STELLINGEN
behorende bij het proefschrift
Mechanistic Studies of the Stress-Corrosion Cracking Behaviour of Oriented Cu30Zn Single Crystals in NaNO₂ Solutions

1. Het ondersteunen van het surface mobility model voor SCC met behulp van waarden van scheurgroei snelheden die zijn gemeten voor combinaties van materiaal en milieu waarbij de scheurgroei snelheid toeneemt met toenemende potentiaal, is niet in overeenstemming met de aan dit model ten grondslag liggende theorie, die leert dat de scheurgroei snelheid onafhankelijk is van de potentiaal.


2. Voor de verificatie van de bewering van Lian en Meletis dat voor de initiatie van SCC een kritische rek aan het materiaaloppervlak bestaat die gelijk is aan de breukrek van het materiaal in lucht, is het wenselijk de initiatie van SCC te onderzoeken met behulp van constante rek snelheidsproeven, waarbij de rek snelheid beduidend lager is dan de rek snelheid van 1·10⁻⁵ s⁻¹ die door deze onderzoekers is toegepast.


3. De observatie van Ashour en Ateya dat de toevoeging van Na₂HPO₄ aan een NaNO₂ oplossing voor α-messing zowel een verlaagde stroom dichtheid in de anodische tak van de polarisatiekromme als een verminderde gevoeligheid voor SCC tot gevolg heeft, toont, in tegenstelling tot hetgeen de auteurs beweren, geenszins aan dat deze verminderde gevoeligheid voor SCC toegeschreven kan worden aan de bemoeilijking van dezincificatie door de aanwezigheid van Na₂HPO₄.


5. Voor het onderzoek naar de invloed van mechanische oppervlaktebehandelingen op putvormige corrosie verdient het aanbeveling het effect te onderzoeken van spanningsvrijgloeien van de behandelde proefstukken, teneinde een onderscheid te kunnen maken tussen de invloed van een veranderde oppervlaktemorfologie en die van veranderde spanningen aan het oppervlak.


6. Indien de kathodische reactie tijdens de propagatie van filiformen op aluminium slechts in het kopgedeelte van de filiformen plaatsvindt, is het waarschijnlijk dat het door Mol et al. geobserveerde verschijnsel dat de aanwezigheid van koperbanen op aluminium bij een bepaalde expositietaal resultert in langere filiformen, toegeschreven kan worden aan een verhoogde initiatiesnelheid.


7. Mits er met een laag zuurstofverbruik aan de kathode wordt gewerkt, is Li₂CO₃/Na₂CO₃ als elektrolyt voor de gesmolten carbonaat brandstofstel te verkiezen boven de standaard Li₂CO₃/K₂CO₃.

8. Indien onderzoek zodanig wordt georganiseerd dat er een nauw contact bestaat tussen degenen die relatief toegespit onderzoek doen en degenen die zich met meer fundamentele onderwerpen bezighouden, is tussen hen een kruisbestuiving te verwachten.

9. Om muziek te laten zweven, moeten de noten eerst staan.

10. Een eendje zie je zelden in z'n eentje.
1. To support the surface mobility model of SCC, the proponents use data for crack velocities which are obtained for material/environment combinations which display a strongly increasing crack velocity with increasing potential. The fact that this dependency is ignored, and that only the maximum values are used for the crack velocity in testing the model, severely calls into question the validity of agreement between experiment and the underlying theory, as claimed by these authors.


2. From the results of their constant strain-rate experiments, Lian and Meletis conclude that a critical surface strain (comparable to the magnitude of strain at ductile fracture in air) is required for the initiation of SCC. To convincingly validate this claim, one is required to employ strain rates which are considerably lower than the value of $1 \cdot 10^{-5}$ s$^{-1}$ which has been used by those investigators.


3. Ashour and Ateya have convincingly shown that the addition of Na$_2$HPO$_4$ to a NaNO$_2$ solution results in a lower current density in the anodic branch of the polarisation curve as well as in a decreased sensitivity to SCC in the case of $\alpha$-brass. What remains entirely unconvincing from their work is their inference that this decreased sensitivity to SCC can be attributed to the the hindering of dezincification by the presence of Na$_2$HPO$_4$.


4. Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) are promising techniques for the investigation of the interaction between deformation and corrosion reactions.
5. For the study of the influence of mechanical surface treatments on pitting corrosion, it is recommended to investigate the influence of stress-free annealing on the behaviour of the treated specimens, in order to distinguish between the influence of changes of the surface morphology and changes of the stresses present near the surface.


6. If the cathodic reaction only occurs in the head region of the filiform during its propagation on aluminium, the effect observed by Mol et al. that the presence of copper traces on aluminium results in longer filiforms for a given exposure time, is likely to be attributed to an increased initiation rate.


7. If the oxygen utilisation at the cathode is kept sufficiently low, a Li$_2$CO$_3$/Na$_2$CO$_3$ electrolyte is preferable to the standard Li$_2$CO$_3$/K$_2$CO$_3$.

8. If research is organised in such a way that a close contact exists between those who carry out relatively applied research and those who are working on relatively fundamental subjects, a cross-pollination between them is to be expected.

9. To let music go, the notes should stand first.

10. One rarely sees a duck alone. (see also Dutch text)
Mechanistic Studies
of the Stress-Corrosion Cracking Behaviour
of Oriented Cu30Zn Single Crystals
in NaNO₂ Solutions
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Onderzoek naar het mechanisme van spanningscorrosie
van georiënteerde Cu30Zn éénkristallen in NaNO₂ oplossingen

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. ir. K.F. Wakker,
in het openbaar te verdedigen ten overstaan van een commissie,
door het College voor Promoties aangewezen,
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1 Introduction

Stress-Corrosion Cracking (SCC) is a process where cracks nucleate and grow in a material due to the interaction between corrosion and a non-cyclic tensile stress. Its result is a brittle appearing failure of the material, which is often unexpected and surprising, since materials are often involved which show highly ductile behaviour in the absence of the corrosion process, and which show a good resistance against general corrosion in the absence of the stress. This extremely treacherous process is a threat to the safety of structures, and its occurrence frequently results in loss of life as well as in large economic losses.

In order to be better able to prevent stress-corrosion cracking, it is desirable to know and understand which circumstances play a role in the SCC process and how changes in these circumstances affect the SCC process. This requires understanding of the mechanism(s) by which SCC occurs. For the purpose of obtaining insight in the mechanism(s) of SCC, research efforts are still ongoing.

The SCC fracture process can be intergranular or transgranular, and the mechanisms by which these occur are generally believed to be different. A further distinction needs to be made between fracture with and without the presence of hydrogen. The present work deals with transgranular stress-corrosion cracking (T-SCC) in situations where no hydrogen is involved.

The present work has been carried out as a collaborative effort between Vanderbilt University, Nashville, TN, USA and Delft University of Technology. During this collaboration the T-SCC behaviour of various model systems are being studied and compared. The investigation of model systems is useful for mechanistic studies, since model systems allow the number of variables to be considerably reduced as compared to more practical systems. In particular, the SCC behaviour of oriented single crystals is studied for different material/environment combinations which display comparable mechanical, but different electrochemical behaviour. These systems comprise, Cu25Au in NaCl solutions, Cu30Zn in de-oxygenated cuprous ammonia solutions, Cu30Zn in NaNO2 solutions and stainless steels in chloride-containing solutions. The goal for the future is to use the results originating from the model systems to develop a theory which can explain and predict the SCC behaviour of material/environment combinations which are more relevant in practice.

The electrochemistry and the SCC behaviour of oriented Cu30Zn single crystals in NaNO2 solutions is the subject of this thesis. The goal of this work is to obtain a systematic knowledge of the influence of the mechanical and electrochemical conditions
on the SCC behaviour for this material/environment combination and to find explanations for the observations. It is a further goal to compare the observations with those which have been reported for the other systems and to investigate which theories can be used to explain observed differences between the systems. An important theory in this respect is the Corrosion-Assisted Cleavage model which has been developed by Flanagan and Lichter et al., and which successfully explained the SCC behaviour of oriented Cu25Au single crystals in NaCl solutions [1-14].

The remainder of the thesis contains the following parts: Chapter 2 provides a review of the literature concerning observations on T-SCC cracking of Cu-base alloys as well as models which have been proposed to explain T-SCC. Following a description of the experimental set-up in chapter 3, the results of investigations of the electrochemical behaviour of flat Cu and Cu30Zn electrodes in NaNO2 solutions are presented in chapter 4. In chapter 5 a general overview of the results of the investigation of the SCC behaviour of oriented Cu30Zn single crystals in NaNO2 solutions is given. Chapters 6, 7 and 8 focus on specific aspects of the SCC behaviour, i.e. the fractography, the load and current behaviour and the mass transport in the crack respectively. In chapter 9 the differences between the Cu30Zn/NaNO2, the Cu30Zn/Cu(I)ammonia, and the Cu25Au/NaCl systems are discussed in terms of different SCC models. This is followed by a summary of the chapters.
2 Observations on T-SCC of Cu-base alloys and models for T-SCC, literature review

2.1 Observations on the role of electrochemistry and deformation in stress-corrosion cracking

It is certainly not known in all cases which electrochemical and mechanical conditions lead to a high sensitivity to SCC. However, for a large variety of material/environment combinations observations do exist on the roles of electrochemistry and deformation. These general observations and concepts have been described in a large number of review papers [15-21], and are briefly discussed in this section.

*Role of electrochemical processes*

The existence of a role of electrochemical processes in stress-corrosion cracking is clearly indicated by the observation that the occurrence of SCC is strongly dependent on the environment as well as on the electrode potential, since these parameters influence the kind of electrochemical reactions which occur and the rate of these reactions.

A first observation is that SCC is often found in material/environment combinations and at values of the electrode potential, where the material is covered by a surface layer which protects the material against general corrosion [15-17]. Examples of surface layers which can result in such passivity include oxides and dealloyed or ennobled layers. A general concept is that passive layers maintain a "sharp" crack geometry by preventing the crack walls from spreading laterally by dissolution [15,16].

A second observation is that the sensitivity for SCC, as for instance expressed by the crack velocity, usually increases with increasing electrode potential [3,15-17,22, 23]. Since a higher electrode potential results in a higher rate of the anodic reaction, it is strongly suggested that the crack velocity increases with increasing rate of the anodic reaction.

The observation that the formation of a passive layer as well as high rates of the anodic reaction favour SCC seems contradictory. Therefore, it is often claimed that SCC occurs under conditions showing an intermediate repassivation rate, i.e. where the passivation rate is not so fast that the anodic reaction can hardly occur, but fast enough to maintain the sharp crack geometry [15-18]. However, this concept is certainly not valid for all systems. For instance, Cu25Au in NaCl solutions is very sensitive to SCC at potentials at which the repassivation rate is very high [8,9,11].
Role of stress and deformation
There is common agreement that, though a stress is required to obtain SCC, the plastic deformation rate is a critical factor in the SCC mechanism [17-21]. The importance of dynamic strain is demonstrated in slow strain rate tests, in which a slow strain rate is imposed on specimen, while the specimen is exposed to an environment. In such tests it is often found that SCC only occurs within a certain range of strain rates, i.e. above a minimum value and below a maximum value for the strain rate [18,20,24]. The presence of a minimum strain rate shows that a strain rate rather than a certain value of the strain is important in SCC. Above this minimum the crack velocity generally increases with increasing strain rate up to a certain value, where general yielding starts to predominate over SCC. The importance of plastic deformation can also be demonstrated in slow strain rate tests, if the straining is started in the elastic domain. In these tests it is found that crack nucleation occurs at the onset of yielding [25].

Due to the importance of the strain rate in SCC, the slow-strain rate experiments are commonly employed in SCC testing.

Corrosion-deformation interactions
The observation that stress-corrosion cracking only occurs under situations where a material is exposed to an environment as well as to a stress has led to the concept of corrosion-deformation interactions, i.e. the idea that deformation affects the corrosion process and that corrosion affects the deformation process [21]. An example of the situation that dynamic deformation affects a corrosion process is the observation that localised corrosion at slip-planes occurs while the material is strained simultaneously with its exposure to the solution, whereas such localised corrosion does not occur if the material is only strained prior to exposure to the solution [21,26]. An example of the situation that corrosion affects a deformation process is the observation of enhanced creep of during anodic dissolution of copper [27-29]. Some workers explain this as being caused by the increase of dislocation motion due to vacancies produced by anodic dissolution [27]. However, the enhanced creep has also been proposed to be the result of an increasing stress, the latter being caused by the continuously decreasing cross section by dissolution while the load remained constant [28,29]. The concepts of corrosion-deformation interactions are often incorporated in models for SCC which are presently being developed, such as, e.g., the corrosion-enhanced plasticity model [30,31,32] and the corrosion-assisted cleavage model [1-3,10,11] which have been described in section 2.5.
2.2 Appearance of the fracture surface in T-SCC of Cu-base alloys

Transgranular stress corrosion fracture surfaces have a cleavage-like appearance, which is especially surprising for fcc materials, which are highly ductile in the absence of the environment. The characteristics of the fracture surfaces were reviewed by Pugh in 1985 [33]. In this section, the following features, which were considered to be generally present in T-SCC in the review by Pugh, are described and evaluated.

1. The fracture surfaces consist of crystallographic, parallel, but displaced, primary facets separated by steps that are generally also crystallographic in appearance. This is illustrated using a schematic representation of the fracture surface in figure 2.1. The orientation of the facets and faces are known in some cases.
2. The opposite fracture faces match and interlock in a number of systems.
3. The average direction of the steps between facets define "river lines" which are approximately perpendicular to the crack front and, hence, approximately parallel to the crack direction.
4. Undercutting occurs at the intersection of the steps with the primary facets.

For α-brass in both cuprous and cupric ammonia solutions [26,33,34], pure copper in nitrite solutions [34], and Cu25Au in chloride solutions [1-6,9], the orientation of the primary facets has been determined to be {110}. Since this thesis is dealing with these materials, the fractography will be discussed using a (110) stereographic projection which has been depicted in figure 2.2. The primary (110) facets are intersected by four

![Figure 2.1a Schematic representation of (110) primary facets](image)

![Figure 2.1b Schematic representation of the situation, where what appear to be (110) facets actually consist of alternating (111) and (111) steps, which intersection with the (110) primary facets are [112] and [112] respectively. The occurrence of undercutting has been indicated as well.](image)
\{111\} type planes, where the (111) and (11\overline{1}) planes are the primary slip planes which make an angle of 35.3° with the primary (110) facets and where the (111) and (111) planes are orthogonal to the primary (110) facets.

For the systems mentioned above, it is often reported that the steps, which separate the primary (110) facets, consist of alternating (111) and (111) planes which are orthogonal to the (110) facets. The intersection of the (110) facets with the (111) and (111) steps are [112] and [112] respectively, and if the (111) and (111) steps alternate, the fracture surface shows a zig-zagging pattern consisting of the [112] and [112] directions.

The following sequence of processes is generally believed to result in this "facet-step" morphology. The primary facets form first. Since the primary facets lie on different levels, their growth results in the formation of ligaments, i.e. pieces of material which connect the primary facets. After failure of the ligaments steps are present between the primary facets. Since overlapping of the primary facets occurs at their edges, the steps are undercut.

The fracture on primary \{110\} facets and crystallographic appearance of the steps were first considered to be generally applicable for \(\alpha\)-brasses. However, since the Pugh's review [33] new observations have shown that the mentioned features of the facets and the steps are not as general as was believed earlier, and that the appearance of the facets and steps is dependent on both the electrochemical as well as the mechanical conditions. These observations will now be discussed.

**Primary facets**
Dickson et al. made a systematic study of the fracture surface and in particular of the details on the primary facets as a function of the stress intensity factor \(K\) for polycrystalline Cu30Zn under constant load conditions in ammonia solutions [35]. For

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**Figure 2.2** Stereographic projection showing the sign convention used in the present work. The primary facets are defined as (110). Four \{111\} type planes are available, where the (111) and (111) planes are the primary slip planes which make an angle of 35.3° with the primary (110) facets. The two other \{111\} type planes, i.e. (111) and (111), are orthogonal to the primary (110) facets, and their intersections with the primary (110) facets are [112] and [112] respectively.
intermediate K values, i.e. higher than 5 MPa·m$^{0.5}$ [36], he claims that what appear to be (110) facets actually consist of alternating (111) and (111) micro-facets. This is illustrated in figure 2.1b. Experimental evidence for this claim consisted of the observation of striations parallel to the [110] direction, which correspond to the intersection of the (111) and (111) micro-facets with each other. The size of the alternating (111) and (111) micro-facets, as estimated from the distance between the striations, was determined to be on the order of 0.5-1 μm and was found to increase with increasing K. For low K values, i.e. lower than 5 MPa·m$^{0.5}$ [36], the primary facets clearly had a (110) orientation and possible alternating (111) and (111) facets could not be resolved by SEM.

In this respect it should be noted that the presence of [110] striations alone may not necessarily be evidence for the presence of alternating (111) and (111) micro-facets with each other since the intersection of a (111) or (111) plane with a (110) facets is also parallel to the [110] direction. As Flanagan has pointed out [37], [110] striations can also be produced by slip steps on (110) facets.

**Steps**

Crystallographic (111) and (111) steps for Cu30Zn have been found in bending, constant load, and constant extension rate tests in cupric ammonia solutions as well as in cuprous ammonia solutions [26,35,38,39]. Evidence for the importance of mechanical conditions is provided by observations in the cupric ammonia system showing that the steps become less crystallographic when the stress intensity increases [38,39]. Furthermore, Kaufman and Fink claim for the same system that the steps are not crystallographic under constant displacement conditions which they attribute to the occurrence of less deformation prior to fracture [39]. However, it should be noted that their SEM photo's do not illustrate this claim, since the photo which is used to show the absence of serrated steps is made at such a low magnification that serrated steps would not be visible anyway.

An effect of electrochemical conditions on the appearance of the steps is reported if a cuprous ammonia solution is used instead of a cupric ammonia solution for randomly oriented Cu30Zn single crystals in a constant extension rate test [40]. For the cuprous ammonia solution the steps seem to be less equally distributed over the surfaces and are more concentrated in distinct river lines. Further, the crystallography of the steps is less pronounced. While not particularly mentioned by their authors, some other work performed on the cuprous ammonia system, seems to support this observation, since the fractography presented there does not show pronounced serrated steps either [41]. An effect of the electrochemical conditions on the appearance of the steps is also found for Cu25Au single crystals in chloride and sulphate solutions under bending and constant extension rate conditions [5]. In these systems the steps are (111) and (111), but they become less crystallographic if the potential is decreased. This may be an indication that the anodic dissolution process facilitates the failure of the ligaments.
2.3 Evidence for discontinuous crack propagation

There is a tremendous amount of evidence that crack propagation in T-SCC can be discontinuous. This idea is strengthened by the observation of the cleavage-like fracture surfaces. If such cracks were to propagate by real cleavage, discontinuous crack advance would be required in order to account for the observed average crack velocities, which are 8 to 11 orders of magnitude lower than the propagation rate of real cleavage cracks which is of the order of the speed of sound. Because it is important for the development of mechanistic models for SCC to know whether or not discontinuous crack propagation is an essential feature of T-SCC, the evidence will be evaluated in this section. The evidence for discontinuous crack propagation, reported in the literature, consists of six different types of observations. These observations are:

1. Crack arrest markings (CAMs)
2. A critical, minimum value of the crack propagation distance in a load pulsing test
3. The sudden and discontinuous appearance of a crack trace at a side of a specimen
4. Discrete acoustic emission signals during crack propagation
5. Current peaks during crack propagation
6. Discontinuous load drops in a slow strain rate test

1. Crack arrest markings (CAMs)
   Crack arrest markings (CAMs) are offsets on the fracture surface which are produced by plastic strain at the crack tip during a period of crack arrest. CAMs can only be detected if the strain has produced an offset on the fracture surface large enough to be detected by the SEM. For α-brass and admiralty metal in tarnishing ammonia solutions this has been found to be the case in the overload region in constant load (CL) tests and for relatively high crosshead speeds in slow strain rate (SSR) tests [38,42,43].

2. A critical, minimum value of the crack propagation distance in a load pulsing test
   Since CAMs are often too small to be resolved their absence does not disprove discontinuity of cracking. In order to resolve this question Hahn, Slattery and Pugh used a load pulsing test where markings of the crack front were produced by load pulses which were periodically superimposed on an otherwise constant load [44,45]. The workers varied the time intervals between the pulses and found that, as long as the time intervals between the pulses were above a critical value, a one to one correspondence existed between the number of pulses and the number of crack front markings. Such a one to one correspondence indicated that at each position along the entire crack front a crack advance event had occurred within each interval. However, at time intervals below the critical value, the number of crack front markings was less than the number of pulses, indicating that the crack had not moved between each load pulse. From this it was concluded that the cracks spend some time being arrested, after which a discrete event of crack advance occurs, which duration is so small that the load pulse can not mark the position of the crack front during such an event. The crack advance distance
corresponding to this critical time interval was thought to represent the crack advance distance for a crack-advance event.

In this respect the comment is given that the load pulses possibly affect the crack propagation behaviour. It is further noted that the observations described above only provide indirect evidence for discontinuous cracking and that they can also be interpreted in a different way. E.g. it can be argued that a load pulse will blunt and arrest an otherwise continuously propagating crack and that the critical time interval mentioned above corresponds to the time required for crack re-nucleation.

3 The sudden and discontinuous appearance of a crack trace at a side of a specimen

Edeleanu and Forty describe observations where an optical microscope is used to view the trace of a SCC crack at the side of a randomly oriented Cu30Zn single crystal under three point bending in an ammonia solution [46,47]. They report a repetitive process consisting of the sudden appearance of a fine crack, terminating at a pre-existing slip band, the widening of this fine crack due to continued slip and the appearance of a new fine crack starting at the shear band where the previous fine crack was stopped. The time between the successive crack advance events was on the order of a minute [46]. The crack advance distance between two arrests can be estimated from the micrographs and is generally 2 to 4 μm. Another observation was that the application of additional stress immediately after the appearance of the fine crack resulted in opening of the fine crack, but not in further crack advance. However, the application of additional stress at the time where a new fine crack was expected, resulted in a visible crack advance.

In relation with these observations it is noted that a crack is only visible with an optical microscope, if the crack has opened up sufficiently. E.g. if a discontinuous crack advance event were to occur by cleavage, for which an atomically sharp crack is required, this will never be visible using an optical microscope, unless slip has opened up the crack on the order of 1000 atomic distances. Thus, the sudden appearance of a new fine crack is only evidence for a crack which suddenly opens up. Therefore, one can not distinguish between discontinuous crack advance, where each crack advance event is followed by deformation, and continuous crack growth, where deformation occurs discontinuously, e.g. due to the discontinuous failure of ligaments.

4 Discrete acoustic emission signals during crack propagation

The experiments by Edeleanu and Forty were repeated by Beggs, Hahn, and Pugh [48] who combined the trace observations with acoustic emission studies. They also performed three-point bending tests on Cu30Zn and Admiralty Metal mono-crystals in a 15 M ammonia solution. They confirm the sudden appearances of fine cracks as found by Edeleanu and Forty. The workers report that, except for low stress intensities where the amplitude of acoustic emissions is expected to be low, each appearance of a fine crack was preceded by a discrete acoustic emission signal, from which they conclude that the acoustic emission signals originate from discrete events of crack advance. A delay-time of 3 to 4 seconds between the acoustic emission and the detection of the fine
Table 2.1 Crack propagation distance per crack advance event, $\Delta x$, crack arrest time, $\Delta t$, and average crack velocity $v_{\text{crack, av}}$ in Cu-base alloys as reported by various workers. SSR = slow strain rate, CL = constant load.

<table>
<thead>
<tr>
<th>material</th>
<th>environment</th>
<th>loading mode</th>
<th>$\Delta x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>admiralty metal, single crystals, random orientation</td>
<td>1 M ammonia (tarnishing)</td>
<td>SSR-test, $v_{\text{crossh.}} = 51 \mu m \cdot s^{-1}$ CL-test, 0.1% yield stress</td>
<td>5 $\mu m$</td>
</tr>
<tr>
<td>admiralty metal, single crystals, random orientation</td>
<td>15 M ammonia</td>
<td>four-point bending</td>
<td>$\approx 12.5 \mu m$ (calc. from $\Delta t$ and $v_{\text{crack, av}}$)</td>
</tr>
<tr>
<td>Cu30Zn, single crystals</td>
<td>15 M cuprous ammonia</td>
<td>SSR-test $v_{\text{crossh.}} = 0.07 \mu m \cdot s^{-1}$</td>
<td>0.5 $\mu m$</td>
</tr>
<tr>
<td>admiralty metal, polycrystals</td>
<td>ammonia solutions</td>
<td>CL test</td>
<td>no min. value $&lt; 1 \mu m$</td>
</tr>
<tr>
<td>Cu30Zn, single crystals, random orientation</td>
<td>ammonia solutions</td>
<td>3 point bending</td>
<td>$\approx 2-4 \mu m$</td>
</tr>
<tr>
<td>Cu30Zn + admiralty metal, single crystals, random orientation</td>
<td>15 M ammonia</td>
<td>bending</td>
<td>10 $\mu m$ for short cracks 2 $\mu m$ for long cracks</td>
</tr>
<tr>
<td>Cu30Zn, polycrystals</td>
<td>1 M NaNO$_2$</td>
<td>in tension, constant displacement</td>
<td>1 $\mu m$</td>
</tr>
<tr>
<td>pure copper, single crystals</td>
<td>1 M NaNO$_2$</td>
<td>SSR-test, $v_{\text{crossh.}} = 0.007-0.03 \mu m \cdot s^{-1}$</td>
<td>1-3 $\mu m$</td>
</tr>
<tr>
<td>pure copper, single crystals</td>
<td>1 M NaNO$_2$</td>
<td>SSR-test, $v_{\text{crossh.}} = 0.025 \mu m \cdot s^{-1}$</td>
<td>2 $\mu m$</td>
</tr>
<tr>
<td>disordered Cu25Au single crystals ${110} &lt;001&gt;$</td>
<td>0.6 M NaCl</td>
<td>SSR-test, $v_{\text{crossh.}} = 0.04 \mu m \cdot s^{-1}$</td>
<td>$\approx 200 \mu m$, short cracks $\approx 50 \mu m$, long cracks</td>
</tr>
<tr>
<td>Cu25Au sin. cryst. disorder ${110} &lt;110&gt;$ ordered ${110} &lt;001&gt;$</td>
<td>0.6 M NaCl</td>
<td>SSR-test, $v_{\text{crossh.}} = 0.04 \mu m \cdot s^{-1}$</td>
<td>CONTIN.</td>
</tr>
</tbody>
</table>
*) Current peaks and acoustic emissions are probably no evidence for discontinuous cracking in this system, since they most likely originate from the discontinuous release of gas bubbles.

<table>
<thead>
<tr>
<th>$\Delta t$</th>
<th>$v_{\text{crack, av}}$</th>
<th>technique</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>not given</td>
<td>not given</td>
<td>CAMs</td>
<td>[38,42,43]</td>
</tr>
<tr>
<td>250 s</td>
<td>0.05 $\mu$m·s$^{-1}$</td>
<td>acoustic emission, no CAMs</td>
<td>[38]</td>
</tr>
<tr>
<td>$\approx$ 3 s (calcul. from $v_{\text{crack, av}}$ and $\Delta x$)</td>
<td>0.13 $\mu$m·s$^{-1}$</td>
<td>CAMs (sometimes)</td>
<td>[10,26]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>load pulsing</td>
<td>[44,45]</td>
</tr>
<tr>
<td>$\approx$ min. 60 s</td>
<td>0.03-0.07 $\mu$m·s$^{-1}$ (calculated from $\Delta t$ and $\Delta x$)</td>
<td>surface trace</td>
<td>[46,47]</td>
</tr>
<tr>
<td>240 s for short cracks</td>
<td>0.04 $\mu$m·s$^{-1}$, long cracks (calc.)</td>
<td>surface trace + acoustic emission</td>
<td>[48]</td>
</tr>
<tr>
<td>15 s for long cracks</td>
<td>0.13 $\mu$m·s$^{-1}$, short cracks (calc.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\approx$ 10 s *)</td>
<td>0.1 $\mu$m·s$^{-1}$</td>
<td>current peaks + acoustic emission + CAMs</td>
<td>[49,50]</td>
</tr>
<tr>
<td>100 s (calc.)</td>
<td>0.01-0.03 $\mu$m·s$^{-1}$</td>
<td>CAMs (always) + current peaks + acoustic emission *)</td>
<td>[51]</td>
</tr>
<tr>
<td>300 s (from peaks and AE *)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 s (calc.)</td>
<td>0.01 $\mu$m·s$^{-1}$</td>
<td>CAMs (sometimes)</td>
<td>[52]</td>
</tr>
<tr>
<td>120 s, $E = +$ 400 mV SCE</td>
<td></td>
<td>load drops + current transients + CAMs</td>
<td>[1-3,6,9]</td>
</tr>
<tr>
<td>500 s, $E = +$ 350 mV SCE CONTINUOUS</td>
<td></td>
<td>no load drops no current transients no CAMs</td>
<td>[1-3,6,9]</td>
</tr>
</tbody>
</table>
crack was attributed to the necessity of creep to occur in order to make the fresh crack visible by the optical microscope.

5 Current peaks during crack propagation
As the creation of fresh surface during advance of the crack will give rise to the flow of a current which can be measured if the specimen is anodically polarised, observations of discrete current peaks during SCC cracking have been used as evidence for discontinuous cracking. Newman, Sieradzki and Sabatini present data showing a correlation between acoustic emission events and current peaks for α-brass and copper in NaNO₂ solutions under anodic polarisation [49-51]. However, gas bubbles are formed in these systems, and the release of these gas bubbles can both result in an acoustic emission signal as well as in the sudden exposure of fresh surface resulting in a current transient [9] As long as it is not possible to distinguish between the effect of gas bubbles and phenomena related to crack advance, these data may not be used as evidence for discontinuous crack growth. Flanagan, Lichter and co-workers observed current transients associated with discontinuous events of crack advance for certain crack growth directions in disordered Cu25Au single crystals in NaCl solutions [1-3,9].

6 Discontinuous load drops in a slow strain rate test
For oriented Cu25Au single crystals tested under slow strain rate conditions in NaCl solutions under anodic polarisation, discontinuous cracking was found to result in the occurrence of discrete load drops which coincided with current peaks [1-3,9]. These discrete load drops, which were several seconds in duration, were associated with the advance of the crack resulting in a decrease of the load supporting section of the specimen, while the stress in the unfractured part of the sample remained constant at the yield stress. An important observation was that the discontinuity of cracking was related to the crack propagation direction, i.e. crack growth on {110} facets in the <001> direction was discontinuous, whereas crack growth on {110} facets in the <110> direction was continuous. The results obtained for the Cu25Au/NaCl system will be described in more detail in section 2.4.

Table 2.1 gives an overview of the studies on the discontinuous nature of T-SCC crack propagation. This overview shows that there is a strong variation of the values for the crack propagation distance, Δx, and the crack arrest time, Δt. These differences are likely to be attributed to differences in the mechanical and electrochemical conditions. However, no explanations are available on the precise relation between these conditions and the observed differences. In the present evaluation it has further been argued that the use of data as evidence for discontinuous crack propagation is not appropriate or doubtful in a number of cases. The most important observation is that in the Cu25Au/NaCl system discontinuous cracking is found for crack propagation in certain directions, whereas this phenomenon is not found for crack propagation in other directions. This observation casts doubts on possible claims that discontinuous crack propagation is an essential feature for T-SCC.
2.4 SCC behaviour of oriented single crystals as observed by Flanagan, Lichter and co-workers

In this section, a description is given of the SCC behaviour of oriented Cu25Au single crystals in 0.6 M NaCl solutions in an experimental set-up employed by Flanagan, Lichter, and co-workers [1-14,26,53]. This work is of particular interest, since the experiments have provided new and detailed experimental information on SCC features comprising:

- the relation between the crack propagation direction and the discontinuity of crack propagation.
- the influence of the potential on the re-nucleation time following crack arrest
- instantaneous crack velocity between periods of crack arrest and the influence of the potential on the instantaneous crack velocity
- fractography

Since understanding of the electrochemistry of the Cu25Au/NaCl system is important for the interpretation of the experimental results on the SCC behaviour of this system, the electrochemical behaviour of a flat Cu25Au electrode in NaCl solutions as determined by Flanagan, Lichter, and co-workers is described first. Following a description of the experimental procedures for the SCC tests, the experimental results on the SCC behaviour of the Cu25Au/NaCl system as well as a method for analysing

Figure 2.3 Anodic branch of the voltammogram of Cu25Au in 0.6 M NaCl measured at a scan rate of 0.08 mV.s⁻¹. The potential region in which SCC is observed has been indicated as well [8].

Figure 2.4 Current response of Cu25Au in 0.6 M NaCl following a potential step from the rest potential to + 400 mV SCE [9].
the results are given. The description of the experimental results does not include the fractography as this has already been described in section 2.2. Eventually the SCC behaviour of oriented Cu30Zn single crystals in de-oxygenated cuprous ammonia solutions which was tested by Yong Ling in the same experimental set-up, will briefly be described.

**Electrochemical behaviour of a flat Cu25Au in NaCl solutions**

Figure 2.3 shows the anodic branch of the voltammogram for a Cu25Au single crystal in a 0.6 M NaCl solution as measured by Lee et al. [8]. This voltammogram shows a plateau region in which the current density has a constant, "passive" value of several $\mu$A$\cdot$cm$^{-2}$. This plateau is attributed to the selective dissolution of a several monolayers of Cu leaving an ennobled gold layer behind which acts like a passive film. Above a critical potential at $E = +420$ mV SCE, the current density rises with increasing potential. In this potential region massive dissolution of Cu occurs, where the remaining Au forms a sponge-like structure [4]. Figure 2.4 shows the current response following a potential step from the rest potential to $+400$ mV SCE, this value being

---

**Figure 2.5a**  {110}\(<001\>\) or type I specimen as used by Flanagan and Lichter [1-3,9]. The intersection of the primary {111} slip planes with the {110} fracture surface coincides with the crack front.

**Figure 2.5b** Side view of a {110}\(<001\>\) specimen showing that slip on the primary slip planes results in mechanical blunting of the crack tip.
below the critical potential and in the potential domain where SCC is observed [9]. This step results in a current which is initially high, but which quickly decreases to a low background value. By calculating the charge density which has passed until the current density has decreased to its background value, it can be shown that passivity is already achieved by the selective dissolution of a few monolayers of Cu. This passivity is achieved within a second.

**Experimental procedures for the SCC experiments [2,3,6,9,11]**
The workers used disordered single crystalline Cu25Au specimens which were coated except for a notch which was made at one side of the specimen. This coating served two purposes. The first purpose was to allow only one crack to be nucleated. This was achieved by the presence of the coating, since crack nucleation is only possible at sites where the material is exposed to the solution. The second purpose was to reduce the background current during anodic polarisation of the specimen, so that reliable measurements could be obtained of the current associated with the propagation of the crack.

---

**Figure 2.6a** (110)<110> or type II specimen as used by Flanagan and Lichter [1-3, 9]. The intersection of the primary (111) slip planes with the (110) fracture surface does not coincide with the crack front.

**Figure 2.6b** View of a (110)<110> specimen in the crack propagation direction showing that slip on the primary slip planes only jogs the crack tip without blunting it.
The specimens had a \(<110>\) tensile axis, which resulted in a fracture surface which was orthogonal to the tensile axis. The nominal crack growth direction, which is the intended crack growth direction, i.e. the direction orthogonal to the specimen side in which the notch is made, was varied. The two mostly studied nominal crack growth directions were \(<001>\) and \(<110>\). The specimen types used in these cases were referred to as \{110\}<001>\) or type I and \{110\}<110>\) or type II respectively. An important difference between these two orientations is the orientation of the two primary slip planes with respect to the nominal crack front, which has been illustrated in figures 2.5 and 2.6. In the case of \{110\}<001>\) crack growth, the crack front coincides with the intersection of the primary \{111\} slip planes with the \{110\} fracture surface, allowing mechanical blunting of the crack tip. In contrast, for \{110\}<110>\) crack growth, thus orthogonal to \{110\}<001>, the intersection of the primary \{111\} slip planes and the \{110\} fracture surface does not coincide with the crack front, in which case slip only jogs the crack tip without opening or blunting it.

Tensile tests were performed in a 0.6 M NaCl solution, where the specimens were strained in the directions parallel to the tensile axis using a slow, constant crosshead speed, i.e. several hundredth's of micrometers per second which corresponded, in the absence of a crack, to a strain rate of \(2 \times 10^{-6}\) s\(^{-1}\). Straining was started in the elastic domain. At the onset of the plastic domain, as indicated by the deviation of the linearity in the load-time diagram, a potential of \(+450\) mV SCE was applied which resulted in a quick nucleation of the crack. Following this nucleation, the potential was decreased to the value to be investigated, which mostly lay in the domain between \(+350\) mV and \(+400\) mV SCE.

During these "slow strain rate" (SSR) test, the load and current were monitored. Both parameters were used to obtain information on the propagation of the crack. The idea behind the load measurements was that a decrease of the unfractured cross section in front of the crack is expected to be reflected in the load, since the load is the product of the stress in the load bearing section and the surface area of the load bearing section. The idea behind the current measurements was that the creation of fresh surface due to the advance of the crack is expected to give rise to a current, since the freshly created surface becomes exposed to the solution while this surface is under anodic polarisation.

\textit{Crack propagation [1-3,6,9-11]}

The crack propagation behaviour appeared to be different for the \{110\}<001>\) and the \{110\}<110>\) orientation.

In the case of \{110\}<001>\) crack growth, the load showed periods of a few seconds during which the load decreased fast. These \textit{load drops} alternated with periods on the order of a few minutes during which the load did not decrease. Each load drop was associated with a current transient. The fracture surface showed crack arrest markings, which were 50 to 200 \(\mu\)m apart, and each crack arrest marking coincided with a shear band on the side of a specimen. The number of crack arrest markings was equal to the number of load drops and the number of current transients. The time interval between the periods of crack advance decreased with increasing potential, being approximately
500 s for $E = +350$ mV SCE, 250 s for $E = +380$ mV SCE, and 120 s for $E = +400$ mV SCE [6]. This showed that the re-nucleation time occurs faster at higher potentials.

In the case of $\{110\}<110>$ crack growth, the load decreased continuously without showing discrete drops [1,2,9]. The current did not show peaks, and remained at a constant level. No crack arrest markings were present. From these observations it was concluded that in this system $\{110\}<001>$ crack growth is discontinuous, whereas $\{110\}<110>$ is continuous.

**Calculation of the instantaneous crack velocity using the load and current data [3]**

The workers showed that it was possible to use the load and current data to calculate the instantaneous crack velocity, which is the velocity of the crack during the actual advance of the crack. This analysis is described by the present author in a slightly different way than the way of the authors themselves, but the essence of the description is the same. For the $\{110\}<001>$ orientation, where crack growth is discontinuous, the relation between the instantaneous crack velocity and the average crack velocity is visualised in formula 2.1, as well as in figure 2.7.

\[
V_{\text{crack, av.}} = \frac{\Delta x}{\Delta t_{\text{arrest}} + \Delta t_{\text{prop.}}} = \frac{\int v_{\text{crack, inst.}}(t) \, dt}{\Delta t_{\text{arrest}} + \Delta t_{\text{prop.}}}
\]  

(2.1)

where:

- $V_{\text{crack, av.}}$ = average crack velocity
- $\Delta x$ = crack propagation distance covered between two periods of crack arrest
- $\Delta t_{\text{arrest}}$ = duration of a period of crack arrest
- $\Delta t_{\text{prop.}}$ = duration of a period of crack advance
- $v_{\text{crack, inst.}}(t)$ = instantaneous crack velocity as a function of time

**Figure 2.7** Schematic representation of the instantaneous crack velocity as a function of time during discontinuous $\{110\}<001>$ crack growth in the Cu25Au/NaCl system at potentials $\approx 350$-400 mV, SCE.
For the $\{110\}<110>$ orientation, where crack growth is continuous, the instantaneous crack velocity is equal to the average crack velocity under the assumption that the latter is constant during the course of an experiment.

For the discontinuous, $\{110\}<001>$ crack growth, the instantaneous crack velocity was calculated in two independent ways, which gave the same results. The first method was based on the load data, and the second method was based on the current data. For the analysis of the load data it was assumed that the stress in the unfractured cross section remained at a constant yield stress. If the yield stress is constant, which is the case as long as the single crystalline specimen is in the easy glide, the load is proportional to the unfractured cross section, and the load decrease rate is, for a constant length of the crack front, proportional to the instantaneous crack velocity. This is illustrated in formulas 2.2a and 2.2b.

\[
F = \sigma_y A \quad (2.2a)
\]

\[
\frac{dF(t)}{dt} = \sigma_y \frac{dA(t)}{dt} = -\sigma_y I_f v_{\text{crack, inst.}}(t) \quad (2.2b)
\]

where:

\(F\) = load
\(A\) = surface area of the unfractured cross section of the specimen
\(\sigma_y\) = yield stress
\(t\) = time
\(I_f\) = length of the crack front

For the analysis of the current data, it was assumed that the repassivation rate was sufficiently high, so that the current could be considered to be proportional to the surface area production rate and thus to the instantaneous crack velocity in the case of a constant length of the crack front. The relation between the current and the crack velocity is indicated in formula 2.3.

\[
I(t) = -2q \frac{dA(t)}{dt} = 2q I_f v_{\text{crack, inst.}}(t) \quad (2.3)
\]

where:

\(I(t)\) = current after subtraction of the background current
\(q\) = charge density passed until repassivation

Since it was found that the predictions for the instantaneous crack velocity using the load and current data gave identical results, it was concluded that the load decrease rate as well as the current were appropriate measures for the surface area production rate and for
the instantaneous crack velocity in the case of a constant length of the crack front. Assuming a constant length of the crack front it was found for the discontinuous \{110\}<001> crack growth that a period of crack advance consists of a period of approximately a second in which the crack velocity increases from zero to a maximum value followed by a period of a few seconds in which the crack velocity decreases again to zero. The maximum in the crack velocity was found to be higher for higher potentials being several tens of \(\mu\text{m} \cdot \text{s}^{-1}\) for \(E = +380 \text{ mV SCE}\) and several hundreds of \(\mu\text{m} \cdot \text{s}^{-1}\) for \(E = +450 \text{ mV SCE}\).

The analysis described above can only be carried out for if the assumptions are valid. For the interpretation of the load data, the assumption was that the stress in the unfractured cross section remained at a constant yield stress. For the interpretation of the current data, the assumption was made that the repassivation rate was sufficiently high to consider the current to be proportional to the instantaneous crack velocity. The latter assumption is for instance not valid in the limiting case that the repassivation only starts after the crack has already been arrested. A current peak is then found of which the height is proportional to the crack advance distance, instead of the instantaneous crack velocity.

Work on the Cu30Zn/Cu(I)ammonia system by Yong Ling [53]

Yong Ling used the same experimental set-up as described above to investigated the SCC behaviour of Cu30Zn single crystals in de-oxygenated solutions containing 5 M NH\(_3\), 0.16 M Cu\(^+\) and an excess of Cu powder. This solution will be referred to as Cu(I)ammonia solution in the rest of this thesis. Most SCC experiments in this solution were performed at the rest potential, where selective dissolution of Zn occurs, i.e. the anodic reaction consists of the oxidation of Zn to form dissolved ions and the cathodic reaction consists of the reduction of Cu\(^+\) to form metallic Cu.

The SCC behaviour in the Cu30Zn/Cu(I)ammonia system appeared to be different from the behaviour of the Cu25Au/NaCl system. For \{110\}<001> specimens discontinuous crack propagation was only found at a microscopic scale, i.e. small markings were present on the fracture surface which were less than 1 \(\mu\text{m}\) apart. Another difference was that the average orientation of the fracture surface deviated strongly from \{110\} in the case of \{110\}<110> specimens.

2.5 Proposed models for T-SCC

Though many models have been proposed to account for T-SCC, it is more or less possible to divide the models in a relatively small number of categories based on the way by which the crack actually advances, e.g. by dissolution, cleavage, vacancy capture or localised deformation. In this section a selection of models has been made, where the above mentioned categories are represented.
2.5.1 Slip-Dissolution model

The slip-dissolution model describes a mechanism, where the crack propagation occurs by dissolution at the tip of the crack [19,22,54,55]. A process is envisaged, where a film is periodically ruptured at the crack tip by slip. Following each rupture event the crack propagates by dissolution until a new film has been formed. This new film is ruptured again, and the process is repeated. When the slip-dissolution model is operative, the average crack velocity, $v_{\text{crack, av.}}$, can be derived based on Faraday's second law [55].

$$v_{\text{crack, av.}} = \frac{M}{nF\rho} \bar{i}_{\text{tip}}$$  \hspace{1cm} (2.4a)

$$\bar{i}_{\text{tip}} = \frac{1}{t^*} \int_0^{t^*} i_{\text{tip}}(t) \, dt$$  \hspace{1cm} (2.4b)

where:

- $M$ = atomic weight
- $n$ = number of electrons transferred per atom dissolved
- $F$ = Faraday's number
- $\rho$ = density
- $\bar{i}_{\text{tip}}$ = mean current density at the crack tip
- $t$ = time after creation of the fresh surface by film rupture
- $i_{\text{tip}}(t)$ = current density at the crack tip as a function of $t$, i.e. repassivation transient in crack
- $t^*$ = time between two rupture events

In order to use the slip-dissolution model to predict the crack velocity, various methods have been used to estimate $i_{\text{tip}}(t)$ and $t^*$. A method often used for estimating $i_{\text{tip}}(t)$ is the method where $i_{\text{tip}}(t)$ is considered to be equal to the current response which is measured when a fresh surface is suddenly exposed to the solution while the specimen is polarised at a potential in the potential domain for SCC cracking. These current responses can be measured in experiments, where the passive film is suddenly removed mechanically by scratching or rapid straining or in experiments where the potential is suddenly stepped from a value where no anodic reaction occurs to a more positive value in the potential domain for SCC cracking. The value of $t^*$ is often approximated by making assumptions regarding the crack tip strain rate and the required strain to rupture a film. There is a significant number of systems, where a good correlation between the predicted values and measured values for $v_{\text{crack, av.}}$ is obtained [22,23,56-58]. However for other systems, e.g. the Cu25Au/NaCl system, it has been proved that the measured crack velocities are orders of magnitude higher than the crack velocities which would be expected based on the slip-dissolution model [6].
The strongest evidence for the slip-dissolution model consists of the frequently observed correlation between the predicted and measured crack velocities, and this correlation has also been reported for T-SCC of α-brass in NaNO₂ solutions. However, this model cannot account for the fractographic features in transgranular SCC, such as the matching surfaces and the undercutting. Further, if this model were to result in fracture on a crystallographic plane in fcc materials, the {111} slip planes would be expected to be the favourable fracture plane instead of the observed {110} planes, since moving dislocations are a preferential site for dissolution. Now, the slip-dissolution model is mainly applied to intergranular SCC.

2.5.2 Film-Induced Cleavage (FIC) model
The film-induced cleavage model, as proposed by Sieradzki and Newman [49,59], describes a mechanism, where the crack propagates by discontinuous cleavage. This model envisages a crack advance event as a process where the failure of a film with appropriate properties results in the nucleation of a brittle crack which propagates beyond the film into the unaffected substrate until it is blunted by plastic deformation. In an earlier version of the model, the film-substrate atomic misfit and the film thickness where considered to be an important parameter affecting the possibility of film-induced cleavage [49]. Later, the importance of a film with a nanoporous morphology was emphasised [55]. In most cases the film responsible for nucleation is considered to be a dealloyed layer. However, the possibility that an oxide or other types of layer can produce film-induced cleavage is not excluded.

In this model the role of corrosion consist of the formation of the required surfaces film, and it explains why a higher electrode potential would result in a higher average crack velocity, i.e. if the potential is higher, the period required for the formation of the film with sufficient properties for crack nucleation is expected to be shorter. This model explains observations where crack growth is found to occur in a discontinuous way. However, it fails to explain situations where no discontinuous crack growth is found, which is e.g. the case for {110}<001> type crack growth in Cu25Au single crystals in NaCl solutions. Though evidence for the nucleation of a crack in a dealloyed layer which subsequently propagates in the unaffected substrate is reported [4], the film-induced cleavage model fails to explain situations where the presence of layers having a nanoporous morphology can be excluded, such as for crack growth in Cu25Au in NaCl solutions below the critical potential for dealloying [1-3,6,9].

2.5.3 Corrosion-Enhanced Plasticity (CEP) model
The corrosion enhanced plasticity model has been proposed by Magnin et al. to account for fracture where hydrogen effects play a role as well as for SCC fracture where anodic processes are involved [30-32]. According to this model the crack propagation process comprises the following stages. Corrosion occurs at the {111} slip plane at the crack tip and enhances plasticity on this plane because of hydrogen absorption or vacancy
production by anodic dissolution. Emitted dislocations interact with obstacles such as precipitates, grain boundaries or Lomer locks, and pile-ups are formed increasing the local stress. If the obstacles are strong enough a crack embryo is formed at the obstacle, and the crack is opened up along the \{111\} plane. This process is then repeated on the other \{111\} plane, symmetrical to the general crack plane.

The Corrosion enhance plasticity model gives an explanation for observations of fracture on alternating \{111\} facets, thereby forming an average \{110\} crack [30,35,60]. It further explains recent finding by Magnin et al, Yong Ling and the author of the present work showing that there is a relation between the appearance of the fracture surface and the crack propagation direction [31,32]. In this respect the model predicts that the appearance of the fracture surface should change significantly if the crack front does not contain the \{111\} slip planes, which is e.g. the case for \{110\} \langle110\rangle crack growth. In this model, the role of corrosion is indirect, i.e. it is proposed to enhance the slip activity at the crack tip.

2.5.4 Surface Mobility model

The Surface-Mobility SCC mechanism, as proposed by Galvele [16], postulates that elementary step for crack propagation consists of the capture of a vacancy by the stressed tip. A theory is proposed according to which the crack velocity \(v_{\text{crack}}\) is given by formula 2.5:

\[
v_{\text{crack}} = \frac{D_s}{L} \left[ \exp \left( \frac{\sigma a^3}{kT} \right) - 1 \right]
\]  

(2.5)

where

\(D_s\) = coefficient of surface self-diffusion

\(L\) = diffusion distance of the vacancies

\(s\) = elastic surface stress at the tip of the crack

\(a\) = atom size

\(k\) = Boltzmann constant

\(T\) = temperature

The role of the environment is proposed to consist of affecting \(D_s\), where it is claimed that the presence of a compound with a low melting point on the crack walls has the effect of increasing \(D_s\), and, therefore, \(v_{\text{crack}}\).

Support for this model originates from the observation that in a number of material/environment combinations SCC cracking is only found at potentials where a low-melting compound can be formed [16]. Further, it is found for a number of systems that quantitative predictions for the crack velocity corresponded to the maximum crack velocities measured in those systems. However, in this respect it should be noted that the model does not explain the observation that an increasing
potential results in an increasing crack velocity, i.e. in the formula 2.5 the electrode potential is not a variable, unless one of the variables is a function of the electrode potential. It is also noted that the model does not explain the fractographic features found in T-SCC. It is further remarkable that this model proposes the growth of primary facets to occur vacancy by vacancy, which idea shows similarities with the later version of the Corrosion Assisted Cleavage model which proposes the advance of the primary facets to occur by a atom by atom dissolution.

2.5.5 Corrosion-Assisted Cleavage (CAC) model
The Corrosion-Assisted Cleavage (CAC) model as developed by Flanagan, Lichter and co-workers was originally proposed to account for the observed SCC-behaviour of oriented Cu25Au single crystals in NaCl solutions [1-3,10,11], which has been described in section 2.4. The model comprises a theory for re-nucleation of an arrested crack, for crack propagation, and for crack arrest.

In the proposed re-nucleation process a major role is played by dissolution along a \{111\} shear band emanating from the arrested crack, thereby producing a \{111\} corrosion slot. Calculations have been presented showing that, if such a \{111\} corrosion slot approaches a Lomer-Cottrell lock against which dislocations are piled up, the stress state at the lock becomes more favourable for opening up the lock. It is proposed that opening up the lock results in a crack nucleus and that the local stress field of a crack nucleated at one lock will trigger the nucleation at neighbouring locks. As the neighbouring locks lay at different levels, the neighbouring crack nuclei are also expected to lay at different levels, which is used to explain that the fracture surface consists of co-parallel but displaced facets. The fact that the Burgers vector of the involved Lomer-Cottrell locks is in the \{110\} plane is seen as an explanation for the observation that the co-parallel facets are \{110\} [1,2]. More recent calculations involve the analysis of the stress field around \{111\} corrosion slots, where the crack-opening stresses acting on various low index planes intersecting with the \{111\} slot are compared for different orientations of the tensile axis. These calculations indicate that, for all tensile axes, except for the \{100\} tensile axis, the crack-opening stress at the tip of \{111\} slots is highest for \{110\} planes [14]. Though the original Lomer-Cottrell lock mechanism is not discarded, the initiation at a \{111\} corrosion slot followed by a transition to fracture on \{110\} planes is now more generalised.

The propagation process comprising the growth of sharp \{110\} microcracks is designated as corrosion-assisted cleavage (CAC), and in an earlier version of the model CAC was envisaged as a cleavage process where $K_{fc}$ is lowered by the corrosive environment [1,2]. More recently, it is described as a stress-enhanced dissolution, i.e. atom by atom crack advance by preferential dissolution at the crack tip, where the stress is highest [11,12]. The growth of the microcracks, which occurs at different levels, is restricted by the presence of ligaments which connect the microcracks. The failure of the ligaments is presumed to occur by shear and/or corrosion.
Arrest of the crack is believed to occur after the increase of the stress intensity due to the increasing crack length has resulted in the activation of a major slip band which on its turn results in the blunting and subsequent arrest of the crack. Since slip can only blunt the crack tip if the slip planes are parallel to the crack front, whereas the slip only jogs the crack tip in other cases, discontinuous crack propagation is only expected for crack growth in the \{110\}<001> direction, which has been illustrated in figures 2.5 and 2.6. This used to explain the observation that crack \{110\}<001> growth in disordered Cu25Au crystals in NaCl solutions is discontinuous, whereas \{110\}<110> crack growth in this system is continuous.

Van der Wekken offers an alternative explanation for the occurrence of discontinuous cracking in the Cu25Au/NaCl system which is based on calculations of the salt concentrations in the crack tip region during crack propagation [61]. The anodic reaction occurring in the crack tip region during crack advance involves the oxidation of Cu to form Cu$^{2+}$ ions, which enter the crack solution. Following nucleation of the crack, the Cu$^{2+}$ concentration of in the crack tip region rises which can proceed as long as the solubility product of a copper chloride salt is not exceeded. The calculations by Van der Wekken indicate that the onset of the decrease of the crack velocity, which is found to occur approximately one second following the crack renucleation, coincides with the moment where the solubility limit of CuCl$_2$ has been reached. Therefore, he proposes that the decrease of the crack velocity is the result of the precipitation of the salt, since this precipitation will retard or block further dissolution in the crack tip region which is necessary for crack propagation. This decrease of crack propagation rate is expected to increase the probability of crack blunting, if the slip planes have the appropriate orientation with respect to the crack front, i.e. for \{110\}<001> crack growth. According to this model the crack can renucleate by a similar renucleation mechanism as described by the CAC model after the salt has dissolved to a sufficient extent. For continuous \{110\}<110> crack growth a steady state situation is envisaged, where the salt concentration at the crack tip is continuously at the saturation concentration of CuCl$_2$, while the concentration at the crack mouth is zero.

2.5.6 Differences between SCC models
In table 2.2 an overview has been given of various processes which are considered to play a role in the SCC mechanism. For each process it has been indicated which role they play according to the different models. It has also been indicated if the models describe which features are required for the processes to be effective in producing SCC.

In table 2.2 it can be seen that the models propose various roles for the processes considered to be relevant in SCC. However, in many cases the models describe the roles of these processes in general terms and they do not describe if certain features are necessary for producing SCC. Therefore, it is often difficult to test the validity of the models by experiment or to discriminate between the models.
Table 2.2  Processes relevant in SCC, proposed roles and requirements for these processes according to various SCC models

<table>
<thead>
<tr>
<th>process</th>
<th>role</th>
<th>required features</th>
<th>model</th>
</tr>
</thead>
<tbody>
<tr>
<td>formation of passive film/</td>
<td>localising corrosion</td>
<td>sufficient reduction of general</td>
<td>general concept</td>
</tr>
<tr>
<td>surface layers</td>
<td></td>
<td>corrosion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>injecting crack in substrate</td>
<td>nanoporous structure</td>
<td>FIC model</td>
</tr>
<tr>
<td></td>
<td>increasing surface self-</td>
<td>low melting point</td>
<td>surface mobility</td>
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<tr>
<td></td>
<td>diffusion coefficient</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dissolution</td>
<td>propagation of the crack</td>
<td>slip-diss. model, later version</td>
<td>CAC model</td>
</tr>
<tr>
<td></td>
<td>dissolution of ligaments</td>
<td></td>
<td>earlier version CAC model</td>
</tr>
<tr>
<td></td>
<td>vacancy production</td>
<td></td>
<td>CEP model</td>
</tr>
<tr>
<td>vacancy capture</td>
<td>propagation of the crack</td>
<td></td>
<td>surface mobility model</td>
</tr>
<tr>
<td>stress</td>
<td>produce plastic deformation</td>
<td></td>
<td>general concept</td>
</tr>
<tr>
<td></td>
<td>accelerating dissolution</td>
<td></td>
<td>CAC model (later version)</td>
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<tr>
<td></td>
<td>rate</td>
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<tr>
<td></td>
<td>reduce energy of</td>
<td></td>
<td>surface mobility model</td>
</tr>
<tr>
<td></td>
<td>formation of vacancies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dynamic strain</td>
<td>rupture film by slip</td>
<td>within &quot;strain-rate window&quot;</td>
<td>slip dissolution model</td>
</tr>
<tr>
<td></td>
<td>film failure resulting in</td>
<td></td>
<td>FIC model</td>
</tr>
<tr>
<td></td>
<td>crack injection</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>enhancing corrosion on</td>
<td></td>
<td>CAC model</td>
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<tr>
<td></td>
<td>slip planes leading to</td>
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<tr>
<td></td>
<td>crack nucleation</td>
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<td></td>
<td>shearing ligaments</td>
<td></td>
<td>cleavage models</td>
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<tr>
<td></td>
<td>produce localised</td>
<td></td>
<td>plasticity models</td>
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<tr>
<td></td>
<td>plasticity necessary for</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>crack propagation</td>
<td></td>
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</tbody>
</table>
2.6 Goals of this work in the light of the literature

In section 2.2 and 2.3 features which are often reported to be characteristic for transgranular stress-corrosion cracking have been described and evaluated. Based on this evaluation it has been concluded that, though some features are indeed often observed in T-SCC, the appearance of the features as reported by the various workers can vary strongly. Features of which the appearance has been found to vary strongly comprise the fractographic details and the discontinuity of crack propagation. A general impression which arises from this evaluation is that the differences in the appearance of these features are likely to be attributed to differences in the mechanical and electrochemical conditions. However, in many cases no systematic knowledge is available on the precise relation between these conditions and the appearance of T-SCC.

In section 2.5, various proposed models for T-SCC have been discussed, and it has been described for which features they provide explanations and which roles they attribute to electrochemical and electrochemical factors, like, e.g., passivation, dissolution and deformation. In order to investigate the general applicability of these models, it would be interesting to know if these models can explain changes in the SCC behaviour which occur if the mechanical and electrochemical conditions are varied.

In this light, the purpose of the work presented in this thesis is twofold. A first goal is to obtain a systematic knowledge of the influence of the mechanical and electrochemical conditions on the SCC process. A second goal is to investigate to which extent the models for SCC can explain the observed influence of these conditions on the SCC behaviour. In order to achieve these goals experiments are performed as a part of a broader project in which the T-SCC behaviour of various material/environment conditions are compared, where the material/environment combinations are chosen with the intention that they show comparable crystallography, but different electrochemical behaviour.

In the present work the electrochemistry of Cu30Zn in NaNO₂ solutions as well as the SCC behaviour of oriented Cu30Zn single crystals in NaNO₂ solutions are studied. The observations are compared with the observations as described in section 2.4, i.e. the observations for the Cu25Au/NaCl system, which has been studied by various workers in the group of Lichter and Flanagan [1-14], as well as with the observations for the Cu30Zn/Cu(I)ammonia system which has been studied by Yong Ling who worked the same group [53].

For the comparison of the different systems, a good understanding of the electrochemistry is required, as the electrochemical behaviour of the systems is the varied parameter. In the present work the electrochemistry of the Cu30Zn/NaNO₂ system is studied using polarisation techniques in combination with analyses of the electrode surfaces by Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) and analyses of the solution by Atomic Adsorption Spectroscopy (AAS) or Inductively Coupled Plasma - Optic Emission Spectroscopy (ECP - OES). The results of the electrochemical studies are described in chapter 4.
For the investigation of the SCC behaviour of the Cu30Zn/NaNO₂ solutions, the technique is used which has been developed within the group of Lichter and Flanagan, and which has been described in section 2.4. The reason for using this technique is that it has shown to give good experimental control and that it allows a detailed and systematic study of the following SCC features.

- fractography
- discontinuity of crack advance
- instantaneous crack velocity between crack arrests
- re-nucleation time following an arrest of the crack

as a function of:

- nominal crack propagation direction
- electrode potential
- crosshead speed

The results of the study of the SCC behaviour are described in chapters 5-8.

The comparison of the SCC behaviour of the Cu30Zn/NaNO₂ system with that of the Cu25Au/NaCl system and the Cu30Zn/Cu(I)ammonia system is described in chapter 9.
3 Experimental procedures

3.1 Production of α-brass single crystals and preparation of the specimens

Alpha brass single crystals were produced using the Bridgeman technique. The Bridgeman apparatus, of which a detailed description can be found in reference [26], is depicted schematically in figure 3.1. A high purity graphite mould (1) was used in which "pencil" shaped ingots could be obtained, i.e. cylindrical bars which had a diameter of 19 mm and a point of 30° at one end. The mould was placed vertically in a quartz tube (2) which was closed at the bottom. The top of the quartz tube could be sealed using a cap (3) which was equipped with an inlet and outlet for gas in order to back-fill the tube with ultra high-purity argon gas prior to the melting and solidification procedures. The stationary quartz tube was surrounded by a cylindrical furnace (4) which could be raised along the quartz tube with a constant rate.

The crystals were obtained in two steps. First, a mixture of high purity Cu metal shot (Johnson Matthey, 99.9%) and high purity Zn metal shot (Belmont Metal, 99.9%) were melted, and held at a temperature of 1200 °C for several hours before cooling in the furnace. After cutting off the top portion, where impurities and porosity were usually found, the ingots were replaced in the mould, and re-melted, where the temperature in the furnace was maintained at 1100 °C. Then, single crystals were grown by raising the furnace at a speed of 2 cm per hour. The composition of the single crystals was checked by performing both Energy Dispersive Spectroscopy (EDS) and X-ray Fluorescence (XRF) on samples cut from the mid-point and end of the ingots. The Zn contents varied between 29 and 31%.

The orientation of each crystal was determined using the Laue back-reflection method of which the principles have been described in reference [62]. Following etching in a 30% HNO₃ + 70% H₂O solution during several minutes in order to remove possible surface contamination and deformation, the single crystal was placed in a goniometer, which allowed it to be rotated around two orthogonal axes. Then, Laue photos were made from which the crystal orientation was determined. Depending on the orientation of the crystal, the desired specimen orientation, and the expected material loss, a cutting scheme was designed. After the crystal had been brought in the desired orientation, the crystal in the goniometer was placed in a spark cutting machine, and slabs were cut having two parallel low index reference planes. Following mechanical polishing and etching in a 15% (NH₄)₂S₂O₈ solution, Laue photo's were made to verify
the orientation of the reference plane, and to determine the next cutting direction. After having been glued to a device which could be adapted to a low speed diamond saw, each slab was cut into specimens. The specimens then had dimensions of approximately 35 x 3 x 0.8-1.5 mm. The diamond saw was also used to cut a 0.4 mm deep notch in one of the small sides of specimens. Acetone was used to dissolve the glue after the cutting was finished. Mechanical polishing of the specimens with successively finer abrasives to 1 μm diamond paste, and subsequent etching in a 15% (NH₄)₂S₂O₈ solution were then performed, during all of which an attempt was made to minimise surface deformation. After Laue photo's had been made of some of the specimens, all specimens were sealed in quartz capsules under argon pressure, and homogenised at 850 °C for two weeks. Most specimens did not recrystallise during this heat treatment. In the instances where recrystallisation had occurred, this could easily be seen under the microscope without prior etching of the specimens.

Following the homogenising, the specimens were coated using an elastic and transparent rubber-like glue. Only the specimen ends (which were to be tightened in the grips) and the notch were left uncovered.

![Diagram](image)

**Figure 3.1** Schematic representation of the Bridgeman apparatus used to grow α-brass single crystals (not drawn to scale)
3.2 Tensile test system and corrosion test cell

The set-up used to perform the slow strain-rate (SRR) tests is depicted schematically in figure 3.2. A tensile testing system (Alfred J. Amsler & Co.) was used, where a DC motor was used to drive the crosshead (1) at a constant rate which could be varied between $3 \times 10^{-10}$ and $3 \times 10^{-7}$ m s$^{-1}$. A load cell (2) (Kyowa, type LT-100KF), suitable for loads up to 100 kg, was attached to the fixed end (3) of the tensile tester.

The tensile tester was equipped with devices (4) into which the corrosion test cell, assembled separately from the tensile tester, could be inserted as a unit. The specimen, (5) was tightened within stainless steel grips (6) which were inside fibre-glass grip holders (7), and where rubber caps were used to prevent contact of the grips with the solution. The grip holders were screwed on pull rods (8,9) of which the upper (8) was made of stainless steel and the lower (9) of zircalloy, where an oxide prevented electrical contact between the lower rod and the solution. The solution was kept within a HDPE (high density polyethylene) container (10) on which a transparent Plexiglas lid was screwed. The lower pull rod was fixed to the cell using a rubber O-ring (11), whereas the upper pull rod could move freely. The opening in the cell for the upper pull rod was also used as the outlet for the nitrogen gas which entered the cell at (12). For the connection of the specimen as a working electrode, the fibre glass grip holder contained a hidden contact between the stainless steel grip, and thus the specimen, and a wire (13) which led to a contact at the edge of the cell. The counter electrode was a platinum wire (14). A saturated calomel electrode (SCE) reference electrode (15) was placed in a separate container which was connected with the main cell using a tube which ended in a capillary (16) close to the notch in the specimen. In order to prevent distortion of the current measurements, the reference electrode compartment was placed in a steel Faraday cage (17). Shielded coaxial cables (18,19,20) were used for the connection of the three electrodes with a low noise, battery fed potentiostat (Jaisse, Model 1002, 1002T-NC). A computer controlled data acquisition system (Difa Measuring Systems, D_tac100, version 3.31) was used to record the load, current, and potential data. During an experiment the specimen, and in particular the position of the crack front was monitored using a high resolution video camera (magnification 100x).

Further experimental details are given in chapter 4 (section 4.2), chapter 5 (section 5.2), chapter 6 (section 6.2), and chapter 8 (section 8.2).
Figure 3.2 Schematic representation of the corrosion test cell used in the SSR tests (not drawn to scale)
4 Electrochemistry

4.1 Introduction

It is believed that the role of the electrochemical processes in SCC can only be studied if the electrochemical behaviour of the investigated material/environment combination is known. Therefore, a systematic study of the electrochemical behaviour of the pure Cu in NaNO₂ solutions as well as of Cu30Zn in NaNO₂ solutions has been made.

The electrochemistry at a flat electrode has been investigated using polarisation studies. These polarisation studies included linear sweep voltammetry at different rates and chronoamperometric experiments. In addition to these polarisation experiments the electrode surfaces have been analysed using a scanning electron microscope (SEM) and X-ray photoelectron microscopy (XPS). Analyses of the solution composition following polarisation have been performed as well. Based on the results obtained on flat electrodes, an attempt has been made to describe the electrochemistry in the crack tip area which is likely to be different from that at a flat electrode. These results have been used to evaluate which electrochemical processes occurring in the crack tip region can play a role in the SCC mechanism. The description of the crack tip chemistry is further used as a basis for an analysis of the transport processes in the crack which has been presented in chapter 8.

Literature on the electrochemical behaviour of the Cu/NaNO₂ and α-brass/NaNO₂ system

Transgranular stress corrosion cracking of copper and α-brass in NaNO₂ solutions has been reported to occur in the pH region between 6.2 and 12 and in the potential range between −200 and +250 mV SCE, but it has mostly been studied at potentials between −100 and +100 mV SCE [23,49,51,52,57,58,63-66]. In this system a surface film is formed which consists mainly of Cu₂O [56,67,68], which can be accompanied by ZnO (in the case of α-brass) and CuO at potentials equal or higher than +100 mV and +200 mV SCE respectively [67]. The majority of the studies on the Cu/NaNO₂ and α-brass/NaNO₂ systems report the presence of films which are dark and visible with the naked eye [23,57,64,66,67], having a thickness of several hundreds of nanometers [67]. It is noteworthy that the pH values in those studies are either equal or lower than 9 or not mentioned, in which case it is likely that they were in the same range. Potentiodynamic scans measured at low rates under those conditions seem to show features of "classic" passivating systems, i.e. starting from the rest potential in
the anodic direction, the current density shows an increase which is followed by a
decrease after which the current density remains constant until a second increase occurs
[57,64,66,68]. However, in the passive appearing potential domain, the value of the
current density remains higher than 100 μA·cm⁻², thereby indicating that only marginal
protection and "passivity" is achieved. In contrast to these results, potentiodynamic
scans measured in solutions with pH values of 10 and higher show a potential region
where the current densities have low and "passive" values [56,58]. These scans show a
breakdown potential which increases with increasing pH and decreasing NO₂
concentration, and above which a current rise occurs which is accompanied by the
formation of a visible, thick oxide [56,58]. The current responses at initially bare
surfaces have been studied by potential stepping [68] and by scratching and rapid
straining experiments [23,56,57,67,69]. Depending on the pH, the NO₂ concentration
and the applied potential, various sequences of decay rates are found [56,67], the decays
being the result of the oxide layer becoming more protective. In some instances an
initial decay is followed by a current increase which some workers attribute to the
occurrence of pitting [56]. However, Cassagne, who reports a current rise following an
initial decay in stepping experiments on Cu in 1 M NaNO₂ of pH = 9, attributes the
current rise to the breakdown of an initially passive film to form a thick precipitated
layer [68]. By combining these results with ellipsometric studies, he concludes that this
breakdown is a time dependent process, the required time for breakdown being shorter
for higher potentials [68]. Thus, based on these data, it is concluded that two different
morphologies of the oxide films can be present in the Cu/NaNO₂ and α-brass/NaNO₂
systems, i.e. the film may be thin and protective, and it may be thick and unprotective.
The thick and unprotective form is favoured by higher potentials, increasing NO₂
concentrations and decreasing values of the pH.

*Proposed relations between the electrochemical behaviour of the Cu/NaNO₂ and α-
brass/NaNO₂ system and SCC*

SCC cracking in the Cu/NaNO₂ and the α-brass/NaNO₂ systems is most likely related
to the conditions where the film is thick and porous. This is suggested by the fact that
the majority of the SCC studies on α-brass in NaNO₂ solutions do not even mention
the possibility of the two morphologies of the oxide, and only report the presence of
films which are dark and visible with the naked eye [23,57,64,66,67]. Studies
performed on α-brass at pH values of higher than 10, where the thick oxide is only
formed in localised areas, indicate that cracks are only present in those areas [58].
Conditions leading to a shift in the breakdown potential above which this localised
formation of thick oxide occurs, result in a similar shift of the critical potential for
cracking [58]. The observation that SCC is found under the conditions were the thick,
preumably precipitated, oxide forms, is particularly relevant for the application of the
film induced cleavage model, which attributes great importance to the properties of the
surface films [59,70], to this system. In order to attempt to apply this model to pure
Cu, where de-alloying is, obviously, impossible, it is speculated by some workers that
in this case a porous structure is formed at the metal-solution interface which would be the result of micro-pitting [68,71].

Many studies report an increase of the crack velocity with increasing potential and with increasing NO$_2$ concentration [23,52,56-58,64]. Since higher potentials and higher NO$_2$ concentrations are found to result in higher anodic reaction rates, it is commonly accepted that, like in other systems [22], the anodic reaction rate controls the crack velocity. However, there is no consensus about the nature of the processes associated with the anodic dissolution which are apparently controlling the crack velocity. From the point of view of the dissolution models [19,22,54,55], propagation of the crack is the anodic dissolution at the crack tip, and many attempts have been made to use Faraday's law to correlate the measured crack velocities with the current densities flowing at a bare surface, see section 2.5.1. Reasonable correlations are reported when this fresh surface is created by rapid straining [23,56-58]. However, these results are controversial due to the uncertainty in the estimation of the area of this freshly created surface [69]. From the point of view of the film-induced cleavage model, the anodic step comprises the formation of a film of a critical thickness, which is expected to occur faster at higher potentials [69]. In general, many other models comprise an anodic step, and it must be concluded that it is not possible to distinguish between those models on the basis of the observation of an increasing crack velocity with increasing potential, when the anodic step is rate-controlling.

Based on the idea that an intermediate repassivation rate is an essential requirement for crack propagation in anodic dissolution mechanisms, see section 2.5.1, the repassivation characteristics measured after rapid straining have been analysed [56]. That study, which was performed for different NO$_2$ concentrations at pH = 10, shows various slopes within one experiment, so that the interpretation is quite complex. In spite of these difficulties, the workers conclude that whenever SCC was found, regions of an intermediate repassivation rate are detected. A doubtful aspect of this work is that it does not take into account the fact that the pH value in the cracks is likely to be lower than 10, whereas the pH is known to influence the nature of the oxide and thus the repassivation characteristics. Similar to the idea of an intermediate repassivation rate, is the idea that the current density at a bare surface, $i_b$, should be higher than the current density at a filmed surface, $i_s$, which can be expressed in the ratio $i_b/i_s$. This ratio is reported to be higher than 10 whenever SCC is found [57].

Workers investigating the concept of the surface mobility model [16], speculate that an adsorbed layer of Cu(NO$_2$)$_2$ is present in the crack tip region which behaves like a low melting point compound [58].
4.2 Experimental

Polarisation studies
The polarisation experiments were carried out in a Greene-cell, which contained 0.7 dm³ test solution as well as the work electrode and two counter electrodes. A separate container containing a saturated calomel electrode was connected with the main cell using a salt bridge with a Haber-Luggin capillary which could be placed close to work electrode. Deaeration of the cell was obtained by bubbling N₂ gas through the solution. The solution was stirred using a magnetic stirring device. A computer controlled potentiostat, Eco®, type PGSTAT 20 was used in all experiments.

The copper was provided as a polycrystalline, 99.999% purity, cylindrical bar, annealed in an argon atmosphere at 550 °C during 12 hours. From this bar test cylinders were cut using a diamond blade. The Cu30Zn test material was available in the form of 99.99% purity, randomly oriented single crystalline slabs out of which test cylinders were obtained by spark machining. After an etching treatment, performed to remove the surface layer originating from the spark machining, the Cu30Zn cylinders were placed in a quartz tube backfilled with argon gas, and homogenised at 850 °C during 2 weeks. The Cu and Cu30Zn cylinders were soldered to wires and embedded in a resin. Only a circular area was then available to be exposed to the solution, with an surface area of 0.385 cm² for the Cu and varying between 0.20 and 0.34 cm² for the Cu30Zn. Extreme care was taken to avoid the presence of any crevice between the resin and the electrode. Before every experiment the electrodes were wet-ground down to 600 grit SiC paper, followed by mechanical polishing down to 1 μm using diamond paste. The last polishing step was followed by ultrasonically rinsing in alcohol after which the electrode was dried in a stream of air. The embedded specimen could be screwed on a holder. The Pt and Zn cylindrical test electrodes were not embedded in a resin and were directly screwed on a specimen holder consisting of stainless steel axis which was separated from the solution by a glass tube and a teflon ring.

All test solutions were prepared using milli-Q distilled water and analytical grade chemicals. A NaOH solution was used to bring the pH of the solution to the desired values of 9 or 11. In this respect it should be noted that the natural pH of the 1 M NaNO₂ and 1 NaAc solutions is already close to 9.

Prior to every experiment, the test solution was deaerated during at least 16 hours. The cell was then opened, and the work electrode, of which the last polishing step had been carried out less than 60 minutes before testing, was quickly immersed after which the cell was closed. In order to remove any oxide which may have formed during the exposure to air, a cathodic pretreatment was carried at a potential E = -800 mV SCE during 60 s. In potentiodynamic scanning experiments, the cathodic treatment was immediately followed by scanning in the anodic direction, starting from E = -800 mV SCE. In the case of the chronoamperometric experiments, the cathodic pre-treatment was followed by a period where the electrode was left at its rest potential until it had obtained a stable value, which was usually the case after 60 s. The potential was then instantaneously stepped from the rest potential to the value of interest. For each
potential two separate experiments were performed. The first experiment covered the first 10 seconds following the step, where the sampling rate was 0.002 s⁻¹. The second experiment covered the 10,000 seconds after the step where the sampling rate was 2 s⁻¹.

Analyses of the surface films
For the SEM and XPS studies on Cu and Cu30Zn surfaces following anodic polarisation, rectangular electrodes were used which were not embedded in a resin. These electrodes were coated using a rubber-like coating, leaving only one side exposed to the solution having an area of 0.50 cm². Following the polarisation experiment, the coating was removed by hand, which took a few seconds, and the electrode was rinsed with alcohol, dried in a stream of air, and stored in a deiccator before the SEM and XPS studies were performed.

Analyses of the solutions
Polarisation experiments which would be followed by analyses of the solution composition were performed using a cell containing a relatively small volume of solution (40 ml). This cell contained a polycrystalline work electrode with a relatively large exposed surface area (= 3 cm²) as well as the reference electrode. In order to minimise the possibility that the products of interest, formed at the work electrode, would react at the counter electrode and in order to be able to distinguish between pH changes resulting from reactions at the work electrode and those at the counter electrode, the counter electrode was placed in a separate compartment. The two compartments were connected with a salt bridge which contained the same solution as the test solution. This bridge retarded the transport of the species of interest between the two compartments without being able to avoid it completely. However, this set-up appeared to be suitable to obtain the desired information. It should be noted that this set-up can not be used if the currents become too high. Therefore, only relatively low overpotentials were applied which resulted in relatively low currents (< 1 mA).

The experiments were performed as follows. Immediately before filling the two compartments with the priory deaerated 1 M NaNO₂ test solution, the pH of the solution was measured. Then, the electrodes were immersed, and the polarisation experiment was started. This comprised either imposing a constant potential during 1000 s or scanning from the rest potential in the anodic direction to a given value. Immediately after the polarisation experiment, the pH was measured in both compartments, after which a fraction of the solution of the work electrode compartment was taken for the determination of the Cu and Zn content. These analyses were performed using either Atomic Adsorption Spectroscopy (AAS) or Inductively Coupled Plasma - Optic Emission Spectroscopy (ICP - OES).
4.3 Results

4.3.1 Electrochemical behaviour of Cu and Cu30Zn in 1 M NaNO₂ solutions of pH = 9

Polarisation studies
Figure 4.1 shows voltammograms for Pt, Zn, Cu and Cu30Zn electrodes in a deaerated 1 M NaNO₂ solution of pH = 9, obtained by scanning in the anodic direction from an initial potential of −800 mV SCE at a rate of 0.2 mV·s⁻¹. Of particular interest in the voltammograms is the potential domain for SCC for Cu and Cu30Zn, which has been indicated in figure 4.1.

The purpose of the measurement on Pt was to investigate the extent to which species in the solution react in the potential domain of interest. For Pt in this domain an anodic plateau appears to be present whose value is two or more orders of magnitude lower than the current densities measured for the other electrodes. Although the absence of high reaction rates of the NO₂ ions at a Pt electrode does not preclude their occurrence at other electrodes, it will be assumed that the current densities in the anodic domains of the other electrodes originate predominantly from the oxidation of the electrode material.

In the case of a Zn electrode the current density starts to increase strongly at a potential far below the domain for SCC. In the domain for SCC the current density remains high indicating that massive dissolution occurs. This is confirmed by the

![Voltammograms for Pt, Zn, Cu, and Cu30Zn in a deaerated 1 M NaNO₂ solution of pH = 9. The scan rate was 0.2 mV·s⁻¹.](image_url)
observation of white flakes in the solution, which presumably consist of ZnO or Zn(OH)$_2$ and by the fact that at the end of the experiment the electrode was partially dissolved. Thus, the ZnO or Zn(OH)$_2$ which is formed during anodic polarisation of Zn in 1 M NaNO$_2$ solution of pH = 9 appears not to be protective.

The voltammograms for the Cu and Cu30Zn electrodes show a rest potential which is usually around E = −250 mV SCE. Above the rest potential a quasi-Tafel region is found where the logarithm of the current density increases approximately linearly with increasing potential. In this region the initially bright electrode surface obtains a dull appearance and small gas bubbles are found to adhere at the Cu and Cu30Zn electrodes. At a potential of −100 mV SCE a plateau region starts where the current remains more or less constant, a factor 5 higher for Cu30Zn than for Cu. At the transition from the Tafel to the plateau region, the two electrodes are already completely dark brown or black indicating that a surface layer has already been formed in the Tafel region.

In the case of Cu30Zn the plateau region is followed by a sharp decrease of the current density at E = −20 mV SCE. This is followed by two peaks occur after which the current remains essentially constant, but at a lower level. If the solution is not stirred, an increase of the current is found starting at E = +150 mV SCE, which appears to be the result of the formation of large, shallow pits.

In the case of Cu, the current remains approximately constant until E = +100 mV SCE. At this potential the current density increases by three orders of magnitude forming a sharp peak. This peak is the result of copper entering the solution which was established by using atomic absorption spectrometry (AAS) to analyse the solution before and after the peak. After this large current peak the electrode is completely covered by a salt layer, which is presumably Cu(NO$_2$)$_2$. Despite the interesting phenomena occurring at potentials higher than +100 mV SCE, attention is focused on the potential region below this value, since this is the region where most of the SCC experiments have been done, both in the literature as well as in the present work.

Figure 4.2 shows the response of the current density for Cu and Cu30Zn electrodes following an instantaneous potential step from the rest potential a to more positive value in the range from −200 mV SCE to +100 mV SCE. After a first second where the current decreases with time, a period follows in which the current density stays constant or even increases slightly with time. In both periods the values of the current density are higher for higher potentials. After the period of approximately constant current density, the current density starts to decrease, the onset of which occurs earlier for higher potentials. The rate by which this decrease occurs is not constant within a same experiment and differs for the different potentials. For all potentials, the current density eventually reaches a "passive" value on the order of 1 μA·cm$^{-2}$. At all potentials the initially bright and shiny specimen surface becomes gradually more dull during the course of the experiment and is eventually dark brown or black. Except for the potential of −200 mV SCE gas bubbles adhering to the electrode are visible at all potentials.
Figure 4.2a-g  Current response for Cu and Cu30Zn in a deaerated 1 M NaNO₂, pH = 9 solution following stepping from the rest potential (−260 - −240 mV SCE) to a more positive value E in the domain of SCC.
Both the changing colour as well as the finally occurring decrease of the current density to a passive value strongly indicate that a film is formed at the potentials investigated. A remarkable feature is the presence of a period where the current does not decrease, thereby indicating that the film grows without becoming more protective. The charge densities passed until the onset of the final current decrease have been plotted as a function of the potential in figure 4.3a and vary between 0.02 and 0.05 C-cm\(^{-2}\) in most cases. These values indicate that approximately 120 to 300 atom layers must have been oxidised before further growth of the film results in an increase of the protection. A further indication of the poor protective properties of the film is given by the high charge densities which must pass until the passive values of the current density are achieved. The values of these, which have been given in figure 4.3b, are dependent on the potential and vary between 0.1 C-cm\(^{-2}\) and 1.5 C-cm\(^{-2}\), corresponding to the oxidation of ≈ 600 to 9000 atom layers.

The presence of a stage, where film growth occurs without this leading to an increase in protection against further oxidation, can also explain the counterintuitive observation that the formation of a film can give rise to a Tafel region in voltammograms. Figures 4.4a and 4.4b show voltammograms for Cu and Cu30Zn measured at different scan rates. Above the rest potential a Tafel region appears to be present in all cases of which the length increases with increasing scan rate, i.e. with increasing scan rate the potential where the current density deflects from its linear E vs. \(\log i\) relation shifts to higher values. This is consistent with the idea that the Tafel

\[\text{Figure 4.3a} \quad \text{Charge density passed until the current density, after having been approximately constant, starts to decrease in the chronoamperometric experiments of figure 4.2.}\]

\[\text{Figure 4.3b} \quad \text{Charge density passed until the current density has achieved a "passive value" (10}^{-6} \text{-} 10^{-5} \text{ A-cm}^{-2}\) in the chronoamperometric experiments of figure 4.2.}\]
Figure 4.4a Voltammograms for Cu in a deaerated 1 M NaNO₂ solution of pH = 9 for different scan rates.

Figure 4.4b Voltammograms for Cu30Zn in a deaerated 1 M NaNO₂ solution of pH = 9 for different scan rates.
region is associated with the stage in which the growth of the oxide does not result in protection against further corrosion and that the end of the Tafel region is determined by the end of this stage. If this end is related to a certain charge density which has passed, then a higher scan rate is expected to result in an elongation of the Tafel region, since, for a given E-i relation, the charge density passing during a scan between two potentials is lower for a higher scan rate. More support for the idea that the Tafel region corresponds to the stage where the growth of the oxide does not result in protection against further corrosion is given by the observation that the values of the current density in this stage in the chronoamperometric experiments correspond to the current densities in the Tafel regions of the voltammograms. This applies in particular for Cu30Zn.

**SEM and XPS studies**

The products which are present on the Cu and Cu30Zn electrodes in the various stages during the potentiodynamic scanning experiments of figure 4.1 were investigated by SEM and XPS after interrupting these scans at different potentials. Figures 4.5 and 4.6 show SEM photo's of the surfaces of Cu and Cu30Zn electrodes at the potentials E = −200, −100, and +100 mV SCE. On both materials grains appear to be formed. The grains found at E = −200 mV SCE are distributed more or less homogeneously over the surface. They do not touch each other and their size is on the order of 100 nm. At E = −100 mV SCE, which is approximately the transition from the Tafel region to the plateau region in the potentiodynamic scans, the surface is completely covered with grains. The grains impinge, and their size varies from 50 to 400 nm. At E = +100 mV SCE, the photo's do not differ significantly from those made at E = −100 mV SCE. It should be noted that it appeared to be more difficult to produce focused SEM photo's for Cu30Zn than for Cu. This may be the caused by differences in the film properties between the two materials, e.g. by a smaller conductivity in the case of Cu30Zn.

XPS analyses were performed after interrupting the scans at two different potentials, i.e. −100 mV SCE and +100 mV SCE. Except for one experiment, only the composition of the outer part of the films was determined, since the film thickness is much larger than the penetration depth of the beam, which is not more than 10 nm. In one experiment an attempt was made to obtain a qualitative idea of possible differences in composition between the outer part of the film and the inner part. For this purpose the specimen was polished under a low angle, so that the film was removed from a part of the surface. Then, the XPS analysis could be performed at the transition from metal to the film.
Figure 4.5 SEM photos of the oxide present on polycrystalline Cu after interrupting potentiodynamic scans at various potentials in a deaerated 1 M NaNO₂ solution of pH = 9. The start potential was – 800 mV SCE. The scan rate was 0.2 mV SCE. Figure 4.1 shows the voltammogram in this potential region.
Figure 4.6 SEM photos of the oxide present on single crystalline Cu30Zn after interrupting potentiodynamic scans at various potentials in a deaerated 1 M NaNO₂ solution of pH = 9. The start potential was −800 mV SCE. The scan rate was 0.2 mV SCE. Figure 4.1 shows the voltammogram in this potential region.
Table 4.1  XPS analyses of the surface films formed on Cu and Cu30Zn in a 1 M NaNO₂ solution of pH = 9 after potentiodynamic scanning at a rate of 0.2 mV·s⁻¹ from $E = -800$ mV SCE to an end potential. Except for the experiment indicated by *, the analyses were performed on the outer part of the film. The experiment indicated by * represents an analysis at the transition from the metal to the film.

<table>
<thead>
<tr>
<th>end pot. (mV SCE)</th>
<th>Cu</th>
<th>Cu⁺</th>
<th>Cu²⁺</th>
<th>Zn</th>
<th>Zn²⁺</th>
<th>O</th>
<th>O_con</th>
<th>N</th>
<th>C_con</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>-100</td>
<td>0</td>
<td>34</td>
<td>-</td>
<td>-</td>
<td>17</td>
<td>15</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>+100</td>
<td>0</td>
<td>45</td>
<td>1</td>
<td>-</td>
<td>16</td>
<td>17</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td>Cu30Zn</td>
<td>-100</td>
<td>0</td>
<td>33</td>
<td>0</td>
<td>3</td>
<td>21</td>
<td>9</td>
<td>1</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>+100</td>
<td>0</td>
<td>43</td>
<td>1</td>
<td>0</td>
<td>18</td>
<td>13</td>
<td>1</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>+100*</td>
<td>13</td>
<td>21</td>
<td>0</td>
<td>2</td>
<td>15</td>
<td>9</td>
<td>3</td>
<td>33</td>
</tr>
</tbody>
</table>

Table 4.1 shows the possible constituents of the film formed during the polariisation experiment, as well as certain contaminations on the surface, i.e. carbon resulting form the XPS equipment, indicated by C_{con}, and adsorbed oxygen, indicated by O_{con}. The measurements show little nitrogen which presumably originates from the nitrite ions in the solution. In all cases the film appears to contain oxygen and copper, the latter being predominantly present in the monovalent form and to a smaller extent in the divalent form. Therefore, it is concluded that the layer present on the Cu electrode consists predominantly of Cu₂O and to a much smaller extent of CuO. In the case of the Cu30Zn electrode, the film appears to contain a small amount of zinc as well, of which the form, ZnO or Zn(OH)₂, was not determined. The ratio zinc/copper in the film is much smaller than in the alloy, thereby indicating that most of the zinc has gone into the solution. The analysis of the transition from metal to oxide shows that Cu₂O still predominates over CuO in the inner part of the oxide, and the experiment further suggests that the zinc/copper ratio here in the transition domain is higher than in the outer part of film, but still lower than in the alloy.

Analyses of the solution

Tables 4.2 and 4.3 show the Cu and Zn concentrations in the 1 M NaNO₂ test solutions, c_{Cu,sol} and c_{Zn,sol}, as determined after anodic polarisation of Cu and Cu30Zn electrodes. The anodic treatment consisted of the application of a constant potential during 1000 s. In all cases the applied potentials are in the Tafel region as shown in figure 4.1. Tables 4.2 and 4.3 also show the charge which has flown during the anodic polarisation and which is associated with element Me (where Me can be Cu or Zn), Q_{Me,ox}, as well as the fraction of Q_{Me,ox} which is associated with the Me ions entering the solution following oxidation. The value of this fraction, f_{Me,sol}, teaches to which extent the oxidised Me ions enter the solution and to which extent they remain on the electrode surface, e.g. as an oxide, where f_{Me,sol} = 1 if all Me ions enter the solution, and f_{Me,sol} = 0 if all Me ions remain on the electrode surface.
Table 4.2  Cu concentration, $c_{Cu, sol}$, present in the solution after a charge $Q_{Cu, ox}$ had passed during polarising a Cu electrode (surface area = 3 cm$^2$) in a 1 M NaNO$_2$ solution (volume = 40 ml) at the indicated potentials during 1000 s. The calculation of $f_{Cu, sol}$ has been presented as well.

<table>
<thead>
<tr>
<th>pot. (mV$_{SCE}$)</th>
<th>$Q_{Cu, ox}$ (mC)</th>
<th>$c_{Cu, sol}$ (µmol·l$^{-1}$)</th>
<th>$Q_{Cu,sol.}$ (mC)</th>
<th>$Q_{Cu}^+$ (µmol/l)</th>
<th>$Q_{Cu}^{2+}$ (µmol/l)</th>
<th>$f_{Cu, sol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 160</td>
<td>86.3</td>
<td>1.1</td>
<td>4.2</td>
<td>(8.5)</td>
<td>0.049</td>
<td>(0.098)</td>
</tr>
<tr>
<td>- 140</td>
<td>96.5</td>
<td>1.7</td>
<td>6.6</td>
<td>(13.1)</td>
<td>0.068</td>
<td>(0.14)</td>
</tr>
<tr>
<td>- 120</td>
<td>173</td>
<td>2.5</td>
<td>9.7</td>
<td>(19.3)</td>
<td>0.056</td>
<td>(0.11)</td>
</tr>
</tbody>
</table>

Table 4.3  Cu and Zn concentrations, $c_{Cu, sol}$ and $c_{Zn, sol}$, present in the solution after a total charge $Q_{sum, ox}$ had passed during polarising a Cu30Zn electrode (surface area = 3 cm$^2$) in a 1 M NaNO$_2$ solution (volume = 40 ml). The calculation of $f_{Cu, sol}$ and $f_{Zn, sol}$ has been presented as well.

<table>
<thead>
<tr>
<th>pot. (mV$_{SCE}$)</th>
<th>$Q_{sum, ox}$ (mC)</th>
<th>$Q_{Cu, ox}$ (mC)</th>
<th>$Q_{Zn, ox}$ (mC)</th>
<th>$c_{Cu, sol}$ (µmol/l)</th>
<th>$c_{Zn, sol}$ (µmol/l)</th>
<th>$Q_{Cu,sol.}$ (mC)</th>
<th>$Q_{Zn,sol.}$ (mC)</th>
<th>$f_{Cu, sol}$</th>
<th>$f_{Zn, sol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 140</td>
<td>448</td>
<td>241</td>
<td>207</td>
<td>2.4</td>
<td>32</td>
<td>9.1</td>
<td>248</td>
<td>0.038</td>
<td>1.2</td>
</tr>
<tr>
<td>- 120</td>
<td>489</td>
<td>263</td>
<td>226</td>
<td>3.1</td>
<td>42</td>
<td>12</td>
<td>320</td>
<td>0.046</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The value of $f_{Me, sol}$ has been calculated as follows.

$$f_{Me, sol} = \frac{Q_{Me, sol}}{Q_{Me, ox}} \quad (4.1)$$

where:

$Q_{Me, sol.}$ = charge associated with the element Me in the solution
$Q_{Me, ox.}$ = total charge associated with the oxidation of element Me

$Q_{Me, sol.}$ can be calculated by using equation 4.2.

$$Q_{Me,sol.} = z_{Me,sol.} F V_{cell} c_{Me,sol.} \quad (4.2)$$

where:

$z_{Me,sol.}$ = number of electrons per reacting Me entering the bulk solution
$F$ = Faraday's number (9.65·10$^4$ C·mol$^{-1}$)
$V_{cell}$ = volume of the work electrode compartment (40 ml in the current set-up)
$c_{Me,sol.}$ = Me concentration in the bulk solution after anodic polarisation
It will be assumed that no other reactions occur but the oxidation of the metal. Then, in the case of a copper electrode, \( Q_{Cu,ox} \) is equal to the total charge which has flown during the experiment, \( Q_{sum,ox} \). The value for \( Q_{sum,ox} \) is obtained by integrating the current over the time during the polarisation. However, in the case of a Cu30Zn electrode \( Q_{Cu,ox} \) and \( Q_{Zn,ox} \) have to be calculated by combining equations 4.3 and 4.4.

\[
Q_{sum,ox} = Q_{Cu,ox} + Q_{Zn,ox}
\]

\[
\frac{Q_{Zn,ox}}{Q_{Cu,ox}} = \frac{x_{Zn} \cdot z_{Zn}}{x_{Cu} \cdot z_{Cu}}
\]

where:

\( x_{Zn}/x_{Cu} \) = ratio of the number of Zn and Cu atoms being oxidised. This ratio is assumed to be equal to the ratio of these elements in the alloy, i.e. 0.7/0.3.

\( z_{Zn}, z_{Cu} \) = charge per reaction atom Zn, Cu respectively.

Table 4.2 shows the results of the calculations \( f_{Cu,sol} \) for a Cu electrode. Since the oxidation state of Cu in the solution can not be determined with the techniques used, the values for \( Q_{Cu,sol} \) have been calculated for the possibility that all Cu in the solution would be in the monovalent state \( (z_{Cu,sol} = 1) \) as well as for the possibility all Cu in the solution would be in the divalent state \( (z_{Cu,sol} = 2) \). In table 4.2, it can be seen that \( f_{Cu,sol} = 0.058 \) if \( z_{Cu,sol} = 1 \) and 0.115 if \( z_{Cu,sol} = 2 \). Thus, 88.5% to 94.2% percent of the charge associated with the oxidation of Cu is used to form the surface layer.

Table 4.3 shows the results of the calculation of \( f_{Cu,sol} \) and \( f_{Zn,sol} \) in the case of Cu30Zn electrode. The value for \( z_{Cu} \) is assumed to be equal to 1. The value for \( z_{Zn} = 2 \). According to the calculations, \( f_{Cu,sol} \) is equal to 0.041. This value is slightly lower than the value obtained for a pure Cu electrode. The ratio \( f_{Zn,sol} \) appears to be 1.3. This is certainly not a realistic value, since it is impossible that the total charge of the zinc in the solution exceeds the charge used during its formation. However, these measurements support the results of the XPS analyses of the surface film which showed that the Cu2O film is depleted of Zn, thereby indicating that the Zn must thus have entered the solution.

The fact that the calculated value for \( f_{Zn,sol} \) appears to be higher than 1, indicates that the value for \( Q_{Zn,ox} \) is higher than the value calculated using equations 4.3 and 4.4. Equation 4.4 shows which factors can result in a higher value of \( Q_{Zn,ox} \). The most likely possibility is that the ratio \( x_{Zn}/x_{Cu} \) is actually higher than the ratio in the alloy, which would mean that the fraction of zinc which is oxidised is higher than the fraction of zinc in the alloy and thus that dealloying would occur. This would not be surprising, since dealloying of Cu30Zn is a very common phenomenon.
Tables 4.4 and 4.5 show the values for the pH in the solution before and after the polarisation experiments indicated in tables 4.2 and 4.3. In all cases, the occurrence of the anodic reaction results in a decrease of the pH, which is consistent with the formation of an oxide according to the formation of Cu₂O according to 2 Cu + H₂O → Cu₂O + 2 H⁺ + 2 e⁻. In the cathode department the pH increases, presumably due to the reduction of NO₂ or H₂O.

Table 4.4 pH before and after the experiments indicated in Table 4.2

<table>
<thead>
<tr>
<th>potential (mV SCE)</th>
<th>Q_sum (mC)</th>
<th>pH_start</th>
<th>pH_end</th>
</tr>
</thead>
<tbody>
<tr>
<td>-160</td>
<td>86.3</td>
<td>8.2</td>
<td>7.6</td>
</tr>
<tr>
<td>-140</td>
<td>96.5</td>
<td>8.2</td>
<td>7.4</td>
</tr>
<tr>
<td>-120</td>
<td>173</td>
<td>8.2</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Table 4.5 pH before and after the experiments indicated in Table 4.3

<table>
<thead>
<tr>
<th>potential (mV SCE)</th>
<th>Q_sum (mC)</th>
<th>pH_start</th>
<th>pH_end</th>
</tr>
</thead>
<tbody>
<tr>
<td>-140</td>
<td>152</td>
<td>8.8</td>
<td>8.4</td>
</tr>
<tr>
<td>-120</td>
<td>448</td>
<td>8.2</td>
<td>7.4</td>
</tr>
<tr>
<td>-100</td>
<td>489</td>
<td>8.7</td>
<td>8.0</td>
</tr>
</tbody>
</table>

4.3.2 The influence of the nitrite concentration and the pH

Figure 4.7 shows the voltammograms for Cu electrodes in 1 M Na₂SO₄, NaNO₃, and NaAc solutions of pH = 9, measured by scanning at a rate of 0.2 mV·s⁻¹. In these solutions a current plateau is present below E = 0 mV SCE, where the current density is a factor 40 to 100 lower than in the case of a 1 M NaNO₂ solution. In the plateau regions in the Na₂SO₄, NaNO₃, and NaAc solutions the appearance of the electrode remains unchanged, in contrast to the situation in the NaNO₂ solution, where the electrode obtains a dark appearance. For the Na₂SO₄, NaNO₃ solutions the current density shows a strong rise above E = 0 mV SCE which continues until the end of the experiment. This is probably related to the oxidation of Cu to Cu²⁺, since the equilibrium potential of this reaction is just below the potential where the rise of the current density starts. At the end of these experiments the electrode appears to have become thinner, which effect could be seen with the naked eye, thereby indicating that massive dissolution has occurred. In the case of NaAc solutions a current rise occurs above E = + 100 mV SCE. Inspection with an optical microscope revealed that this rise is due to the occurrence of extensive pitting.

The influence of the NO₂ ions on the electrochemical behaviour of Cu and Cu30Zn was also studied by varying the NO₂ concentration. Figures 4.8a and b show the voltammograms for Cu and Cu30Zn in 0.1 M and 1 M NaNO₂ solutions, measured by scanning at a rate of 0.2 mV·s⁻¹. In the potential domain above the rest potential, where the current increases strongly with increasing potential, the current densities are a factor 10 to 20 lower for the 0.1 M solution. Darkening of the electrode surface occurs, but to a smaller extent than in the 1 M solution. In the 0.1 M solution the current density shows a maximum at E = -50 mV SCE, after which it decreases strongly, thereby indicating that protection against further oxidation is achieved. In the case of
the 1 M solutions this decrease does not occur for Cu and only occurs for Cu30Zn after a much higher charge density has passed. Since, except for the Zn in the case of Cu30Zn, the charge is predominantly used for the formation of the film, it can be concluded that, in this potential domain, further oxidation is retarded by a significantly smaller thickness of the film in the 0.1 M solution. However, above $E = +50$ mV SCE, the current density rises again which is presumably due to the further growth of the porous film, which is indicated by a further increase of the darkness of the electrodes.

Figures 4.9a and b reveal the influence of the NO$_2$ concentration on the voltammograms for Cu and Cu30Zn, measured at a relatively high scan rate, i.e. 20 mV·s$^{-1}$. It can clearly be seen that the current densities increase with increasing NO$_2$ concentration.

Figures 4.10a and b show voltammograms for Cu an Cu30Zn respectively, measured in 1 M NaNO$_2$ solutions for pH values of 9 and 11. For the solution of pH = 11 the voltammograms show a lower rest potential than for the solution of pH = 9. Above the rest potential the voltammograms measured at pH = 11 show a plateau in which the current density is 1 to 2 orders of magnitude lower than in the same potential domain for pH = 9. In this plateau domain, the electrode becomes slightly dull, but it does not obtain the dark appearance which is found in the same potential domain for pH = 9. Upon exceeding a "breakdown" potential the current density starts to rise quickly, which is accompanied by the formation of a visible, black layer on the electrode surface.

![Figure 4.7](image.png)  
**Figure 4.7** Voltammograms for Cu in deaerated 1 M NaNO$_2$, NaNO$_3$, Na$_2$SO$_4$, and NaAc solutions of pH = 9, measured at a scan rate of 0.2 mV·s$^{-1}$. 
**Figure 4.8a** Voltammograms for Cu in deaerated 0.1 M and 1 M NaNO₂ solutions of pH = 9, measured at a scan rate of 0.2 mV·s⁻¹.

**Figure 4.8b** Voltammograms for Cu30Zn in deaerated 0.1 M and 1 M NaNO₂ solutions of pH = 9, measured at a scan rate of 0.2 mV·s⁻¹.
Figure 4.9a Voltammograms for Cu in deaerated NaNO₂ solutions of various concentrations, measured at a scan rate of 20 mV·s⁻¹. pH = 9.

Figure 4.9b Voltammograms for Cu30Zn in deaerated NaNO₂ solutions of various concentrations, measured at a scan rate of 20 mV·s⁻¹. pH = 9.
Figure 4.10a Voltammograms for Cu in deaerated 1 M NaNO₂ solutions of pH = 11 and pH = 9, measured at a scan rate of 0.2 mV s⁻¹.

Figure 4.10b Voltammograms for Cu₃₀Zn in deaerated 1M NaNO₂ solutions of pH = 11 and pH = 9, measured at a scan rate of 0.2 mV s⁻¹.
4.3.3 **Reactions, equilibria and mass transport**

In this section, reactions which are thought to be relevant in the Cu/NaNO$_2$ and CuZn/NaNO$_2$ systems will be described. Then, analyses will be made of the mass transport resulting from the occurrence of some of these reactions. These analysis show for which reactions the maximum possible transport rates are sufficient to be able to account for the measured reaction rates. These analyses further show that the NO$_2^{-}$ ions play a necessary role in mass transport without which the measured reaction rates cannot be obtained.

**Reactions and equilibria**

Reactions which are thought to be relevant will be given below. Values for the equilibrium potential $E$ are always given in Volts with respect to the Saturated Calomel Electrode (SCE).

An extensive treatment of the chemistry of NO$_2^{-}$ solutions can be found in references [72-74]. For the present work the following reactions are considered to be relevant.

$$H^+ + NO_2 \rightleftharpoons HNO_2 \quad K_5 = \frac{a_{HNO_2}}{a_{H^+} \cdot a_{NO_2}} = 10^{3.35} \quad (4.5)$$

$$3HNO_2 \rightleftharpoons H^+ + NO_3^- + 2NO (g) + H_2O \quad K_6 = \frac{a_{H^+} \cdot a_{NO_3} \cdot a_{H_2O}^2}{a_{HNO_2}^3} = 10^{1.72} \quad (4.6)$$

Reaction 4.5 explains why the pH of an initially neutral solution shifts from 7 to approximately 9 after addition of NaNO$_2$ to form a 1 M solution. The occurrence of the dissociation reaction 4.6, where NO can escape as a gas, is favoured by lower values of the pH and results in instability of acidic NO$_2$ containing solutions, so that it is impossible to work at low values of the pH.

Copper can dissolve as a cuprous and cupric ion, see equations 4.7 and 4.8. Cupric ions can form complexes with nitrite ions, see equations 4.9, 4.10 and 4.11.

$$Cu \rightleftharpoons Cu^+ + e^- \quad E_{Cu/Cu^+} = 0.279 + 0.0591 \cdot \log a_{Cu^+} \quad (4.7)$$

$$Cu \rightleftharpoons Cu^{2+} + 2e^- \quad E_{Cu/Cu^{2+}} = 0.096 + 0.0295 \cdot \log a_{Cu^{2+}} \quad (4.8)$$

$$Cu^{2+} + NO_2 \rightleftharpoons Cu(NO_2)^+ \quad K_9 = \frac{a_{Cu(NO_2)^+}}{a_{Cu^{2+}} \cdot a_{NO_2}} = 10^{1.26} \quad (4.9)$$

$$Cu^{2+} + 2NO_2 \rightleftharpoons Cu(NO_2)_2 \quad K_{10} = \frac{a_{Cu(NO_2)_2}}{a_{Cu^{2+}} \cdot a_{NO_2}^2} = 10^{1.48} \quad (4.10)$$

$$Cu^{2+} + 3NO_2 \rightleftharpoons Cu(NO_2)_3 \quad K_{11} = \frac{a_{Cu(NO_2)_3}}{a_{Cu^{2+}} \cdot a_{NO_2}^3} = 10^{1.08} \quad (4.11)$$
Reactions involving Cu₂O and CuO are given by equations 4.12, 4.13, 4.14, and 4.15. The formation of Cu(OH)₂, which is less stable than CuO [75], has not been considered in the present work.

\[
\begin{align*}
2 \text{Cu} + \text{H}_2\text{O} &\iff \text{Cu}_2\text{O} + 2 \text{H}^+ + 2 \text{e}^- & E_{\text{Cu/Cu}_2\text{O}} &\iff 0.230 - 0.0591 \cdot \text{pH} \quad (4.12) \\
\text{Cu}_2\text{O} + \text{H}_2\text{O} &\iff 2 \text{CuO} + 2 \text{H}^+ + 2 \text{e}^- & E_{\text{Cu}_2\text{O/CuO}} &\iff 0.428 - 0.0591 \cdot \text{pH} \quad (4.13) \\
\text{Cu}_2\text{O} + 2 \text{H}^+ &\iff 2 \text{Cu}^{2+} + \text{H}_2\text{O} + 2 \text{e}^- & E_{\text{Cu}_2\text{O/Cu}^{2+}} &\iff -0.038 + 0.0591 \cdot \text{pH} + 0.0591 \cdot \log a_{\text{Cu}^{2+}} \quad (4.14) \\
\text{Cu}^{2+} + \text{H}_2\text{O} &\iff \text{CuO} + 2 \text{H}^+ & K_{15} = \frac{a_{\text{Cu}^{2+}}}{a_{\text{H}^+}} &\iff 10^{7.89} \quad (4.15)
\end{align*}
\]

Figure 4.11 represents the Pourbaix diagram for copper which has been constructed by using the equations 4.8 through 4.15. The lines which are not bold and which border the Cu²⁺ domain represent the case where no NO₂ is present and where the Cu²⁺ activity is equal to 10⁻⁶. The bold lines represent the case where the NO₂ activity is equal to 1 and where the sum of the activities of the Cu(NO₂)²⁻(x⁻) species is equal to 10⁻⁶. Figure 4.12 shows the Pourbaix diagram for zinc [75], where the Zn²⁺ activity is equal to 10⁻⁶.

**Figure 4.11** Pourbaix diagram for Cu. The thin lines surrounding the Cu²⁺ domain are valid in the absence of NO₂ for a Cu²⁺ activity of 10⁻⁶. The bold lines apply for a 1 M NO₂ containing solution where the sum of the Cu²⁺ and Cu(NO₂)²⁻(x⁻) activities is equal to 10⁻⁶.

**Figure 4.12** Pourbaix diagram for Zn, calculated for a Zn²⁺ activity of 10⁻⁶.
Figure 4.11 shows that the presence of the NO$_2^-$ ion results in an enlargement of the domain where the dissolved Cu(NO$_2$)$_{x}^{(2-x)+}$ species is stable and in a reduction of the domains of stability for Cu, Cu$_2$O and CuO. However, as has been indicated by the dashed lines which represent the anodic domains up to $E = +100$ mV SCE in the polarisation curves in figures 4.1 and 4.10, Cu$_2$O and CuO are still the stable species at these potentials for pH = 9 and pH = 11. Therefore, the main conclusion from figure 4.11 is that it is not surprising that the anodic current densities in the polarisation curves up to $E = +100$ mV SCE are found to originate predominantly from the formation of a copper oxide, except for the current densities associated with the oxidation of zinc in the case of brass. It should be noted that at potentials above –104 mV SCE for pH = 9, CuO is stable instead of Cu$_2$O which was found by the XPS measurements. This is understandable, since there is much evidence that the formation of CuO is preceded by the formation of Cu$_2$O [75], so that the predominance of Cu$_2$O at the higher potentials may be a matter of kinetics. Figure 4.12 shows that Zn(OH)$_2$ and HZnO$_2$ are the stable species at the potentials and pH values where the polarisation curves in figures 4.1 and 4.10 show an anodic domain. Apparently the biggest fraction of the Zn(OH)$_2$ is not incorporated in the surface layer as is indicated by the XPS measurements and by the analyses of the solution composition.
Mass transport
If there are uncertainties about the occurring reactions at the electrode, knowledge of the maximum transport rates of the species involved in a given reaction can be helpful in determining if a measured current density can be attributed to that reaction alone. Therefore, a description of the mass transport occurring during the stationary flow of the reactions mentioned above as well as a calculation of the maximum transport rates of the species involved in those reactions will now be provided. This description will be based on the diffusion layer model by Nernst, where it is assumed that diffusion is restricted to a stagnant layer adjacent to the electrode in which mixing by convection does not occur and where diffusion only takes place in the direction perpendicular to the electrode. In the solution outside this layer perfect mixing is assumed to take place. If solute transport by migration is neglected, the particle flux, as calculated by Fick's first law, is proportional to the concentration gradient in the Nernst diffusion layer, see formula 4.16. The current density corresponding to this flux can be calculated by Faraday's law, see formula 4.17.

\[ J_x = D_x \frac{c_x^{\text{electr}} - c_x^{\text{bulk}}}{\delta} \]  
\[ i = n_x F J_x \]

where:

- \( J_x \) = flux of species x
- \( D_x \) = diffusion coefficient of species x
- \( c_x^{\text{electr}} \) = concentration of species x at the electrode
- \( c_x^{\text{bulk}} \) = concentration of species x in the bulk solution
- \( \delta \) = thickness of the Nernst diffusion layer
- \( i \) = current density
- \( n_x \) = number of electrons transferred per reacting particle x
- \( F \) = Faraday's number (9.65 \times 10^4 \text{ C mol}^{-1})
Figure 4.13 Schematic representation of the stationary concentration profiles during the anodic dissolution of Cu, where reactions 4.7 - 4.11 occur.

Figure 4.14 Maximum current densities for Cu in a 1 M NaNO₂ solution, corresponding to the maximum transport rates, calculated for the situation depicted in figure 4.13, where \( c_{\text{bulk}}^{\text{Cu}^{2+}} = 0 \), \( D_x = 10^{-9} \text{ m}^2\text{s}^{-1} \), and \( \delta = 5 \times 10^{-5} \text{ m} \). Both the voltammograms from figure 4.1, measured at a scan rate of 0.2 mV s⁻¹, and the current densities at \( t = 1 \text{ s} \) in the chronoamperometric experiments from figure 4.2 have been plotted for Cu and Cu30Zn in a 1 M NaNO₂ solution of pH=9. The calculated lines also represent the "equilibrium concentrations" where the y-axis gives the values corresponding to the calculated lines for the divalent Cu(NO₂)₂⁺⁻³ species. In order to obtain the equilibrium concentrations corresponding to the calculated line for the monovalent Cu⁺ species the values at the y-axis have to be multiplied by 2.
Figure 4.13 shows a schematic representation of the stationary concentration profiles for the situation where dissolution of Cu occurs to form Cu\(^+\) and Cu\(^{2+}\) according to reactions 4.7 and 4.8 respectively, and where the NO\(_2\) forms complexes with Cu\(^{2+}\) according to reactions 4.9, 4.10, and 4.11. For the diffusion of Cu\(^+\) from the electrode a concentration gradient is established involving this species alone. However, since the Cu\(^{2+}\) can form complexes with NO\(_2\), transport of Cu\(^{2+}\) from the electrode can occur by diffusion of Cu\(^{2+}\) as well as by diffusion of Cu(NO\(_2\))\(_x\)(2-x)\(^+\). The oxidation reactions to form Cu\(^+\) and Cu\(^{2+}\) can not proceed if the increase of the Cu\(^+\) and Cu\(^{2+}\) concentrations at the electrode results in an increase of the corresponding equilibrium potential which exceeds the applied potential. Thus for each value of the potential the maximum possible concentration gradients, for Cu\(^+\) and Cu\(^{2+}\) can be calculated, when the equilibrium activities for these species as calculated by the Nernst equation are used to approximate the maximum concentration at the electrode. The maximum possible concentration gradients for the Cu(NO\(_2\))\(_x\)(2-x)\(^+\) complexes can be approximated by using the equilibrium constants from equations 4.9, 4.10, and 4.11 to calculate the Cu(NO\(_2\))\(_x\)(2-x)\(^+\) activities corresponding to the maximum Cu\(^{2+}\) activity for a given potential. For the latter calculation neglecting the decrease of the NO\(_2\) concentration at the electrode seems to be plausible as long as the as the values for the Cu(NO\(_2\))\(_x\)(2-x)\(^+\) concentration are of a lower order of magnitude than the bulk NO\(_2\) concentration.

Using formulas 4.16a and 4.17a the maximum transport rates and the corresponding current densities can be calculated for the situation described above. The results have been plotted in figure 4.14 for a 1 M NaNO\(_2\) solution using the following values, i.e.

\[ c_{\text{Cu}^+}^{\text{bulk}}, c_{\text{Cu}^{2+}}^{\text{bulk}} = 0, D_x = 10^{-9} \text{ m}^2\text{s}^{-1},\text{ and } \delta = 5 \times 10^{-5} \text{ m}. \]

\[ J_x^{\text{max}} = D_x \frac{\delta c_x^{\text{eq}} - c_x^{\text{bulk}}}{\delta} \quad (4.16a) \]

\[ I_{\text{sum}}^{\text{max}} = F \left( J_{\text{Cu}^+}^{\text{max}} + 2 \cdot J_{\text{Cu}^{2+}}^{\text{max}} + 2 \cdot J_{\text{Cu(NO}_2\text{)}_x}^{\text{max}} + 2 \cdot J_{\text{Cu(NO}_2\text{)}_2}^{\text{max}} + 2 \cdot J_{\text{Cu(NO}_2\text{)}_3}^{\text{max}} \right) \quad (4.17a) \]
Figure 4.15 Schematic representation of the stationary concentration profiles during Cu$_2$O formation, where reactions 4.12, 4.5, and 4.18 occur.

Figure 4.16 Maximum current densities for Cu in a 1 M NaNO$_2$ solution, corresponding to the maximum transport rates, calculated for the situation depicted in figure 4.15, where $c_{\text{H}^+}^{\text{bulk}} = 10^{-9}$ mol·l$^{-1}$, $c_{\text{H}^+}^{\text{bulk}} = 10^{-5}$ mol·l$^{-1}$, $D_{\text{NO}_2^{-}HNO_2} = 10^{-9}$ m$^2$·s$^{-1}$, $D_{\text{H}^+} = 10^{-8}$ m$^2$·s$^{-1}$, $D_{\text{OH}^-} = 5 \times 10^{-9}$ m$^2$·s$^{-1}$ and $\delta = 5 \times 10^{-5}$ m. Both the voltammograms from fig. 4.1, measured at a scan rate of 0.2 mV·s$^{-1}$, and the current densities at $t = 1$ s in the chronoamperometric experiments from fig. 4.2 have been plotted for Cu and Cu30Zn in a 1 M NaNO$_2$ solution of pH = 9. The calculated lines for H$^+$ and HNO$_2$ also represent the "equilibrium concentrations" where the y-axis gives the values corresponding to the calculated H$^+$ line. In order to obtain the equilibrium concentrations corresponding to the calculated HNO$_2$ line, the values at the y-axis have to be multiplied by 10.
Figure 4.15 shows the stationary concentration profiles at the electrode which correspond to the following situation for the formation of Cu$_2$O according to reaction 4.12. The occurrence of reaction 4.12 results in the production of H$^+$ ions. The diffusion of H$^+$ from the electrode can occur as H$^+$ itself, and as HNO$_2$ after reaction with NO$_2$ according to reaction 4.5. This situation results in an increase of the H$^+$ and HNO$_2$ concentrations and in a decrease of the NO$_2^-$ concentration at the electrode. Removal of H$^+$ from the electrode can also occur according to reaction 4.18, resulting in a decrease of the OH$^-$ at the electrode.

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad (4.18) \]

If the pH at the electrode decreases to such an extent that the equilibrium potential exceeds the applied potential, reaction 4.12 can not proceed. Thus, for each potential a maximum H$^+$ concentration and a minimum OH$^-$ concentration at the electrode can be calculated by the Nernst equation. By using the equilibrium constant from equation 4.5, the maximum HNO$_2$ concentration corresponding to the maximum H$^+$ concentration can be calculated. For the calculation of the latter neglecting the decrease of the NO$_2^-$ concentration at the electrode is considered to be plausible as long as the calculated values for HNO$_2$ are of a lower order of magnitude than the NO$_2$ concentration. In all calculations the concentrations are assumed to be equal to the activities.

Using formulas 4.16a and 4.17b the maximum transport rates and the corresponding current densities can be calculated for the situation described above. The results have been plotted in figure 4.16 for a 1 M NaNO$_2$ solution of pH = 9 using the following values, i.e. $c_\text{H}^\text{bulk} = 10^{-9}$ mol·l$^{-1}$, $c_\text{OH}^\text{bulk} = 10^{-5}$ mol·l$^{-1}$, $D_\text{H}^+ = 10^{-8}$ m$^2$·s$^{-1}$, $D_\text{OH}^- = 5·10^{-9}$ m$^2$·s$^{-1}$, $D_{\text{NO}_2\text{HNO}_2} = 10^{-9}$ m$^2$·s$^{-1}$, and $\delta = 5·10^{-5}$ m.

\[ j_{\text{sum}}^{\text{max}} = F\cdot(J_{\text{H}^+}^{\text{max}} + J_{\text{HNO}_2}^{\text{max}} - J_{\text{OH}^-}^{\text{max}}) \quad (4.17b) \]

Figures 4.14 and 4.16 also show a part of the voltammograms from figure 4.1 as well as the current densities at $t = 1$ s in the chronoamperometric experiments from figure 4.2, all measured for Cu and Cu30Zn in a 1 M NaNO$_2$ solution of pH = 9. From figure 4.14 it becomes clear that the dissolution of Cu as Cu$^2+$, Cu$^{2+}$, and Cu(NO$_2$)$_2^{(2-x)+}$ alone can not account for the measured current densities, since the latter exceed the maximum possible current densities by far. However, the Cu$_2$O formation reaction in combination with reactions 4.5 and 4.18 can account for the measured current densities, since the latter are on the same order as the maximum possible current densities. Thus, these calculations are consistent with the observation that the formation of an oxide occurs instead of the dissolution of Cu dissolution of Cu as Cu$^2+$, Cu$^{2+}$, and Cu(NO$_2$)$_2^{(2-x)+}$. It can further be concluded that the oxide formation reaction gives an opportunity for the occurrence of high reaction rates in the lower potential domain, which does not exists at lower values of the pH, where the formation of the oxide is impossible.
It should be noted that in the absence of NO₂, in which case reaction 4.5 is not available, the maximum possible current densities are much lower if an alternative for reaction 4.5 is not available, so that it would then be impossible to obtain the current densities which are found in the Cu/NaNO₂ system. An alternative for reaction 4.5 is not available in the case of NaNO₃ and Na₂SO₄ solutions, so that the reaction rates found for the Cu and Cu30Zn in a 1 M NaNO₂ solutions are not possible in those systems and are also not found, see figure 4.7. In the case of NaAc solutions, an alternative for reaction 4.5 is available, i.e.

\[ H^+ + Ac^- = HAc \quad K_{19} = \frac{[HAc]}{[H^+][Ac^-]} = 10^{4.75} \] (4.19)

However, despite the fact that the possibilities for solute transport in NaNO₂ and NaAc solutions are comparable, the current densities in former system are two orders of magnitude higher than in the latter, see figure 4.7. This shows that possibilities for solute transport are necessary, but not always sufficient to obtain high reaction rates.

The observation that the measured current densities in the Cu/NaNO₂ system are of the same order of magnitude as the calculated maximum current densities indicate that the diffusion rates must dominate the reaction rates. This suggests that the current densities should be dependent on stirring. A higher stirring rate has indeed the effect of higher current densities. However, since the reaction under study is an oxide formation reaction, this effect may also be due to an effect of the stirring on the oxide formation process, which is particularly likely if the oxide is formed by a dissolution-precipitation process. Thus, this experiment gives no proof for the idea that the reaction is under diffusion control. Another reason why the reaction would not be under diffusion control, is the possibility that reaction 4.6 follows reaction 4.12 and 4.5, which results in the following sum reaction.

\[ 2 \text{Cu} + 3 \text{NO}_2 \rightarrow \text{Cu}_2\text{O} + \text{NO}_3 + 2 \text{NO (g)} + 2 \text{e}^- \] (4.20)

For this reaction diffusion restrictions only occur if the NO₂ becomes depleted at the electrode, which occurs, in the case of a 1 M solution, at high reaction rates. The likelihood of the occurrence of reaction 4.6 is big, since gas bubbles are mostly found to adhere to the electrode during anodic polarisation. However, no information is available on the rate by which reaction 4.6 occurs. If the rate of reaction 4.6 is high, diffusion restrictions are only expected if a NO₂ depletion occurs at the electrode, which occurs at high reaction rates. If the rate of reaction 4.6 is slow, the situation described in figures 4.15 and 4.16 is likely to apply, and diffusion control is expected to be present over the whole potential domain. In both cases the NO₂ is playing a necessary role in the solute transport. However, as will be discussed now, this is probably not its only role.
4.4 Discussion

4.4.1 General description of the electrochemical behaviour of the Cu/NaNO₂ and Cu30Zn/NaNO₂ systems at a flat electrode

The present work shows that a pronounced feature of the anodic polarisation behaviour of Cu and Cu30Zn in 1 M NaNO₂, pH = 9 solutions consists of the growth of a porous Cu₂O film, which formation can continue at high rates as long as a relatively high thickness has not been achieved. This oxide has a dark brown or black appearance, and is visible in the SEM as grains having diameters varying between 50 and 500 nm. The poor protective properties of the film are indicated by high current densities in voltammograms, as well as by high initial current densities followed by a slow decay in chronoamperometric experiments, where, depending on the potential, charge densities corresponding to the oxidation of 600 to 9000 atom layers must have passed before the initially high current densities have dropped to "passive" values. For pure Cu, mass transport considerations and analyses of the solution following anodic polarisation have shown, that the rates of other reactions than those involving the oxide formation are certainly negligible at potentials between the rest potential and E = ~ 50 mV SCE, but most likely also up to potentials of 0 mV SCE. In the case of Cu30Zn, analyses of the solution following anodic polarisation have shown that the oxide formation is accompanied by the dissolution of Zn which enters the solution. These measurements also suggest that dealloying takes place, since the amounts of Zn in the solution are higher than would be predicted if the oxidation of Cu and Zn would occur at rates proportional to their concentrations in the bulk metal. For potentials of + 50 mV SCE and higher, indications are present that the dissolution of copper to form dissolved ions occurs in addition to the other reactions.

In 1 M NaNO₂ solutions of pH = 11 the oxide is more protective than for pH = 9 which is indicated by the voltammograms of figure 4.10 which show lower "plateau" current densities as well as by the absence of the formation of a black layer in this plateau domain. However, these voltammograms show a breakdown potential above which an increase of the current occurs which is accompanied by the formation of a black layer. The presence of such a breakdown potential at pH = 11 and its absence at pH = 9, is consistent with the literature which indicates that thick tarnish layers are formed in the whole anodic potential domain for situations where the pH ≤ 9 or where the pH is not mentioned [23, 57, 64, 66, 67], but where the existence of a breakdown potential is reported for the formation of this tarnish layer when the pH is 10 or higher [56, 58].

It is suggested that the behaviour described above is characteristic for Cu and Cu30Zn in NO₂ containing solutions, since it was not found in other investigated solutions, i.e. Na₂SO₄, NaNO₃, and NaAc, solutions. As can be seen in figure 4.7, voltammograms measured at a rate of 0.2 mV·s⁻¹ in these solutions, show plateau's where the current density varies between 2 and 5 μA·cm⁻². These values, which are a factor 40 to 100 lower than the plateau value found for Cu in a 1 M NaNO₂ solution,
indicate the absence of high formation rates of Cu$_2$O. This is consistent with the observation that, unlike the situation in NaNO$_2$ solutions, no dark films are formed. Further support for the idea that the NO$_2^-$ ion enhances, somehow, the formation of porous Cu$_2$O can be derived from the observation that voltammograms measured at low and high scan rates, show in both cases increasing current densities for increasing NO$_2^-$ concentrations, see figures 4.8 and 4.9.

4.4.2 Proposed roles for the NO$_2^-$ ions

For the explanation or rationalisation of the role of the NO$_2^-$ ions in the observed electrochemical behaviour, three possibilities will be considered, i.e. a role in mass transport, a deteriorating effect on the Cu$_2$O film properties, and a catalysing effect on one of the steps of the reaction mechanism of the Cu$_2$O formation.

The mass transport considerations presented in section 4.3.3 have shown that reaction 2 Cu + H$_2$O $\rightarrow$ Cu$_2$O + 2 H$^+$ + 2 e$^-$ can not proceed at the measured rates, if the transport of H$^+$ ions from the electrode can only occur by diffusion. Namely, due to the increase of the H$^+$ concentration at the electrode, which would result from this situation, the H$^+$ activity at the electrode would exceed the value where reaction 2 Cu + H$_2$O $\rightarrow$ Cu$_2$O + 2 H$^+$ + 2 e$^-$ is in equilibrium, in which case the continued occurrence of the anodic reaction is impossible. However, it has been shown that the H$^+$ concentration at the electrode can sufficiently be reduced due to the occurrence of reaction H$^+$ + NO$_2^-$ $\rightarrow$ HNO$_2$, presumably in combination with reaction 3 HNO$_2$ $\rightarrow$ H$^+$ + NO$_3^-$ + 2 NO (g) + H$_2$O. Therefore, a necessary role of the NO$_2^-$ ions consists of sufficiently reducing the H$^+$ concentration at the electrode surface during the occurrence of reaction 2 Cu + H$_2$O $\rightarrow$ Cu$_2$O + 2 H$^+$ + 2 e$^-$. However, it is doubtful if this role alone can explain all features of the observed electrochemical behaviour. E.g. 1 M NaNO$_2$ solutions of pH = 11, where the H$^+$ removal can even occur slightly faster than in pH = 9 solutions due to a higher OH$^-$ concentration in the bulk, show significantly lower Cu$_2$O formation rates at potentials below the breakdown potential, thereby suggesting that the film properties are also important. A second example is the comparison of the anodic behaviour of Cu in 1 M NaAc, Na$_2$SO$_4$, NaNO$_3$ solutions of pH = 9, where the possibility of reaction H$^+$ + Ac$^-$ $\rightarrow$ HAc in the NaAc solutions allows faster H$^+$ removal than in 1 M Na$_2$SO$_4$ and 1 M NaNO$_3$ solutions. As has been shown in figure 4.7, no significant differences in Cu$_2$O formation rates are found, which indicates that increased possibilities for H$^+$ removal do not necessarily result in higher Cu$_2$O formation rates. Therefore, it is concluded that the role of the NO$_2^-$ ions in reducing the H$^+$ concentration at the electrode is necessary, but not sufficient to explain all features of the observed electrochemical behaviour.

It is clear that the high Cu$_2$O formation rates can only proceed as long as the film does not become protective, and it can be speculated that the NO$_2^-$ ions play a role in impeding formation of thin, protective film. Support for this idea can be found in the voltammograms in figure 4.8, measured at a slow scan rate in 0.1 and 1 M NaNO$_2$ solutions of pH = 9. Starting from the rest potential, the current density initially
increases with increasing potential for both concentrations. However, the moment where a subsequent decrease of the current density occurs, indicative for the oxide becoming protective, is different, i.e. for the lower concentration it occurs after a significantly smaller charge density has passed than for the higher concentration. Since it has been shown that, except for the Zn in the case of Cu30Zn, the charge is predominantly used for the formation of the film, it can be concluded that in the 0.1 M solution protection against further oxidation is achieved by a significantly thinner film than in the 1 M solution. This can be interpreted as evidence that the NO$_2^-$ ions, somehow, impede the formation of a protective film. The idea of the NO$_2^-$ ions having a deteriorating effect on the film properties is also supported by the observations in the literature for 1 M NaNO$_2$ solutions of pH = 10, where a breakdown potential, above which the thick oxide is formed, has been found to shift to lower potentials with increasing NaNO$_2$ concentrations [56,58].

A third possibility for the role of the NO$_2^-$ ions could comprise a catalysing effect on the Cu$_2$O formation rates. Namely, it is not clear if the absence of a protective film necessarily leads to high oxide formation rates. It may be the case that the reaction mechanism of the Cu$_2$O formation involves a slow step which determines the reaction rate. It can be speculated that the NO$_2^-$ ions, somehow, catalyse the Cu$_2$O formation reaction by accelerating this step. Support for a catalysing effect can be found in the voltammograms in solutions of pH = 9 for different NaNO$_2$ concentrations, which have been presented in figures 4.8 and 4.9. These voltammograms show a potential domain in which an approximately linear relationship exists between the logarithm of current density and the potential. In this domain, where the oxide is apparently not effective in providing protection against further oxidation, the current densities are significantly higher for higher NaNO$_2$ concentrations, which could be explained as a catalytic effect of the NO$_2^-$ ions on the Cu$_2$O formation rate.

Summarising, it has been concluded that the NO$_2^-$ ions play a necessary role in maintaining a sufficiently low H$^+$ concentration at the electrode surface during the occurrence of the reaction 2 Cu + H$_2$O $\rightarrow$ Cu$_2$O + 2 H$^+$ + 2 e$^-$. Other roles of the NO$_2^-$ ions remain a matter of speculation, but support could be found for the idea that the NO$_2^-$ ions impede the formation of a thin, protective film, as well as for the idea that NO$_2^-$ ions accelerate the reaction kinetics of the Cu$_2$O formation. Possibly, a combination of the latter two functions gives the right picture. At any rate, it can be concluded that, despite the fact that their role in the Cu$_2$O formation mechanism is not clear, the NO$_2^-$ ions are necessary to promote high rates of Cu$_2$O formation.

4.4.3 Description of the expected chemistry in the crack tip region

Based on the on the observed electrochemical behaviour on flat electrodes an attempt will now be made to describe the electrochemical behaviour expected in the occluded space of the crack tip region.

For a flat electrode conclusive evidence has been provided that, besides the dissolution of Zn in the case of Cu30Zn, the formation of Cu$_2$O is certainly the
dominant reaction for potentials between the rest potential and \(-50 \text{ mV SCE}\). This evidence is based on the combination of analyses of the surface layer and the solution composition, see section 4.3.1, as well as on mass transport calculations, see section 4.3.3. As has been illustrated in figure 4.14, the mass transport calculations show that the oxidation of Cu to form \(\text{Cu}^+\) and \(\text{Cu(NO}_2\text{)}^{(2-x)+}\) ions can not occur at the rates measured in the polarisation experiments. Namely, due to the resulting increase of the \(\text{Cu}^+\) and \(\text{Cu(NO}_2\text{)}^{(2-x)+}\) concentrations at the electrode, the equilibrium potential for their formation reactions would exceed the applied potential, in which case their continued formation would be, obviously, impossible. Similar calculations show that oxidation of Cu to form \(\text{Cu}_2\text{O}\) can occur at the rates measured in the polarisation experiments, since the transport possibilities for the \(\text{H}^+\) ions produced during this reaction are sufficient, see figure 4.15. In general, it has been concluded for this potential domain, that the \(\text{Cu}_2\text{O}\) formation rates corresponding to the maximum transport rates for the \(\text{H}^+\) ions produced during this reaction are orders of magnitude higher than the dissolution rates as \(\text{Cu}^+\) and \(\text{Cu(NO}_2\text{)}^{(2-x)+}\) corresponding to their maximum transport rates.

Unlike the situation at a flat electrode, it is not possible to determine which reaction predominates at the crack tip. First, two possible situations will be described for pure Cu. Then, these situations will be extended for Cu30Zn.

In the first situation, reaction 2 \(\text{Cu} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2 \text{H}^+ + 2 \text{e}^-\) occurs at the crack

\[
\begin{align*}
2 \text{Cu} + \text{H}_2\text{O} & \rightarrow \text{Cu}_2\text{O} + 2 \text{H}^+ + 2 \text{e}^- \quad (4.12) \\
\text{H}^+ + \text{NO}_2^- & \rightarrow \text{HNO}_2^- \quad (4.5) \\
(\text{Zn} & \rightarrow \text{Zn}^{2+} + 2 \text{e}^-) \quad (4.21)
\end{align*}
\]

**Figure 4.17** Schematic representations of the concentration profiles in the crack for Cu and Cu30Zn in NaNO\(_2\) solutions, if reactions 4.12, 4.5, and 4.21 in the case of Cu30Zn, occur at the tip of the crack, and in the region behind the crack tip as long as passivity has still not been achieved. The magnitude of the \(\text{H}^+\) and HNO\(_2\) concentration gradients will be diminished if reaction 4.5 is followed by reaction 4.21, i.e. 3 HNO\(_2\) \rightarrow \text{H}^+ + \text{NO}_3^- + 2 \text{NO} \ (g) + \text{H}_2\text{O}\)
tip as well as behind the crack tip. In a similar way as has been done for a flat electrode in figure 4.15, the $H^+$, HNO$_2$, and NO$_2$ concentration profiles in the crack, corresponding to this situation, have been represented schematically in figure 4.17. It should be noted that the OH$^-$ concentration profile, which is not essential for the idea, has been omitted for the sake of simplicity. Just as at a flat electrode the magnitude of the $H^+$, HNO$_2$ concentration gradients may be diminished if the HNO$_2$ dissociates according to reaction $3 \text{HNO}_2 \rightarrow \text{H}^+ + \text{NO}_3 + 2 \text{NO} \,(g) + \text{H}_2\text{O}$. Figure 4.17 shows the occurrence of acidification, but not to the extent that the Cu$_2$O formation is prevented at the crack tip. This requires that the $H^+$ activity at the crack tip is equal or lower than the value where the Cu$_2$O formation reaction is in equilibrium, and that the $H^+$, HNO$_2$, and NO$_2$ concentration gradients extend to the tip of the crack.

In the second situation, acidification prevents the formation of the Cu$_2$O at the crack tip. Concentration profiles representing this situation have been depicted schematically in figure 4.18, showing a region behind the crack tip, where the $H^+$ and HNO$_2$ activities are equal to values where the reactions

\[

c_{\text{H}^+} \rightarrow \text{Cu}^+ + e^- \quad (4.7)
\]

\[
(Zn \rightarrow Zn^{2+} + 2 e^-) \quad (4.21)
\]

\[
2 \text{Cu}^+ + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ \quad (4.22)
\]

\[
2 \text{Cu} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ + 2e^- \quad (4.12)
\]

\[
\text{H}^+ + \text{NO}_2 \rightarrow \text{HNO}_2 \quad (4.5)
\]

**Figure 4.18** Schematic representations of the concentration profiles in the crack for Cu and Cu30Zn in NaNO$_2$ solutions, if reaction 4.7, and 4.21 in the case of Cu30Zn, occur at the crack tip, while reactions 4.12 and 4.5 are in equilibrium over some distance behind the crack tip. Behind this region reaction 4.22 occurs in combination with reaction 4.12, which continues as long as passivity has still not been achieved. The magnitude of the $H^+$ and HNO$_2$ concentration gradients will be diminished if reaction 4.5 is followed by reaction 4.6, i.e.

\[
3 \text{HNO}_2 \rightarrow \text{H}^+ + \text{NO}_3 + 2 \text{NO} \,(g) + \text{H}_2\text{O}
\]
and \( \text{H}^+ + \text{NO}_2 \leftrightarrow \text{HNO}_2 \) are in equilibrium. In this region the occurrence of reaction 2 \( \text{Cu} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2 \text{H}^+ + 2 \text{e}^- \) is prevented, since the otherwise occurring increase in \( \text{H}^+ \) activity would result in a rise of the equilibrium potential above the applied potential. Thus, another reaction must occur at the crack tip, e.g. the reaction \( \text{Cu} \rightarrow \text{Cu}^+ + \text{e}^- \). However, the \( \text{Cu}^+ \) activities where this reaction is in equilibrium are very low for the considered potential region, which excludes the possibility of large diffusion distances through the crack solution.

Namely, this low equilibrium activity sets an low upper limit for the increase of the \( \text{Cu}^+ \) activity at the crack tip. The alternative possibility of \( \text{Cu}^+ \) removal is the formation of the \( \text{Cu}_2\text{O} \) at some distance behind the crack tip according to reaction 2 \( \text{Cu}^+ + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2 \text{H}^+ \). Thus, the main difference between the two possibilities consists of the location of the \( \text{Cu}_2\text{O} \) formation, either at or behind the crack tip. However, for both situations it can be argued that the \( \text{Cu}_2\text{O} \) formation rate is determining the crack tip reaction rate. This is obvious for the first situation, where the \( \text{Cu}_2\text{O} \) formation occurs at the crack tip. However, if the reaction \( \text{Cu} \rightarrow \text{Cu}^+ + \text{e}^- \) occurs at the crack tip, as is proposed in the second possibility, its rate is expected to be dependent on the rate at which the \( \text{Cu}^+ \) removal can occur, this being dependent on the rate of reaction 2 \( \text{Cu}^+ + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2 \text{H}^+ \).

If the first situation, indicated in figure 4.17, is considered for \( \text{Cu}30\text{Zn} \) instead of for pure \( \text{Cu} \), the picture does not change essentially, i.e. at the crack tip the formation of \( \text{Cu}_2\text{O} \) is accompanied by the dissolution of \( \text{Zn} \). In this respect it should be noted that it may be possible that a dealloyed layer is continuously present at the crack tip. Namely, it can be imagined that dezincification of a certain number of atom layers occurs, before the dissolution of both elements occurs at rates proportional to their concentrations in the bulk metal. Evidence for dezincification has been obtained by analyses of the solution composition following anodic polarisation of a flat electrode, showing higher amounts of \( \text{Zn} \) in the solution than would be predicted if the oxidation of \( \text{Cu} \) and \( \text{Zn} \) would occur at rates proportional to their concentrations in the bulk metal.

If the second situation, indicated in figure 4.18, is considered for \( \text{Cu}30\text{Zn} \) instead of \( \text{Cu} \), the essence of the picture may change. Namely, a relatively large acidified region can then be imagined, where the \( \text{Cu}_2\text{O} \) formation reaction is impossible, the dissolution rate of \( \text{Cu} \) to form dissolved ions can be neglected, but where the dissolution of \( \text{Zn} \) can occur at high rates. In this respect it is noted that examples exist where the dissolution of the least noble element in a binary alloy alone is sufficient for the propagation of the crack, e.g. \( \text{Cu}30\text{Zn} \) in cuprous ammonia solutions and \( \text{Cu}25\text{Au} \) in \( \text{NaCl} \) solutions. An important consequence of this situation would be that the reaction rate at the crack tip would then most likely be determined by the selective dissolution rate of \( \text{Zn} \) instead of by the \( \text{Cu}_2\text{O} \) formation rate, as was concluded to be the case for pure \( \text{Cu} \). In this respect the following arguments will be made, which are, however, not conclusive. It is not certain that selective dissolution of \( \text{Zn} \) alone is sufficient for crack propagation in this system, i.e. not all systems exhibiting selective dissolution show SCC, e.g. \( \text{Cu}30\text{Zn} \) in \( \text{NaCl} \) solutions [66]. Further, it seems hard to believe that the crack tip reaction rate is not dependent on the \( \text{Cu}_2\text{O} \) formation rate,
whereas the high Cu$_2$O formation rate is the most pronounced feature for Cu and Cu30Zn in NaNO$_2$ solutions, the latter being by far the strongest promoter of SCC cracking of α-brass in non-ammoniacal environments. Finally, it seems not convincing that the actual crack tip reaction is completely different for Cu than for Cu30Zn. Therefore, the most likely explanation is believed to be that reaction rate at the crack tip is dependent on the dissolution rate of Zn in combination with the Cu$_2$O formation rate.

4.4.4 Relation between the electrochemical behaviour of the Cu/NaNO$_2$ and Cu30Zn/NaNO$_2$ systems and SCC

It is an aim of the present work to use the obtained understanding of the electrochemistry of the Cu/NaNO$_2$ and Cu30Zn/NaNO$_2$ system to evaluate which electrochemical processes and characteristic parameters are likely to play a role in the SCC mechanism in this system. Electrochemical processes and characteristics, proposed to be necessary in SCC according to one or more models, have been listed in table 2.2. This table shows that some electrochemical characteristics are only relevant in relation with a particular model, whereas other electrochemical characteristics are more generally relevant in SCC. The more specific features include the formation of a surface layer having appropriate properties to inject a crack in the ductile substrate, which is claimed to be required to allow the film induced cleavage model [49,55] to be operative, and the presence of a compound with a low melting point, which is a requirement for the surface mobility model [16]. Electrochemical features not necessarily related to a particular model include the occurrence of sufficiently high reaction rates at the crack tip and the presence of conditions which decrease the corrosion rates at the crack walls, which are often achieved by the formation of a protective film. The electrochemical characteristics mentioned above will be discussed in relation with the knowledge of the electrochemistry of the Cu/NaNO$_2$ and Cu30Zn/NaNO$_2$ systems. It is further noted that the question whether or not the present results support the possible propagation of the crack by a slip-dissolution mechanism will not be dealt with, since this has extensively been done by other workers [23,56, 57,58], and since this model can not account for the cleavage-like fracture found in this system.

According to the Film Induced Cleavage Model, a surface layer is required to have such properties that a crack, nucleated in this film, is able to penetrate in the ductile substrate. This model is mostly considered for systems showing dealloying, where the importance of the de-alloyed layer lies in its nanoporous morphology [55]. However, it has also been proposed to account for pure Cu in NaNO$_2$ solutions, where dealloying is, obviously, impossible. For this system, it was speculated that micropitting could produce a porous layer having the required properties to produce a brittle propagating crack [68,71]. Based on the results of the present work, the possibility of dealloying in Cu30Zn/NaNO$_2$ as well as the possibility of the formation of a porous layer by
micropitting in Cu/NaNO₂ will now be discussed. In this respect it should be mentioned that it is considered to be unlikely that the thick, probably loosely bonded, oxide allows a crack to be nucleated which is able to penetrate in the ductile substrate.

In section 4.4.3 it has been argued that the dealloying is certainly possible in the Cu30Zn/NaNO₂ system. However, no statement can be made regarding the question as to whether or not this layer has a nanoporous structure as is claimed to be necessary for the occurrence of film induced cleavage. Thus, the present work can neither preclude nor confirm the presence of a dealloyed layer with appropriate properties to inject a crack in the ductile substrate. With regard to Cassagnes speculation that a micropitting process, where Cu dissolves as Cu²⁺, could occur in the Cu/NaNO₂ system, thereby producing a porous layer capable of inducing a brittle popagating crack, the following is noted. He only observes pits in the TEM for a high value of the potential, i.e. E = + 50 mV SCE [68]. For lower potentials, e.g. E = −150 mV SCE, he does not report visible pits, but he derives their existence using an interpretation of electrochemical impedance spectroscopy measurements. It should be noted that the occurrence of pitting due to the reaction Cu → Cu²⁺ + 2 e⁻ is hard to imagine for the lower potentials. Namely, at these potentials the reaction Cu → Cu²⁺ + 2 e⁻ is already in equilibrium for low Cu(NO₂)₂(2-x)⁺ activities, which has been illustrated in figure 4.14. Although an analysis of solute transport in pits is beyond the scope of this work, and will not be made, it can generally be stated that low equilibrium activities have the consequence that the maximum possible rates for mass transport are already achieved at low current densities. In figure 4.14 it has been shown that the current densities corresponding to the maximum possible transport rates at a flat electrode at e.g. E = −100 mV SCE are low, i.e. they are of the order of several μA·cm⁻². The current densities corresponding to the maximum possible transport rates are expected to be even lower in the more confined geometry's of pits. Thus, it is argued that the occurrence of pitting is unlikely at relatively low potentials. Since SCC is still found at those potentials, the present work disagrees with Cassagnes speculation that the SCC of Cu in NaNO₂ solutions occurs by the nucleation of a crack in a porous layer which is formed by micropitting. Since the possibility of dealloying can also be excluded, the applicability of the film induced cleavage model on the Cu/NaNO₂ system, seems to be doubtful.

The surface-diffusion mechanism requires a low melting point compound on the metal surface at the tip of the crack [16]. Rebak et al. state that this model would not be operative if Cu₂O would be present because of its high melting point [58]. However, they expect that acidification prevents the formation of Cu₂O at the crack tip, and that an adsorbed Cu(NO₂)₂ layer is present instead. They further state that Cu₂O is only precipitated behind the crack tip, which idea is similar to the situation depicted in figure 4.18. The likelihood of these ideas will now be discussed in relation with the present work.

A first question is the likelihood of the presence of an adsorbed Cu(NO₂)₂ layer in the lower potential region, e.g. around E = −100 mV SCE. Such a layer would require the presence of Cu²⁺ ions at the surface, and it is questionable if their presence in
significant concentrations is to be expected in a potential domain where the equilibrium activities for Cu(NO₂)_{2-x}^{2-} in the solution are so low, see figure 4.14. A second question is if it is reasonable to expect a divalent Cu(NO₂)₂ layer at the crack tip and a monovalent Cu₂O layer behind the crack tip. Namely, the surface at the crack tip has been exposed to the solution for a shorter time than the surface behind the crack tip. Thus, according to the proposed model, the formation of a divalent Cu(NO₂)₂ layer would precede the precipitation of a monovalent Cu₂O layer, which seems, intuitively, unlikely.

Concluding, the idea that adsorbed Cu(NO₂)₂ layer would be present at the crack tip is not very convincing. If no other low melting point compound is available at the crack tip, the applicability of the surface mobility model to the Cu/NaNO₂ and Cu30Zn/NaNO₂ systems seems not possible.

Finally, an attempt will be made to relate the electrochemical behaviour of the Cu/NaNO₂ and α-brass/NaNO₂ systems to more general requirements for SCC, which are not specific to a particular model. As can be seen in table 2.1, many models do not seem to describe specific required electrochemical features, other than the occurrence of an anodic reaction at the tip of the crack, which has e.g. been proposed to be necessary for corrosion enhanced plasticity [30-32] or corrosion assisted cleavage [1-3,10,11]. Though not always described by the models, it is also to be expected that conditions are necessary which decrease the corrosion rates at the crack walls, which are often achieved by the formation of a protective film. A reason for the requirement of decreased corrosion rates at the crack walls may be that blunting of the crack tip by dissolution has to be avoided. This concept has often been used in relation with the slip-dissolution model, but it may play a role in other models. However, a less frequently mentioned reason for the necessity of decreased corrosion rates at the crack walls relates to the conditions for solute transport in the crack. Namely, higher crack wall corrosion rates lead to higher fluxes of solute and higher currents in the crack. The resulting changes in the composition of the crack tip solution and the resulting IR drops influence the reaction rate at the crack tip, and thus the crack velocity. Thus, the reaction rates at a fresh surface are important, where the repassivation characteristics and the various chemical equilibria are relevant, because of their influence on the conditions for solute transport and, thereby, on the crack tip reaction rates. It is proposed that the ability of system to maintain sufficiently high crack tip reaction rates despite the confined geometry of a crack is a general requirement for SCC, though it is certainly not claimed that meeting this requirement is a sufficient condition to actually obtain SCC.
With regard to the just proposed general, but not necessarily sufficient, requirement for SCC, it is now argued that the following characteristics of the Cu/NaNO₂ and α-brass/NaNO₂ system are factors promoting SCC:

I In the potential domain for SCC, the reaction rate at a bare surface is high, which is presumably due to an effect of the NO₂ ions on the reaction mechanism of the Cu₂O formation.

II The solute transport of the species involved in the Cu₂O formation can occur at high rates due to the following sequence of reactions

\[
\begin{align*}
2 \text{Cu} + \text{H}_2\text{O} & \rightarrow \text{Cu}_2\text{O} + 2 \text{H}^+ + 2 \text{e}^- \\
3 \text{H}^+ + 3 \text{NO}_2^- & \rightarrow 3 \text{HNO}_2 \\
3 \text{HNO}_2 & \rightarrow \text{H}^+ + \text{NO}_3^- + 2 \text{NO (g)} + \text{H}_2\text{O} \\
2 \text{Cu} + 3 \text{NO}_2^- & \rightarrow \text{Cu}_2\text{O} + \text{NO}_3^- + 2 \text{NO (g)} + 2 \text{e}^-
\end{align*}
\]

III The corrosion rates at the crack walls are eventually reduced to passive values.

Chapter 8 will deal with these reactions and the corresponding solute transport mechanisms in the crack in a more quantitative way.

4.5 Conclusions

1 A characteristic feature of the anodic polarisation behaviour of Cu and Cu30Zn in 1 M NaNO₂ solutions of pH = 9 consists of the growth of a porous Cu₂O film, which has a dark brown or black appearance, and which is visible in the SEM as grains having diameters varying between 50 and 500 nm.

2 The formation rate of this Cu₂O film is high, i.e. voltammograms measured in 1 M NaNO₂ solutions of pH = 9 show a current plateau, associated with the Cu₂O formation, where the current density is 2 orders of magnitude higher than in current plateaus found for 1 M NaNO₃, Na₂SO₄, and NaAc solutions of the same pH.

3 In chronoamperometric experiments, the formation of the Cu₂O film is associated with initially high current densities followed by a slow decrease to "passive" values. The "passive" values are only achieved after a charge density has passed which, depending on the potential, corresponds to the oxidation of 600 to 9000 atom layers.

4 The formation of Cu₂O at flat Cu and Cu30Zn electrodes predominates over the dissolution as Cu⁺ and Cu(NO₂)ₓ(2-x⁺) ions, certainly for potentials between the rest potential and – 50 mV SCE, but most likely also for potentials up to 0 mV SCE. At higher potentials, the Cu₂O film is still formed, but its formation is accompanied by the dissolution of Cu to form Cu(NO₂)ₓ(2-x⁺) ions.
In the case of Cu30Zn, the Cu₂O formation is accompanied by the dissolution of Zn which enters the solution. The amounts of Zn in the solution are higher than which would be expected if the oxidation of Cu and Zn would occur at rates proportional to their concentrations in the bulk alloy, thereby indicating that dealloying occurs.

In a 1 M NaNO₂ solution of pH = 11, high rates of Cu₂O formation are only found above a breakdown potential which value lays above the rest potential. Between the rest potential and the breakdown potential the oxide is more protective.

Voltammograms, measured at various scan rates for various NO₂ concentrations at pH = 9, show higher current densities for higher NO₂ concentrations.

During the Cu₂O formation according to reaction 4.12, the NO₂ ions play a necessary role in the mass transport, without which the Cu₂O formation can not occur at the rates measured at a flat electrode. This role consists of maintaining the H⁺ concentration sufficiently low, due to reaction 4.5, presumably in combination with reaction 4.6.

\[
\begin{align*}
2 \text{Cu} + \text{H}_2\text{O} & \rightarrow \text{Cu}_2\text{O} + 2 \text{H}^+ + 2 \text{e}^- \quad (4.12) \\
3 \text{H}^+ + 3 \text{NO}_2^- & \rightarrow 3 \text{HNO}_2 \\
3 \text{HNO}_2 & \rightarrow \text{H}^+ + \text{NO}_3^- + 2 \text{NO} (g) + \text{H}_2\text{O} \quad (4.5)
\end{align*}
\]

The necessary role in mass transport alone is not considered to be sufficient to explain all features of the measured voltammograms, and it is argued that the NO₂ ions have a deteriorating effect of on the film properties as well as a catalysing effect in the Cu₂O formation mechanism.

Based on the knowledge of the electrochemical behaviour at a flat electrode, it is argued that the Cu₂O formation rate determines the crack tip reaction rate in the case of pure Cu for potentials equal or lower than −50 mV SCE, but most likely also for potentials equal or lower than 0 mV SCE. Though it can not be excluded that the rate of dezincification determines the crack tip reaction rate in the case of Cu30Zn, it is considered to be more likely that the crack tip reaction rate is, in analogy to pure Cu, determined by the Cu₂O formation rate.

The following characteristics of the Cu/NaNO₂ and Cu30Zn/NaNO₂ systems have been proposed as general (but not necessarily sufficient) factors promoting SCC.

I In the potential domain for SCC, the reaction rate at a bare surface is high, which is presumably due to an effect of the NO₂ ions on the mechanism of the Cu₂O formation.

II The solute transport of the species involved in the Cu₂O formation can occur at high rates due to the presence of NO₂ ions.

III The corrosion rates at the crack walls are eventually reduced to passive values.
5 General overview of the Stress-Corrosion Cracking behaviour

5.1 Introduction

In this chapter the results of SCC-experiments are described which have been performed on oriented Cu30Zn single crystals in 1 M NaNO₂ solutions of pH = 9. The aim of these experiments was to obtain a general picture of the SCC behaviour of this system on a relatively macroscopic scale, and in particular to obtain an overview on the differences between the SCC behaviour in the Cu30Zn/NaNO₂ system and that of the Cu25Au/NaCl system which has been described in section 2.4. The present description is focused on the detection of possible discontinuous events by load drops, current peaks and crack arrest markings; the average orientation of the fracture surface; and the average crack velocity.

While it is intended in this chapter to provide broad overview of the SCC behaviour in the Cu30Zn/NaNO₂ system, a more detailed description on the fractography and the possibility of discontinuous crack advance has been given in chapters 6 and 7 respectively.

5.2 Experimental

Slow strain rate (SSR) tests were performed using the experimental set-up which has been described in chapter 3. This set-up is essentially identical to that used for the investigation of the Cu25Au/NaCl system, which has been described in section 2.4. The specimen orientations are shown in figures 2.5 and 2.6. The potential, crosshead speed and the specimen orientation were varied.

For each experiment a coated specimen was prepared as described in section 3.1. The coated specimen was tightened in the grips of the corrosion test cell, which has been described in section 3.2. After coating the transition from the specimen to the grips, the lid of the corrosion test cell was closed. The assembled corrosion test cell was then slid in the tensile tester. After the priori deaerated, 1 M NaNO₂, pH = 9 test solution, prepared from milli-Q distilled water and analytical grade chemicals, had been introduced in the corrosion test cell, the cell was connected with the potentiostat and with the nitrogen flow. The specimen was then loaded to approximately 25% of its yield stress. The further procedure varied somewhat on the potentials and crosshead
speeds. For potentials equal or higher than 0 mV SCE, the potential of interest was applied at the onset of the experiment. In this case it was waited until the current had dropped to an (almost) constant background value, after which the straining was started. This was seen as the most desirable procedure, since the interpretation of the current measurements is facilitated if the background value of the current is known. However, for lower values of the potential, this procedure resulted in a difficult crack nucleation, especially if the crosshead speed was low as well. In order to minimise plastic deformation prior to crack nucleation in the case of low potentials, a potential of + 50 or + 100 mV SCE was applied, it was waited until the current had achieved a constant value, after which straining at a crosshead speed of 0.01 μm·s⁻¹ was started. Following nucleation of the crack at this high potential, the potential was lowered to the value of interest. The disadvantage of this method was that the background current was not known and possibly not constant. In those cases the background current was estimated by measuring the current after failure of the sample. During the test the load, current and position of the crack front were monitored.

Table 5.1 is an overview of the experimental conditions of the experiments presented in this chapter.

<table>
<thead>
<tr>
<th>potential (mV SCE)</th>
<th>Crosshead speed (μm·s⁻¹)</th>
<th>specimen orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>-100</td>
<td>3·10⁻³</td>
<td>{110}&lt;001&gt;</td>
</tr>
<tr>
<td>-50</td>
<td>1·10⁻³</td>
<td>{110}&lt;001&gt;</td>
</tr>
<tr>
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<td>1·10⁻²</td>
<td>{110}&lt;001&gt;</td>
</tr>
<tr>
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<td>1·10⁻²</td>
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</tr>
<tr>
<td>+100</td>
<td>1·10⁻²</td>
<td>{110}&lt;001&gt;</td>
</tr>
<tr>
<td>+150</td>
<td>4·10⁻²</td>
<td>{110}&lt;001&gt;</td>
</tr>
</tbody>
</table>

5.3 Results and discussion

Load and current behaviour

In figure 5.1 the general characteristics of the load and current behaviour as well as the position of the crack front as monitored by the video camera is shown for an experiment where the potential is applied at the onset of the experiment and where the straining is started after the current has reached a constant background value. In this particular example a {110}<001> specimen was involved which was tested at a potential of + 50 mV SCE and at a crosshead speed of 0.01 μm·s⁻¹. After having remained at its background value in the elastic domain, the current starts to rise several minutes before the onset of the load decrease. The rise of the current above its background value indicates that fresh surface is produced by either slip or by the combination of slip and crack advance, while the decrease of the load provides certainty
that a crack has nucleated. After a period of increase, which can vary from 15 to 60 minutes, the current reaches a stationary value which usually remains at a constant level during the rest of the experiment. Current peaks are frequently found to be superimposed on the stationary current. However, the direct relation of the current peaks with the crack propagation is uncertain, since they may originate from the discontinuous release of gas bubbles in the crack, which phenomenon is continuously observed following the nucleation of the crack. During the advance of the crack, the load decreases, where smooth changes in the load decrease rate are sometimes observed. However, no process is detected where fast load drops, accompanied by current transients, alternate with longer periods of no load decrease. The latter issue will be treated in greater detail in chapter 7.

In figure 5.2 the effect of an increase of the crosshead speed is illustrated for a \{110\}<001> specimen, tested at a potential of + 50 mV SCE. In the experiment represented by figure 5.2, crack nucleation was achieved at a crosshead speed of 0.01 \(\mu\text{m}\cdot\text{s}^{-1}\), which is the same value as in the experiment represented in figure 5.1. However, at \(t = 185\) minutes, the crosshead speed was increased by a factor 10. Following this increase, there was a momentary increase in load before it once again continued to decrease. Another effect of the increase of the crosshead speed was that the current obtained a stationary value which was higher by a factor 4-6 (after subtraction of the background current). The video camera observations indicated that the higher crosshead speed resulted in an increase of the average crack velocity by a factor of 1.5.

In figures 5.3 and 5.4 the data for the load, current, and position of the crack front are shown for \{110\}<001> specimens, tested at a potential of − 50 mV SCE for two different values of the crosshead speed. In both experiments the crack was nucleated at a potential of + 100 mV SCE and at a crosshead speed of 0.01 \(\mu\text{m}\cdot\text{s}^{-1}\), and the potential was lowered to − 50 mV SCE following nucleation of the crack. For the experiment represented in figure 5.4, the crosshead speed was lowered simultaneously with the decrease of the potential following the nucleation of the crack. In figures 5.3 and 5.4 it can be seen that the load stops decreasing immediately after lowering the potential, subsequently continuing to decrease at a lower rate. This lower load decrease rate suggests a lower crack velocity which is confirmed by the video camera observations. The current correspondingly is seen to establish a new and lower plateau value, which was due to a decrease of the background current as well as to a decrease of the current related to the slower propagation of the crack.

Figures 5.5 and 5.6 display the load and current data obtained during testing of two different specimen orientations, i.e. \{110\}<001> and \{110\}<110>, at a potential of + 100 mV SCE and at a crosshead speed of 0.01 \(\mu\text{m}\cdot\text{s}^{-1}\). The load and current behaviour was comparable for both specimen orientations, i.e. for both experiments the current started to rise above its background value several minutes before the load started to decrease. In both experiments the load decreased smoothly without showing fast drops alternating with periods of no load decrease.
Figure 5.1  Load, current and crack length as a function of time during a SSR test of a $\{110\}<001>$ oriented Cu30Zn single crystal in a 1 M NaNO₂ solution of pH = 9 at $E = +50$ mV SCE and $v_{\text{crossh}} = 0.01 \mu$m·s⁻¹. The load and current have been divided by the specimen thickness. (specimen width = 2.82 mm, pre-cut = 0.42 mm)

Figure 5.2  Load, current and crack length as a function of time during a SSR test of a $\{110\}<001>$ Cu30Zn single crystal in a 1 M NaNO₂ solution of pH = 9 at $E = +50$ mV SCE and $v_{\text{crossh}} = 0.01 \mu$m·s⁻¹ from the onset of the experiment, where $v_{\text{crossh}}$ is changed to 0.1 $\mu$m·s⁻¹ at $t = 185$ min. The load and current have been divided by the specimen thickness. (specimen width = 2.69 mm, pre-cut = 0.38 mm)
Figure 5.3  Load, current and crack length as a function of time during a SSR test of a \{110\}<001> oriented Cu30Zn single crystal in a 1 M NaNO₂ solution of pH = 9 at E = -50 mV SCE, and $v_{crossh} = 0.01 \mu m \cdot s^{-1}$. The crack was nucleated at E = +100 mV SCE, after which the potential was lowered to E = -50 mV SCE at $t = 35$ min. The load and current have been divided by the specimen thickness. (specimen width = 2.64 mm, length pre-cut = 0.38 mm)

Figure 5.4  Load, current and crack length as a function of time during a SSR test of a \{110\}<001> oriented Cu30Zn single crystal in a 1 M NaNO₂ solution of pH = 9 at E = -50 mV SCE, and $v_{crossh} = 0.001 \mu m \cdot s^{-1}$. The crack was nucleated at E = +100 mV SCE and $v_{crossh} = 0.01 \mu m \cdot s^{-1}$, after which E was lowered to -50 mV SCE and $v_{crossh}$ was lowered to 0.001 \mu m \cdot s^{-1} at $t = 75$ min. The load and current have been divided by the specimen thickness. (specimen width = 2.82 mm, length pre-cut = 0.38 mm)
Figure 5.5 Load and current as a function of time during a SSR test of a (110)[001] oriented Cu30Zn single crystal in a 1 M NaNO₂ solution of pH = 9 at $E = +100$ mV SCE and $v_{crossh.} = 0.01 \mu m \cdot s^{-1}$. The load and current have been divided by the specimen thickness.

Figure 5.6 Load and current as a function of time during a SSR test of a (110)[110] oriented Cu30Zn single crystal in a 1 M NaNO₂ solution of pH = 9 at $E = +100$ mV SCE and $v_{crossh.} = 0.01 \mu m \cdot s^{-1}$. At $t = 280$ min. the potential was released, after which the potential was re-applied at $t = 310$ min.. At $t = 220$ min. the organic coating was ruptured unintentionally, so that no useful current measurements are available after $t = 220$ min. The load and current have been divided by the specimen thickness.
In figure 5.6 the load response following a release of and a re-application of the potential is shown. Following a release of the potential at $t = 280$ min., the system attains its open circuit potential (approximately $-200$ mV SCE), and the load stops decreasing almost immediately. Following the re-application of a potential of $+100$ mV SCE at $t = 310$ min, the load resumed its decrease almost immediately. This experiment shows that the decrease of the load is indeed an indication for the propagation of the crack.

Average crack velocity
Except for the onset of cracking, where the video camera is not able to monitor the successive positions of the crack front adequately, the video observations indicate that the crack moves with a constant average velocity during the course of an experiment. In figure 5.7 the average crack velocity has been shown as a function of the potential for both the \{110\}<001> and \{110\}<110> orientation. Up to a potential of $+100$ mV SCE, the average crack velocity increases with increasing electrode potential, suggesting that it is strongly dependent on the anodic reaction rate. At higher potentials an increasing potential does not result in an increase of the average crack velocity, for which an explanation has been given in chapter 8. For \{110\}<110> oriented specimens the average crack velocity is slightly lower than for specimens of the \{110\}<001> orientation.

![Graphs showing average crack velocity](image)

**Figure 5.7** The average crack velocity in oriented Cu30Zn single crystals in 1 M NaNO$_2$ solutions: a) as a function of the potential $E$. The crosshead speed, $v_{\text{crossth}}$, was 0.01 $\mu$m·s$^{-1}$ in all experiments, except for $E = -100$ mV SCE where $v_{\text{crossth}} = 0.003$ $\mu$m·s$^{-1}$, and $E = +150$ mV SCE where $v_{\text{crossth}} = 0.04$ $\mu$m·s$^{-1}$. b) as a function of $v_{\text{crossth}}$. 

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*General overview of the Stress-Corrosion Cracking behaviour*
Figure 5.8  Overview of the fracture surface and one specimen side of a $\{110\}<001>$ oriented Cu30Zn single crystal tested at $E = +50$ mV SCE and $v_{crossh} = 0.01 \text{ \mu m} \cdot \text{s}^{-1}$ for the first 30% of the tests and $v_{crossh} = 0.003 \text{ \mu m} \cdot \text{s}^{-1}$ for the latter 70% of the test. Crack growth direction from the left to the right.

Figure 5.9  Overview of the fracture surface and one specimen side of a $\{110\}<110>$ oriented Cu30Zn single crystal tested at $E = 0$ mV SCE and $v_{crossh} = 0.01 \text{ \mu m} \cdot \text{s}^{-1}$. Crack growth direction from the right to the left.
The influence of the crosshead speed on the average crack velocity has been indicated for two different values of the potential in figure 5.7b. For the region of crosshead speeds investigated it is observed that a tenfold increase of the crosshead speed results in an increase of the average crack velocity by a factor of two. The same relation between average crack velocity and crosshead speed has also been found for \( \{110\}<001> \) oriented Cu30Zn single crystals in Cu(I)ammonia solutions [53]. It is further noted that the values obtained in this investigation of the average crack velocities as well as the dependence of the crack velocity on the crosshead speed appear to be comparable to previously reported results for uncoated polycrystalline \( \alpha \)-brass in 1 M NaNO\(_2\) solutions [23].

As becomes clear from figure 5.7, the maximum observed crack velocity in the Cu30Zn/NaNO\(_2\) is on the order of several micrometers per second. This value is two to three orders of magnitude lower than the maximum observed "instantaneous" crack velocity in the Cu25Au/NaCl system, which is on the order of several tens to hundreds of micrometers per second (See section 2.4).

**General appearance of the fracture surface**

In figure 5.8 the fracture surface is shown for a specimen having the \( \{110\}<001> \) orientation. For the \( \{110\}<001> \) orientation, the average fracture surface is parallel to \( \{110\} \) and perpendicular to the \( <110> \) tensile axis. In contrast, the average fracture surface of a specimen having the \( \{110\}<110> \) orientation deviates strongly from the \( \{110\} \) plane perpendicular to the \( <110> \) tensile axis, which has been illustrated in figure 5.9. This difference between the fracture paths in \( \{110\}<001> \) and \( \{110\}<110> \) specimens was found for all potentials investigated. A difference in fracture path in \( \{110\}<001> \) and \( \{110\}<110> \) specimens has only occasionally been seen for Cu25Au single crystals in NaCl solutions, but not so drastic. In this system the observed average fracture surface is usually \( \{110\} \) perpendicular to the \( <110> \) tensile axis for both orientations. The influence of the "imposed" crack propagation direction on the appearance of the fracture surface is also observed for Cu30Zn single crystals in de-oxygenated cuprous ammonia solutions [53] as well as for Cu in NaNO\(_2\) solutions [31,32].

An exception to the observation of fracture on an average \( \{110\} \) plane for \( \{110\}<001> \) specimens is formed by the observation that a transition can occur from the average \( \{110\} \) plane to an average \( \{111\} \) plane. This phenomenon, shown in figure 5.10, rarely occurs, and requires a high potential, i.e. + 100 mV SCE or higher, and a high crosshead speed, i.e. higher than 0.1 \( \mu \text{m-s}^{-1} \). It is speculated that this phenomenon can be explained as slip-plane dissolution, where the active dissolution of slip planes is favoured by the high potential and the high crosshead speed.

Crack arrest markings, similar to those which have been reported for \( \{110\}<001> \) specimens in the Cu25Au system, have not been found for the combinations of potentials and crosshead speeds investigated. This is consistent with the absence of other indications of discontinuous cracking such as fast load drops, accompanied by current transients, which alternate with periods of constant or slightly rising load.
However, fracture surfaces produced at relatively low crosshead speeds and at high potentials show markings which are perpendicular to the river markings and parallel to the crack front, which can be seen in figure 5.8 and figure 5.11. These markings, 10-15 μm apart from each other, appear as regular differences in colour, and are unlikely to be explained as crack arrest markings. They are not sharp and distinct, do not coincide with the intersection of the primary slip planes with the fracture surface, and they do not correlate with discontinuities in the current and in the load decrease rate.

The combination of the potential and the crosshead speed influences the roughness and

![Figure 5.10](image)

**Figure 5.10** Overview of the fracture surface and one specimen side of a \(\{110\}\langle001\rangle\) oriented Cu30Zn single crystal tested at \(E = +150\) mV SCE and \(v_{\text{cross}} = 4 \times 10^{-1}\) μm·s\(^{-1}\). Crack propagation direction from the right to the left side. The fracture path shows a transition from the average \(\{110\}\) plane to an average \(\{111\}\) slip plane.
irregularity of the fracture surface strongly, which is illustrated in figures 5.11-5.14. Figure 5.11 shows a fracture surface produced during \{110\}<001> crack growth at a potential of +50 mV SCE and at a crosshead speed of 0.01 \mu m \cdot s^{-1}. Under these circumstances a smooth fracture surface is obtained showing river patterns. Figure 5.12 displays the fracture surface obtained in a crack-growth experiment where the initial value of the potential was maintained constant at +50 mV SCE, while the crosshead speed was increased by a factor of 10 from 0.01 \mu m \cdot s^{-1} to 0.1 \mu m \cdot s^{-1}. In this figure the macroscopic crack growth direction is from the left to the right and the centre of the photo shows the moment where the crosshead speed was increased. River patterns are present in the region before the increase of the crosshead speed while many secondary cracks are found in the region where the crosshead speed was high. This shows that an increase of the crosshead speed at the same potential results in a stronger tendency for secondary cracking and in a rougher and more irregular fracture surface.

It is also observed that the tendency for secondary cracking increases with decreasing potential for a constant crosshead speed. This is illustrated in figure 5.13, showing the fracture surface obtained at a potential of \(-50\) mV SCE and at a crosshead speed of 0.01 \mu m \cdot s^{-1}. At a potential of \(-50\) mV SCE excessive secondary cracking is found at a value for the crosshead speed which results in a smooth fracture surface at a potential of +50 mV SCE. However, a tenfold lower crosshead speed for a potential of \(-50\) mV results in a smooth fracture surface, which is illustrated in figure 5.14. Thus, the parameter dominating the appearance of the fracture surface seems to be the plastic deformation rate as determined by the crosshead speed, relative to the rate by which SCC propagation can occur, the latter being strongly influenced by the potential.

The growth of secondary cracks as the result of an increase of the crosshead speed is consistent with the increase of the current which is found to occur following an increase of the crosshead speed, which has been shown in figure 5.2. The fresh surface produced during the growth of the secondary cracks reacts, and forms, thereby, an extra contribution to the current.
Figure 5.11  Higher magnification of fig. 5.8 showing a smooth fracture surface produced during (110)<001> crack growth at E = + 50 mV SCE and \( v_{\text{crossh}} = 0.01 \mu\text{m}\cdot\text{s}^{-1} \). <001> Direction parallel to the horizontal axis of the photo. Actual crack growth direction from the lower left to the upper right corner. Markings, perpendicular to the river lines are present which appear as regular differences in colour.

Figure 5.12  SEM photo illustrating the effect of a sudden increase of \( v_{\text{crossh}} \) from 0.01 \( \mu\text{m}\cdot\text{s}^{-1} \) (left side) to 0.1 \( \mu\text{m}\cdot\text{s}^{-1} \) (right side) at E = + 50 mV SCE. In the region where the crosshead speed is high, many secondary cracks are present and the appearance of the fracture surface is more irregular. (110)<001> Oriented Cu30Zn single crystal. Crack growth direction from the left to the right.
Figure 5.13 Fracture surface produced during \(\{110\}<001>\) crack growth at \(E = -50\) mV SCE and \(v_{crossh} = 0.01\, \mu m\cdot s^{-1}\) showing secondary cracks. Crack growth direction from the left to the right.

Figure 5.14 Smooth fracture surface produced during \(\{110\}<001>\) crack growth at \(E = -50\) mV SCE and \(v_{crossh} = 0.001\, \mu m\cdot s^{-1}\). Crack growth direction from the left to the right.
5.4 Conclusions

1 For \{110\}<001> specimens as well as for \{110\}<110> specimens crack advance is associated with the decrease of the load which does not show load drops similar to those observed for \{110\}<001> specimens in the Cu25Au/NaCl system.

2 Following nucleation of the crack, the current rises to obtain a stationary value which remains at a constant level during the propagation of the crack. Current peaks are frequently found to be superimposed on the stationary current, but their direct relation with crack propagation is uncertain, since it can not be precluded that they originate from the discontinuous release of gas bubbles.

3 Crack arrest markings, similar to those which have been reported for \{110\}<001> specimens in the Cu25Au system, have not been found.

4 The load and current measurements as well as the fractography suggest that crack propagation is macroscopically continuous, i.e. evidence for discontinuous cracking which is observed for \{110\}<001> specimens in the Cu25Au/NaCl system, is not found.

5 Except for the onset of cracking, where the video camera is not able to monitor the successive positions of the crack front adequately, the video observations indicate that the crack moves with a constant average velocity during the course of an experiment.

6 The average crack velocity increases with increasing potential and with increasing crosshead speed. The maximum observed average crack velocity is the order of a few tenth's of a micrometer per second which is two to three orders of magnitude lower than the maximum observed "instantaneous" crack velocity in the Cu25Au/NaCl system.

7 The average orientation of the fracture surface is parallel to the \{110\} plane perpendicular to the \(<110>\) tensile axis for \{110\}<001> specimens, whereas it deviates strongly from this plane for \{110\}<110> specimens.

8 In some exceptional instances the average fracture surface for a \{110\}<001> shows a transition from \{110\} to \{111\}. If this transition occurs, it occurs at high potentials and high crosshead speeds.

9 The combination of the potential and the crosshead speed influences the appearance of the fracture surface strongly. An increasing tendency for secondary cracking is observed for an increasing crosshead speed at a constant potential and for a decreasing potential at a constant crosshead speed.
6 Fractography

6.1 Introduction

In this chapter the results of a study of the fracture surfaces for the Cu30Zn/NaNO₂ system are presented, focused on the following four issues:

It first deals with the question as to what extent the fracture surfaces show the classic features for cleavage-like fracture as described and discussed in section 2.2 for α-brass in ammonia solutions and for Cu25Au in NaCl solutions. These are the presence of matching fracture surfaces, and fracture on {110} type primary facets, which are separated by {111} type steps and which are undercut.

The second issue deals with the difference between the fracture in (110)[001] and (110)[110] specimens. In chapter 5 it was reported that the average orientation of the fracture surfaces was found to be different for these specimen types, i.e., the average orientation of the fracture surface of (110)[001] specimens was found to be (110), whereas the average orientation of the fracture surface of (110)[110] specimens was found to deviate strongly from (110). In this chapter the orientation of the facets which form this deviating plane, has been determined.

The third issue deals with the study of the orientation of the secondary cracks. In chapter 5 it was reported that an increasing crosshead speed increases the tendency for the formation of secondary cracks strongly in the Cu30Zn/NaNO₂ system. In the present section an attempt has been made to determine whether these secondary cracks are {110} type planes or {111} type planes, in which case they could be explained as being the result of slip plane dissolution.

The fourth issue deals with the smoothness of the facets, which is relevant because of the claim by various workers [30,35,60] that what appear to be {110} facets actually consist of alternating {111} facets. Therefore, it has been investigated if evidence for this claim can be obtained.
Figure 6.1 Photo made with an optical microscope showing the trace of a crack, bisecting the traces of the (111) and (111) slip planes. (110)[001] oriented Cu30Zn specimen in a 1 M NaNO₂ solution at a potential of + 100 mV SCE. The crosshead speed was 0.01 μm·s⁻¹. Extensive prior deformation occurred before the crack initiated.

Figure 6.2 SEM photo showing the trace of a crack, bisecting the traces of the (111) and (111) slip planes and terminating at a prior shear band. (110)[001] oriented Cu30Zn specimen in a 1 M NaNO₂ solution at a potential of + 100 mV SCE. The crosshead speed was 0.01 μm·s⁻¹. In this specimen extensive prior deformation had occurred before the crack initiated.
6.2 Experimental

In this work the fracture surfaces have been studied using a JEOL® field emission Scanning Electron Microscope (SEM). In the SEM the specimen can be rotated around two axes, where the angles of rotation could be measured. This capability has been used to determine the orientation of the secondary cracks. The exact procedure for this determination has been given in the text corresponding to figures 6.6, 6.7, 6.8 and 6.9. For the description of the orientations the sign convention has been used which has been given in figure 2.2.

In most cases a working distance of 10-15 mm was used in the SEM, which should be small enough to resolve small alternating facets [36]. In the SEM, a voltage of 5 kV was usually used. In general, it is noted that the investigation of the fracture surfaces is complicated by to the presence of an oxide the thickness of which is several hundreds of nanometers.

6.3 Results and discussion

*Features for cleavage-like fracture*

Figures 6.1 and 6.2 show the trace of a facet on the (110) side of a (110)[001] specimen. On these photo's the traces of two sets of slip planes are visible as well. It can be seen that the crack trace bisects the traces of the slip planes, and that the angles between the crack trace and both traces of the slip planes are close to 35.3°. Although this does not actually prove that the facet is (110), this picture is consistent with the situation that the slip planes are (111) and (111) and that the facet is (110).

Figure 6.3 shows the opposite sides of a fracture surface produced during crack growth in a (110)[001] specimen. On these photos it can be seen that both surfaces are matching. The photo further shows facets which are separated by steps, where the intersection of the steps with the facets are [112] and [112] directions. Figure 6.4, which shows the fracture surface of figure 6.3 after a rotation, reveals that the steps are undercut. It is to be noted that evidence for matching surfaces and crystallographic steps is only observed occasionally. In most cases, steps are present, where the [112] and [112] directions are not pronounced or can not be detected at all, which situation has been illustrated in figure 6.5.

Figure 6.6 shows a fracture surface produced during crack growth in a (110)[001] specimen, where primary (110) facets are connected by secondary {110} type facets which make an angle of 30° with the tensile axis. This shows that the fracture on these secondary {110} type facets can be an alternative for {111} type steps to connect primary {110} type facets growing at different levels.

From figures 6.1 to 6.6 it can be concluded that "classic" features for cleavage-like cracking, which have been reported for α-brass in ammonia solutions and Cu25Au in NaCl solutions, can also be found in the Cu30Zn/NaNO2 system. However, the steps separating the primary facets are generally not crystallographic.
**Figure 6.3** SEM photo's showing matching surfaces showing crystallographic steps (111) and (111) steps which intersection with the primary facets results in [112] and [112] directions respectively. The photo at the right side is in reverse printing, (110)[001] oriented Cu30Zn specimen in a 1 M NaNO₂ solution at a potential of + 100 mV SCE. The crosshead speed was 0.01 μm·s⁻¹.
Figure 6.4 Primary facets showing undercutting after a rotation around the [001] axis. (110)[001] oriented Cu30Zn specimen in a 1 M NaNO₂ solution at a potential of + 100 mV SCE. The crosshead speed was 0.01 μm⋅s⁻¹.

Figure 6.5 Fracture surface not showing crystallographic steps. (110)[001] Oriented Cu30Zn specimen in a 1 M NaNO₂ solution at a potential of + 50 mV SCE. The crosshead speed was 0.01 μm⋅s⁻¹. The nominal crack growth direction and the orientation are indicated above figure 6.3.
Figure 6.6a-d  Example of secondary [110] type facets connecting two primary planes. Figure 6.6a shows a (110)[001] oriented specimen, positioned with its [110] tensile axis parallel to the electron beam and with its [111] direction parallel to the vertical axis of the photo. The relatively dark coloured areas are primary fracture planes, where the dark area in the upper left corner is at a higher level than the dark area in the lower right corner. The orientation of the crystallographic facets connecting these
primary planes is to be determined. After a rotation of 30° around the [111] axis in the
direction indicated by the stereographic projection, the [011] direction becomes parallel
to the horizontal axis of the photo, and figure 6.6b is obtained. The light appearing
facets from figure 6.6a have now just become invisible, indicating that they are
perpendicular to the plane of the photo. Since they also appear to contain the [111]
direction, they must be (011) facets. Figure 6.6c is obtained after rotating the crystal
from the position in fig. a around the [110] axis, so that the [111] direction is parallel
to the vertical axis of the photo. Now, it is clearly seen that the primary planes are
actually connected by two sets of facets, i.e. a set of relatively large facets which have
been identified as (110) in the previous experiment, and a second set of facets which
have a relatively light appearance on the photo. After a rotation of 30° around the [111]
axis in the direction indicated by the stereographic projection, the [011] direction
becomes parallel to the horizontal axis of the photo, and figure 6.6d is obtained. The
largest part of the second set of facets has now just become invisible, indicating that
they are perpendicular to the plane of the photo. Since they also appear to contain the
[111] direction, they must be (011) facets.

(110)[001] Oriented Cu30Zn specimen in a 1 M NaNO₂ solution at a potential of
+ 50 mV SCE. The crosshead speed was 0.01 μm·s⁻¹.
The average fracture plane is not parallel to the (110) plane of the photo, i.e. the area at the left side of the photo is at a lower level than the area at the right side. Two sets of large facets are present, one on the upper side of the photo and another at the lower side. Figure 6.7b shows the set presented in the upper part of figure 6.7a, where [111] direction is now parallel to the vertical axis of the photo. After a rotation of 30° around the [111] axis in the direction indicated by the stereographic projection, the (011) direction becomes parallel to the horizontal axis of the photo, and figure 6.7c is obtained. The large facets, light appearing in figure 6.7b, have now just become invisible, indicating that they are perpendicular to the plane of the photo. Since they also appear to contain the [111] axis, they must be (011) facets. Figure 6.7d shows the set of facets, present in the lower part of figure 6.7b, where the [111] direction is parallel to the vertical axis of the photo and the (110) tensile axis parallel to the electron beam. After a rotation of 30° around the [111] axis in the direction indicated by the stereographic projection, the (011) direction becomes parallel to the horizontal axis of the photo, and figure 6.7e is obtained. The large facets, light appearing in figure 6.7d, have now just become invisible, indicating that they are perpendicular to the
plane of the photo. Since they also contain the [111] axis, they must be (011).

(110)[110] Oriented Cu30Zn single crystal in a 1 M NaNO₂ solution at a potential of 0 mV SCE. The crosshead speed was 0.01 µm·s⁻¹.
Figure 6.8a-c  Example of \( \{110\} \) type secondary cracks. Figure 6.8a shows a (110)[001] oriented specimen, positioned with its [110] tensile axis parallel to the electron beam and with its [111] direction parallel to the vertical axis of the photo. The nominal [001] crack growth direction is from the lower left to the upper right side of
the photo. In the middle of the photo two secondary facets are visible, of which one is going down in the lower part of the photo and the other going up in the upper part of the photo. After a rotation of 30° around the [111] axis in the direction indicated by the stereographic projection, the [011] direction becomes parallel to the horizontal axis of the photo, and figure 6.8b is obtained. The lower facet from figure 6.8a has now just become invisible, indicating that it is perpendicular to the plane of the photo. Since it also appears to contain the [111] direction, it must be a (011) facet. In figure 6.8c, which is obtained after a rotation of 30° in the opposite direction around the same [111] axis, starting from the position in figure 6.8a, the [101] is parallel to the horizontal axis of the photo. Due to this rotation the upper facet has just disappeared, indicating that it is perpendicular to the plane of the photo. Since it also appears to contain the [111] direction, it must be a (101) facet.

A pattern of fine lines is present in the oxide which covers the facets a pattern of fine lines is present. On the primary (110) facet, at the left side of the photo, the fine lines are approximately [110]. On the lower secondary facet, which orientation is (011), fine lines are present as well, and their projection on the (110) plane of the photo is [112]. In the stereographic projection it can be seen that lines which are projected as [112] on the (110) plane must lay in the (111) plane perpendicular to the plane of the photo. Since the fine lines also lay in the (011) facet itself, their direction corresponds to the intersection of (111) with (011), which is [011]. The fine lines on the upper secondary facet, which orientation is (101), are also projected as [112] lines on the (110) plane of the photo and must, therefore, lay in the (111) plane. Since they also lay in the (101) facet itself, their direction must be [101].

(110)[001] Oriented Cu30Zn specimen in a 1 M NaNO₂ solution at a potential of + 100 mV SCE. The crosshead speed was 0.01 μm·s⁻¹.
Figure 6.9a-e  Example of a secondary crack which average fracture surface is not crystallographic, but which consists, at least partly, of a combination of different \(\{110\}\) type facets. Figure 6.9a shows a secondary crack in a \((110)[001]\) oriented specimen, positioned with its \([110]\) tensile axis parallel to the electron beam and with its \([111]\) direction parallel to the vertical axis of the photo. The nominal \([001]\) crack growth direction is from the upper left to the lower right side of the photo. After a rotation of 30° around the \(\{111\}\) axis in the direction indicated by the stereographic projection, the \([101]\) direction becomes parallel to the horizontal axis of the photo, and figure 6.9b is obtained. Now, it can be seen that the facet in the middle of the left side of the crack has just become invisible, indicating that it is perpendicular to the plane of the photo. Since it also appears to contain the \([111]\) direction, it must be a \((101)\) facet. (In order to investigate if lower part of the right side of the crack would is also a \((101)\) facet, lying beneath the primary facet and being perpendicular to the plane of the photo in figure 6.9b, the rotating angle was increased. The facet which became then visible, can be seen in figure 6.9c, which has been obtained after a rotation of 15 more degrees around the \(\{111\}\) axis.)
Figure 6.9d shows the same secondary crack, where the specimen is positioned with its [110] tensile axis parallel to the electron beam and with its [111] direction is parallel to the vertical axis of the photo. After a rotation of 30° around the [111] axis in the direction indicated by the stereographic projection, the [011] direction becomes parallel to the horizontal axis of the photo, and figure 6.9e is obtained. In this example it can not be proven that the facet in the upper part of the left side of the crack is (011). However, this is still strongly suggested, since the intersection of this facet with the primary facet is [111] which corresponds to the intersection of (110) with (011). (It should be noted that the light appearing facet at the extreme left side of figures 6.9d and 6.9e is clearly (011)). Thus, in this secondary crack, which average surface is not crystallographic, at least a (101) and probably also a (011) facet is present.

(110)[001] Oriented single crystal in a 1 M NaNO₂ solution at a potential of + 50 mV SCE. The crosshead speed was 0.1 µm·s⁻¹.
Figure 6.10 Secondary crack produced in a (110)[001] oriented specimen. Crystallographic features cannot be detected. Oriented Cu30Zn single crystal in a 1 M NaNO₃ solution at a potential of + 50 mV SCE. The crosshead speed was 0.1 μm·s⁻¹.
Figure 6.11 SEM photo showing a primary (110) facet at the left side and a secondary (101) facet at the right side. The intersection between both facets is [111]. The primary (110) facet shows a pattern of fine lines parallel to [110]. The secondary (101) facet shows also fine lines which projection on the (110) plane of the photo is [112]. In the stereographic projection it can be seen that lines which are projected as [112] on the (110) plane must lay in the (111) plane perpendicular to the plane of the photo. Since they also lay in the (101) facet itself, their orientation corresponds to the intersection of (111) with (101), which is [101].

(110)(001) Oriented Cu30Zn single crystal in a 1 M NaNO₂ solution at a potential of + 100 mV SCE. The crosshead speed was 0.01 μm-s⁻¹.
Figure 6.12  Higher magnification of figure 6.6b, where the electron beam is parallel to a secondary (011) facet. The photo shows the smoothness of the facet, and does not support the idea that the {110} type primary facets actually consist of alternating {111} type micro-facets.
**Orientation of the facets in the case of (110)[1\overline{1}0] specimens**

Figure 6.7a-e shows the fracture surface of a (110)[110] specimen where the orientation of the facets has been determined by tilting the specimen in the SEM. This tilting experiment shows that fracture has preferentially occurred on secondary {110} type facets which make an angle of 30° with the tensile axis. It is therefore concluded that the deviation of the average fracture surface from (110), which is generally observed for (110)[110] specimens, is the result of fracture on these secondary {110} type facets.

**Orientation of the secondary cracks**

Figure 6.8 shows secondary cracks where tilting in the SEM reveals that they are clearly secondary {110} type facets which make an angle of 30° with the [110] tensile axis. Secondary cracks can also be present which are not crystallographic or not even flat. In figure 6.9 it has been shown that the surface of such secondary cracks can, at least partly, consist of a combination of small and different {110} type facets. However, for other secondary cracks, there is no evidence that they consist of a combination of {110} type facets, which has been illustrated in figure 6.10. Distinct secondary {111} type cracks have not been found, except for the exceptional case which has been discussed in section 5.3, figure 5.8.

**Smoothness of the fracture surface, fine lines**

Generally, the oxide on both the primary as well as the secondary {110} type facets shows a texture which appears as a pattern of fine lines, 0.25-0.5 μm apart, approximately parallel to the, only possible, <110> type direction in that facet. The presence of this pattern on the (110) primary facets is slightly visible in figure 6.3 and in the left part of figure 6.8a. In the middle part of the latter photo, it can be seen that the (011) and (101) secondary cracks show a similar pattern of lines of which it can be shown that they are [011] and [101] respectively. A higher magnification of the fine <110> type lines has been given in figure 6.11.

The presence of these fine <110> type lines is relevant because of the claim by various workers that what appear to be {110} type facets, actually consist of alternating {111} type facets [30,35]. This has been illustrated in section 2.2, figure 2.1b, showing that alternating {111} and {111} facets which build up a (110) plane, result in [110] striations. Figure 6.2, which shows the trace of a (110) crack on the (110) specimen side at high magnification, is of particular interest, since alternating {111} and {111} facets are expected to result in an alternating crack trace. Another possibility to examine the smoothness of the facets is present in figure 6.12 which is a higher magnification of the figure 6.6b, where the electron beam is parallel to a secondary (011) facet. It can be concluded that neither figure 6.2 nor figure 6.12 gives evidence for the idea that the {110} type facets actually consist of alternating {111} type facets, where it is noted that the presence of alternating {111} type facets equal or smaller than 100-200 nm can not be excluded due to resolution limitations and due to the presence of the oxide. Since the observation of fine <110> type lines appears not to be accompanied by evidence for an alternating crack trace it is concluded that it is unlikely that the fine <110> type lines
are the result of alternating \{111\} type facets. An explanation for the fine \langle110\rangle type lines may be that they are the result of slip steps, since slip steps on the \(110\) facets caused by slip on either the \(111\) or the \(111\) slip plane are parallel to \(110\) \([37]\).

### 6.4 Conclusions

1 The fracture surface obtained in the Cu30Zn/NaNO\(_2\) system shows similar characteristics as those reported for \(\alpha\)-brasses in ammonia solutions and Cu25Au in NaCl solutions, i.e. \{110\} type primary facets, separated by steps which are undercut. The steps are generally not crystallographic.

2 While \((110)(001)\) specimens show fracture on primary \(110\) planes, which are perpendicular to the \(110\) tensile axis, \((110)(110)\) specimens show preferential fracture on \{110\} type planes which make an angle of 30° with the \(110\) tensile axis. The fracture on these secondary plains explains that the average fracture surface generally deviates from \(110\) for \(110)(110)\) specimens.

3 The orientation of secondary cracks can sometimes be determined, but sometimes not. In those instances for which the orientation of the secondary cracks has been established, the secondary cracks appear to be of the \{110\} type, making an angle of 30° with the tensile axis. Situations have been found where a secondary crack is formed by a combination of different \{110\} type facets. Distinct \{111\} type secondary cracks have not been found.

4 The \{110\} type facets are, at least on a scale of 200 nm, truly \{110\}. Alternating \{111\} type micro-facets have not been found. Fine \langle110\rangle type lines have been found which are present as a pattern in the oxide. These lines have not been interpreted as evidence for the presence of alternating \{111\} microfacets.
7 Load and current behaviour

7.1 Introduction

In this chapter the load and current behaviour is analysed in a more detailed way than in chapter 5. The purpose of this analysis is to investigate if evidence can be obtained for discontinuous crack propagation in the Cu30Zn/NaNO₂ system.

In chapter 5 the load was reported to decrease smoothly during crack advance, even for \( \{110\}<001> \) specimens. Fast load drops which alternated with periods of constant or slightly rising load decrease were not detected. However, the absence of detectable fast load drops does not preclude the occurrence of discontinuous crack growth. It may, e.g., be possible that the crack advance distance per crack advance event is too small to be detected separately by the load cell. In this respect it is noted that the load cell has shown to be able to pick up load drops in the Cu25Au/NaCl system, where the discontinuous crack advance distances vary between \( = 20 - 200 \mu m \). However, table 2.1 shows that crack advance distances for \( \alpha \)-brasses in ammonia solutions are on the order of \( 0.5 - 5 \mu m \).

In chapter 5 it was also reported that current peaks were detected, but that the interpretation of these current peaks is complicated by the fact that it was also observed that gas bubbles are formed during SCC crack growth in this system, and that the sudden release of these gas bubbles gives rise to current peaks. However, no definite proof is available that all peaks originate from the discontinuous release of gas bubbles.

Given these background, the particular aim of the analysis described in this section is to investigate if the load and current behaviour can in principle be consistent with a discontinuous crack advance process.

7.2 Analysis of the load and current behaviour

In this chapter load and current data obtained in SSR tests as described in chapter 5, are analysed using the basic principles which have been described in section 2.4. In addition, the current behaviour, and in particular the current peaks, are analysed in a slightly different way in order to investigate whether or not the current peaks could be consistent with a discontinuous crack advance process. The different way of analysing the current is necessary because of the low repassivation rate in the Cu30Zn/NaNO₂
Figure 7.1  Values for the crack extension area per peak, $\Delta A$, and the crack extension distance per peak, $\Delta x$, (for a uniformly moving crack front, $w_{front} = 1$ mm), based on the values of the peak frequency, $f_{peak}$ and calculated using formula 7.1.

Figure 7.2  Values for the crack extension area per peak, $\Delta A$, and the crack extension distance per peak, $\Delta x$, (for a uniformly moving crack front, $w_{front} = 1$ mm), based on the values of the peak height, $i_{peak}$ and calculated using formula 7.2.
system, which has the consequence that the current can not considered to be linearly related to the actual crack velocity if the latter shows rapid changes.

The question whether or not the current peaks are consistent with a discontinuous crack advance process is treated based on the idea that the crack extension area per crack advance event can be calculated in two different ways, i.e. by using the frequency of the current peaks and by using the height of the current peaks. If the values which are calculated using these methods are on the same order of magnitude, it can be concluded that the height and the frequency of the current peaks are consistent with a discontinuous crack advance process.

If the current peaks correspond to discrete events of crack advance, the crack extension area and, in the case of a uniformly moving crack, the crack extension distance can be calculated using the peak frequency.

\[
\Delta A = \frac{w_{\text{front}} \cdot v_{\text{crack, av.}}}{f_{\text{peak}}} \quad (7.1a) \quad \Delta x = \frac{v_{\text{crack, av.}}}{f_{\text{peak}}} \quad (7.1b)
\]

where:

\(\Delta A\) = crack extension area
\(\Delta x\) = crack extension distance
\(w_{\text{front}}\) = length of the whole crack front
\(v_{\text{crack, av.}}\) = average crack velocity
\(f_{\text{peak}}\) = peak frequency

The values \(\Delta A\) and \(\Delta x\) can also be estimated from the height of the current peaks, if the simplification is made that the crack extensions occur so fast that the height of the resulting current peaks is proportional to \(\Delta A\) and \(\Delta x\).

\[
\Delta A = \frac{I_{\text{peak}}}{2 \cdot i_{\text{peak}}} \quad (7.2a) \quad \Delta x = \frac{I_{\text{peak}}}{2 \cdot w_{\text{front}} \cdot i_{\text{peak}}} \quad (7.2b)
\]

where:

\(I_{\text{peak}}\) = height of a peak during SCC
\(i_{\text{peak}}\) = peak current density of the repassivation transient (in the micro-crack)

For \(v_{\text{crack, av.}}\), the values from figure 5.7 are used which were derived from the video camera observations. The values of \(i_{\text{peak}}\), which can not be determined during a SCC experiment, are approximated by the peak current densities at \(t = 0.1\) s in the chronoamperometric experiments as plotted in figure 4.2. It should be noted that the values for \(i_{\text{peak}}\) obtained by these experiments have to be treated with certain reservations, since the composition of the solution and the IR drop in the crack is likely to be different from the bulk. In spite of this deficiency, this method will be
Figure 7.3  Load behaviour during \{110\}<001> crack growth, where the potential \( E = +100 \text{ mV SCE} \) and the crosshead speed, \( v_{\text{crossh}} = 0.01 \mu\text{m.s}^{-1} \) until \( t = 115 \text{ s} \). For this combination of the potential and the crosshead speed, which results in a smooth fracture surface, the load decreases smoothly. At \( t = 115 \text{ s} \) the potential was decreased to \(-50 \text{ mV SCE}\). This resulted in a change of the load decrease rate which was detected 15 to 20 seconds after the change of the potential.

Figure 7.4  Load and current behaviour during \{110\}<001> crack growth at \( E = +50 \text{ mV SCE} \) and \( v_{\text{crossh}} = 0.01 \mu\text{m.s}^{-1} \). The load decreases in a rough way showing discontinuities which do not coincide which changes in the current. Large current peaks are present which do not correspond to discontinuities in the load.
used, since it may still give an indication of the order of magnitude.

Using formula 7.1, the values for $\Delta A$ and $\Delta x$, have been calculated and plotted in figure 7.1. Figure 7.2 shows the values for $\Delta A$ and $\Delta x$ corresponding to values of $I_{\text{peak}}$ and $E$ as calculated by formula 7.2. It should be noted that the value of $\Delta A$ which corresponds to a certain value of $I_{\text{peak}}$, is lower for higher potentials, since a higher potential results in a higher $I_{\text{peak}}$.

7.3 Results and discussion

Load measurements
During crack propagation the load is found to decrease without showing fast drops which alternate with periods of constant or slightly increasing load. The appearance of the load decrease during advance of the crack is found to be correlated to the smoothness of the fracture surface. For a smooth fracture surface, which is found for relatively high potentials and relatively low crosshead speeds, see section 5.3, the load is found to decrease smoothly. This is illustrated in figure 7.3 showing the load during crack advance at a potential of +100 mV SCE and at a crosshead speed of 0.01 $\mu$m·s$^{-1}$. For a combination of the potential and crosshead speed resulting in a rough and irregular fracture surface with much secondary cracking, see section 5.3, the load is found to decrease in a rougher way. This is illustrated in figure 7.4 showing the load during crack advance at a potential of +50 mV SCE and at a crosshead speed of 0.1 $\mu$m·s$^{-1}$. It is noted that the irregularities in the load behaviour which are shown in figure 7.4 do not coincide with changes in the current, which would be expected if they were to originate from discontinuities in the crack velocity. The rougher appearance of the load behaviour is likely to be attributed to the rougher and more irregular fracture process which is indicated by the irregular fracture surface obtained under these conditions, which has been illustrated the right part of figure 5.10. Based on these observations, it is concluded that the load behaviour reflects the smoothness of the fracture process. However, despite the fact that irregularities in the load behaviour are found under certain circumstances, there is no indication that these irregularities originate from discontinuous events of crack advance.

Figure 7.3 also shows the load response, if the crack growth rate is decreased by lowering the potential. This illustrates the general observation that a decrease of the crack velocity, as caused by decreasing the potential, is detected within 15-20 seconds. It is not certain if this time delay is to be attributed to the properties of the experimental set-up or to a phenomenon related to SCC. Due to this uncertainty it is considered to be impossible to use the load behaviour for making statements regarding the occurrence of small, discontinuous events of crack advance. However, since a change in the crack velocity is reflected in the load behaviour within 15-20 seconds, a load decrease rate which is constant over a period considerably longer than 15-20 seconds can be considered to be an indication of a constant average crack velocity during that period.
Figure 7.5  Load and current behaviour during \{110\}<001> crack growth at $E = + 50$ mV SCE and $v_{\text{crossh}} = 0.01$ $\mu$m·s$^{-1}$. Regular current peaks are present.

Figure 7.6  Load and current behaviour during \{110\}<001> crack growth at $E = + 100$ mV SCE and $v_{\text{crossh}} = 0.01$ $\mu$m·s$^{-1}$. Current peaks are present. A twofold increase of the peak frequency in the latter 100 seconds does not result in a twofold increase of the load decrease rate. Note that the height of the peaks is one order of magnitude higher than in figure 7.5.
Current measurements
During the SSR experiments current peaks are measured which are similar to those reported by Newman and Sieradzki [49, 50]. Examples of current peaks are given in figures 7.4-7.6. The following general characteristics of the peaks are found.

1. The peaks are characterised by a fast increase followed by a slow decay.
2. The peaks can be very regular over a certain time interval.
3. For a given potential the peak height increases and the peak frequency decreases with increasing crosshead speed and crack length.
4. For a given crosshead speed the height of the peaks increases with increasing potential.

An example of current peaks accompanied by the sudden release of a gas bubbles are the large peaks which are shown in figure 7.4. This evidence for these peaks not being related to discontinuous events is consistent with the observation that the peaks are not accompanied by discontinuities in the load decrease rate. In this respect it is noted that the discontinuous release of gas bubbles has only been observed in experiments performed at high crosshead speeds, resulting in wide cracks and allowing the high resolution camera to observe the solution in the crack. For lower crosshead speeds, where the cracks are too narrow to allow the observation of the solution in the crack, no definite proof is available that the current fluctuations originate from gas bubbles.

An example of the investigation whether or not the peaks can in principle be consistent with a discontinuous crack advance process is given below, where the data from figure 7.5 are used. Figure 7.5 shows the load and current as measured during crack propagation at $E = +50$ mV SCE and $v_{crossh} = 0.01 \mu m \cdot s^{-1}$. In this example $f_{peak} = 0.5 \ s^{-1}$ and $I_{peak} = 0.1 \ \mu A$. According to figures 7.1 and 7.2, which show the calculations for the crack extension area $\Delta A$ based on $f_{peak}$ and $I_{peak}$ respectively, a value of $f_{peak} = 0.5 \ s^{-1}$ corresponds to $\Delta A = 400 \ \mu m^2$, whereas a value of $I_{peak} = 0.1 \ \mu A$ corresponds to $\Delta A = 100 \ \mu m^2$. For a uniform crack front having a length of 1 mm, these values correspond to crack advance distances of 0.4 and 0.1 mm respectively. Since these values are of the same order of magnitude, it can be concluded that in this situation the peaks can be consistent with a discontinuous crack advance process.

However, despite the fact that situations are found where the peaks can be consistent with a discontinuous crack advance process, situations are also found where this consistency does certainly not exist. An example of such a situation is illustrated in figure 7.6. Figure 7.6 shows a load which is decreasing continuously during 200 seconds, from which it can be concluded that the crack is moving with a constant average crack velocity. However, the current peaks are not consistent with a constant average crack velocity, since only 15 peaks are present during the first 100 seconds, whereas 30 peaks of the same height are measured during the latter 100 seconds. If these peaks were to originate from discontinuous events of crack advance, the doubled peak
frequency would have to be associated with a doubled crack velocity and with a double load decrease rate. This is certainly not the case.

Especially at the lower potentials the situation can be found that crack propagation occurs without the presence of any peaks of which an example has been given in figure 7.7. This figure shows the current data for a crack growing at a potential of \(-50\ \text{mV SCE}\) where no peaks can are found larger than 2.5 nA which is the value of the background noise. Since the possibility that discontinuous crack advance events occur resulting in peaks equal or smaller than 2.5 nA cannot be excluded, an estimation is made of the crack extension area, \(\Delta A\), or crack extension distance, \(\Delta x\), resulting in a peak of 2.5 nA. Figure 7.2 shows that peaks of this height would correspond to crack propagation area of 20 \(\mu\text{m}^2\), or a crack propagation distance of 0.02 \(\mu\text{m}\) if the whole crack front of 1 mm were moving uniformly. Although crack extensions of this size can not be excluded by the present work, it should be mentioned that peaks of this size are not the peaks which have been used in the literature as evidence for discontinuous cracking. E.g. Newman and Sieradzki report a peak height of 2.5 \(\mu\text{A}\) for Cu30Zn polycrystals at the same potential [49].

Summarising, it can be concluded that current peaks can originate from the discontinuous release of gas bubbles. It is further found that situations are present where the current peaks can in principle be consistent with a discontinuous crack advance process. On the other hand, situations are also present where the current peaks are certainly not consistent with a discontinuous crack advance process. Given these uncertainties, the current peaks are not considered to be evidence for the occurrence of discontinuous crack advance.

![Figure 7.7](image_url)

**Figure 7.7** Load and current behaviour during \(\{110\}<001>\) crack growth at \(E = -50\ \text{mV SCE}\) and \(v_{\text{crossh.}} = 0.01\ \mu\text{m}\cdot\text{s}^{-1}\). Possible current peaks can not be distinguished from the background noise.
7.4 Conclusions

1 The smoothness of the fracture process is reflected in the smoothness of the load decrease during crack propagation. However, the load measurements do not provide evidence for discontinuous crack advance.

2 Current peaks have been measured. It has been observed that the release of gas bubbles is accompanied by a current peaks.

3 Some situations have been found where the height and the frequency of the current peaks could be consistent with a discontinuous crack advance process.

4 Situations have been found where the height and the frequency of the current peaks are certainly not consistent with a discontinuous crack advance process.

5 It can not be precluded that crack advance occurs discontinuously where the crack extension areas of each crack advance event are on the order of $\approx 100 \, \mu m^2$ corresponding to crack advance distances of $0.1 \, \mu m$ in case of a uniformly moving crack front with a length of 1 mm. These values are smaller than those found in the literature.

6 Given the uncertainties in the interpretation of the current peaks, the current peaks are not considered to be evidence for the occurrence of discontinuous crack advance.
8 Mass transport

8.1 Introduction

In order to investigate which processes determine the crack velocity, it is studied whether or not the crack velocity is restricted by diffusion limitations and/or a potential drop in the crack. This is performed in two different ways. First, the influence of an increase of the viscosity of the solution on the crack velocity is studied, where increasing the viscosity has the effect of decreasing the diffusion coefficients of the solute. Second, the possible presence of restrictions of the crack velocity originating from the conditions for solute transport is investigated by performing mass transport calculations.

8.2 Experimental

Slow strain rate tests are performed on \{110\}\{001\} specimens in a 1 M NaNO₂ solution, where the solvent consists of 50 mass% water and 50 mass% glycerol. The viscosity of this mixture is six higher times than the viscosity of pure water [76]. The slow strain rate tests are performed using the same procedure which has been described in chapter 5.

8.3 Mass transport calculations

*Occurrence of diffusion limitations in the crack for the Cu30Zn/NaNO₂ system*

Based on the description of the electrochemistry of the Cu30Zn/NaNO₂ system which has been given in chapter 4, the following reactions are considered to occur in the crack tip region.

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2 \text{e}^- & (8.1) \\
2 \text{Cu} + \text{H}_2\text{O} & \rightarrow \text{Cu}_2\text{O} + 2 \text{H}^+ + 2 \text{e}^- & (8.2) \\
\text{H}^+ + \text{NO}_2 & \rightarrow \text{HNO}_2 & (8.3) \\
3 \text{HNO}_2 & \rightarrow \text{H}^+ + \text{NO}_3^- + 2 \text{NO (g)} + \text{H}_2\text{O} & (8.4)
\end{align*}
\]
In chapter 4 it is concluded that the crack tip reaction rate is likely to be determined by the rate by which reaction 8.1 and reaction 8.2 can occur. It is assumed that diffusion limitations do not restrict the rate of reaction 8.1, but that diffusion limitations may restrict the rate of reaction 8.2. Though both reaction 8.1 and reaction 8.2 are considered to determine the crack tip reaction rate, and thus the crack propagation rate, it is expected to be likely that the crack propagation rate will be restricted if the rate of reaction 8.2 is limited by diffusion restrictions. In this work it will be calculated whether or not the rate of reaction 8.2, and thus the crack propagation rate, is expected to be restricted by diffusion limitations during SCC crack growth. It will further be calculated if significant potential drops in the crack are expected to influence the crack propagation rate.

The concentration gradients which result from the occurrence of reactions 8.2 and 8.3 are depicted schematically in figure 8.1a. Reaction 8.2 can not occur if the $H^+$ concentration in the crack tip region is higher then the value where reaction 8.2 is in equilibrium. The rate of reaction 8.2 is considered to be restricted by diffusion limitations if the $H^+$ as well as the HNO$_2$ concentration approach the values where reactions 8.2 and 8.3 are in equilibrium, since then the overpotential for reaction 8.2 approaches zero. The $H^+$ and HNO$_2$ concentrations where reaction 8.2 and 8.3 are in equilibrium, i.e. $c^\text{eq}_{H^+}$, $c^\text{eq}_{\text{HNO}_2}$, can be obtained by using the Nernst equation for reaction 8.2 and the equilibrium constant for reaction 8.3. Under the assumption that activities are equal to concentrations, $c^\text{eq}_{H^+}$ and $c^\text{eq}_{\text{HNO}_2}$ given by equations 8.5 and 8.6.

\[
\begin{align*}
c^\text{eq}_{H^+} &= 10^{(E-0.230)/0.0591} \quad (8.5) \\
c^\text{eq}_{\text{HNO}_2} &= 10^{3.35} c^\text{eq}_{H^+} c^\text{eq}_{\text{NO}_2} \quad (8.6)
\end{align*}
\]

where:

\[
\begin{align*}
E &= \text{electrode potential} \\
c^\text{eq}_{\text{NO}_2} &= \text{NO}_2 \text{ concentration at the electrode}
\end{align*}
\]

For the calculation of $c^\text{eq}_{\text{HNO}_2}$, it is noted that a decrease NO$_2$ concentration results in a lower value for $c^\text{eq}_{\text{HNO}_2}$. Therefore diffusion limitations can arise due to a depletion of NO$_2$ in the crack tip regions which results in a lower value for $c^\text{eq}_{\text{HNO}_2}$. Further, the maximum possible transport rate of HNO$_2$ from the crack tip is equal to the maximum possible transport rate of NO$_2$ to the crack tip. Thus, if the transport rate of NO$_2$ is maximal, since its concentration in the crack tip has decreased to zero, the transport rate of HNO$_2$ from the crack tip is maximal as well.

If reaction 8.4 occurs at a sufficiently high rate, the $H^+$ as well as the HNO$_2$ concentration gradients will become smaller, and it could even be possible that they are not present at all, since the successive occurrence of reactions 8.2, 8.3, and 8.4 allows the formations of Cu$_2$O to occur without a net $H^+$ and HNO$_2$ production. This is illustrated by reaction 8.7 showing the sum of reactions 8.2, 8.3 and 8.4.
2 Cu + 3 NO\textsubscript{2} \rightarrow Cu\textsubscript{2}O + NO\textsubscript{3} + 2 NO \textsubscript{(g)} + 2 e^- \quad (8.7)

In this case diffusion restrictions are considered to be present if the NO\textsubscript{2} concentration in the crack tip region reaches zero.

**Calculation of the concentrations in the crack tip region and the potential drop in the crack**

For different proposed situations the H\textsuperscript{+}, HNO\textsubscript{2} and NO\textsubscript{2} concentration will be calculated at the position in the crack, where the crack walls are expected to have just become passivated. This is illustrated in figure 8.1b, showing a schematic representation of the anodic current density along the crack walls for a system where the anodic reaction results in the formation of a protective film. The crack has been drawn schematically in figure 8.1c. A co-ordinate system is used, where the x-axis is chosen to be parallel to the crack growth direction and perpendicular to the crack front. At the point for which the concentration will be calculated, i.e. the point where the crack walls are expected to have just become passivated, x is defined to be equal to zero. The x-coordinate system is defined to move in the same direction and with the same rate as the tip of the crack. The crack mouth is located at x=L. For each species the difference of the concentration between x=0 and x=L, i.e. Δc, will be calculated. The concentration at the crack mouth, i.e. c(x=L) is assumed to be equal to the concentration of the bulk solution, and is, therefore, known. The concentration at x=0, i.e. c(x=0), can be calculated using equation 8.8.

\[
c(x=0) = c(x=L) \pm \Delta c \quad (8.8)
\]

where a plus applies in the right term for species diffusing from the crack tip and a minus applies in the right term for a species diffusing towards the crack tip.

The geometry of the crack in the region for which the mass transport calculations are performed is approximated by a trapezium, where the angle between the crack walls is α. For a constant extension rate test, where gross yielding occurs, the angle α between the crack walls far enough from the crack tip is given by equation 8.9.

\[
\alpha = \frac{v_{\text{crossh}}}{v_{\text{crack}}} \quad (8.9)
\]

where:

- \( v_{\text{crack}} \) = crack velocity
- \( v_{\text{crossh}} \) = crosshead speed, perpendicular to the plane of the crack.
Figure 8.1  (a) Schematic representation of the concentration profiles of the diffusing species in the crack. (b) Schematic representation of the current distribution along the crack walls. (c) Schematic representation of the crack geometry.
The opening of the crack as a function of \( x \) is given by equation 8.10.

\[
h(x) = h_0 + \alpha x
\]

\text{where:}

\[
\begin{align*}
h(x) &= \text{opening of the crack} \\
h_0 &= \text{opening of the crack at } x = 0
\end{align*}
\]

The value for \( h_0 \) is approximated using equation 8.11.

\[
h_0 = \alpha \text{v}_{\text{crack}} t_{\text{pass}}.
\]

\text{where } t_{\text{pass}} \text{ is equal to the time necessary for a fresh surface to achieve complete passivation following the first exposure to the solution. The value for } t_{\text{pass}} \text{ is approximated by the time necessary to achieve complete passivation following a stepping experiment performed on a flat electrode, of which the results have been plotted in figure 4.2.}

The total current, \( I \), is the sum of all current contributions along the crack walls. In the present work it is considered, that the crack is propagating at a constant rate, and that the fresh surface which was created at the time of the nucleation of the crack surface has already become passivated. Under these conditions the current is expected to have a stationary value, \( I_{\text{stat.}} \), which is given by equation 8.12.

\[
I_{\text{stat.}} = 2 Q l \text{v}_{\text{crack}}
\]

\text{where:}

\[
\begin{align*}
Q &= \text{charge density passing the crack walls until complete passivation} \\
l &= \text{length of the crack front}
\end{align*}
\]

For equation 8.12, fresh surface is considered to be produced by the propagating crack only and not by secondary cracks. The stationary current, \( I_{\text{stat.}} \), can be obtained by using the current measurements which have, been performed during the slow strain rate tests and which have, e.g., been plotted in figure 5.1. Figure 5.1 shows subsequently a constant background current while the crack is still not nucleated, a current rise during the initiation of the crack, and an approximately constant current during the crack propagation. The stationary current \( I_{\text{stat.}} \) is taken to be the constant value of the current during the propagation of the crack minus the background current which is measured before the nucleation of the crack. It is further verified if the experimentally determined value for \( I_{\text{stat.}} \) is expected to be reasonable by comparing this value with the calculated value for \( I_{\text{stat.}} \), which is obtained by using equation 8.12. For the calculation of \( I_{\text{stat.}} \) by
using equation 8.12, the crack velocity \( v_{crack} \) is directly obtained from the video camera observations, for which the results have been plotted in figure 5.7. The charge density passing the crack walls until complete passivation, \( Q \), is approximated by the charge density passed during the stepping experiments performed on a flat electrode, for which the results have been plotted in figures 4.2 and 4.3b.

Under the assumption that mass transport in the crack only occurs by diffusion, the flux of a species which is consumed or produced during the reaction is given by equation 8.13:

\[
J(x) = \frac{I_{\text{stat.}}}{nF \alpha I(h_0+\alpha x)} = -D \frac{dc}{dx}
\]  

(8.13)

where:

\( I_{\text{stat.}} \) = stationary current  
\( n \) = number of electrons involved per reacting species  
\( F \) = Faraday's number  
\( l \) = length of the crack front  
\( D \) = diffusion coefficient  
\( c \) = concentration

Integrating equation 8.13 gives the concentration difference between \( x = 0 \) and \( x = L \):

\[
\Delta c = \left[ \frac{I_{\text{stat.}}}{nF \alpha} \ln (h_0+\alpha x) \right]_0^L = \frac{I_{\text{stat.}}}{nF \alpha} \ln \left( \frac{1+\alpha L}{1+\alpha h_0} \right)
\]

(8.14)

In figure 8.2 \( \Delta c \) has been plotted as a function of various values for \( L \), where values have been chosen for \( I_{\text{stat.}}, \alpha, h_0, n, l, \) and \( D \) which are of an order of magnitude applicable to the present work.

Besides the concentration difference \( \Delta c \) between \( x = 0 \) and \( x = L \), the potential difference \( \Delta \phi \) between \( x = 0 \) and \( x = L \) can be calculated as well. The potential drop \( d\phi \) over a distance \( dx \) is given by:

\[
d\phi = \frac{\rho I_{\text{stat.}}}{l \alpha I(h_0+\alpha x)} dx
\]

(8.15)

where:

\( \rho \) = conductivity of the solution

Integrating equation 8.15 gives the potential difference between \( x = 0 \) and \( x = L \):
\[ \Delta \phi = \left[ \frac{\rho I_{\text{stat}}}{1 + \alpha x} \ln \left( \frac{h_0 + \alpha x}{h_0} \right) \right]_0^L = \frac{\rho I_{\text{stat}}}{1 + \alpha L} \ln \left( \frac{1 + \alpha L}{h_0} \right) \]  

(8.16)

For an anodic current, the potential in the solution in the crack tip region is higher than the potential in the bulk solution. This means that the electrode potential at \( x = 0 \) is \( \Delta \phi \) lower than the electrode potential at the crack mouth. In figure 8.2 \( \Delta \phi \) has been plotted as a function of various values of \( L \), where values have been chosen for \( I_{\text{stat}}, \alpha, h_0, L, \) and \( \rho \) to be of an order of magnitude applicable to the present work.

**Note on the interpretation of the results**

For the interpretation of the calculated concentrations, it is noted that they are only expected to approximate the real values within an order of magnitude, since the calculations involve various simplifications which are likely to affect the results. These comprise:

1. The activities are replaced by concentrations
2. Mass transport by migration is not taken into account
3. The part of the crack where the crack walls have not yet become passivated is not considered in the calculations.
4. For the estimation of \( h_0 \) it is assumed that the repassivation characteristics in the crack tip region are the same as those at a flat electrode.

![Figure 8.2](image)

**Figure 8.2** Concentration drop, \( \Delta c \), in the crack between \( x = L \) and \( x = 0 \) as a function of \( L \) and \( h_0 \) for \( I_{\text{stat}} = 1 \) \( \mu A \), \( n = 1 \), \( D = 10^{-9} \) \( m^2 \cdot s^{-1} \), \( l = 1 \) \( mm \), and \( \alpha = 0.05 \). Potential drop, \( \Delta \phi \), in the crack between \( x = L \) and \( x = 0 \) as a function of \( L \) and \( h_0 \) for \( I_{\text{stat}} = 1 \) \( \mu A \), \( \rho = 14 \) \( \Omega \cdot cm \), \( l = 1 \) \( mm \), and \( \alpha = 0.05 \). These values are of the order of the values which are relevant in the present work.
However, despite the fact that the precise values for the concentrations can not be calculated, conclusions can be drawn from the orders of magnitude of the concentrations of the various species.

### 8.4 Results and discussion

**Determination of the influence of an increase of the viscosity of the solution on the crack velocity**

Figure 8.3 shows the crack velocity for \(\{110\} <001>\) specimens as a function of the potential for solutions not containing glycerol as well as for solutions of which the solvent consists of 50 mass% water and 50 mass% glycerol. Figure 8.3 shows that the average crack velocity in a solution not containing glycerol increases with increasing potential up to a potential of +100 mV SCE after which it becomes approximately independent on the potential. Figure 8.3 also reveals that the use of the glycerol-containing solution results in significantly lower crack velocities. Since the effect of glycerol is presumably only to be attributed to the increase of the viscosity of the solution and the resulting decrease of the diffusion coefficients, it can is concluded that the conditions for solute transport in the crack influence the crack velocity. Since the crack velocity in the potential region below +100 mV is also dependent on the potential, it is concluded that in this region the potential as well as the conditions for solute transport influence the crack velocity.

![Figure 8.3](image)

*Figure 8.3 Average crack velocity as a function of the potential measured in solutions not containing glycerol and in solutions containing 50% glycerol. \(\{110\} <001>\) specimens in a 1 M NaNO\(_2\) solution. The crosshead speed, \(v_{crossh}\), was 0.01 \(\mu\)m·s\(^{-1}\) in all experiments except for \(E = -100\) mV SCE, where \(v_{crossh}\) was 0.003 \(\mu\)m·s\(^{-1}\).*
*Determination of the parameters necessary to calculate $\Delta c$ and $\Delta \phi$*

Table 8.1 lists the values for $Q$, $I_{\text{stat}}$, $\alpha$, $t_{\text{pass}}$, and $h_0$ used to calculate $\Delta c$ and $\Delta \phi$ and which have been determined using the method which is described in section 8.3.

**Table 8.1 Values for $Q$, $I_{\text{stat}}$, $\alpha$, $t_{\text{pass}}$, and $h_0$ obtained for experiments performed at different potentials and crosshead speeds. The length of the crack front $l$ is equal to $1\text{mm}$.**

<table>
<thead>
<tr>
<th>pot. (mV SCE)</th>
<th>$v_{\text{crossh.}}$ (µm·s$^{-1}$)</th>
<th>$v_{\text{crack}}$ (µm·s$^{-1}$)</th>
<th>sec. cracks *</th>
<th>$Q$ (C·cm$^{-2}$)</th>
<th>$I_{\text{stat. pred.}}$ (µA) #</th>
<th>$I_{\text{stat. meas.}}$ (µA)</th>
<th>$\alpha$</th>
<th>$t_{\text{pass.}}$ (s)</th>
<th>$h_0$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>0.001</td>
<td>0.016</td>
<td>–</td>
<td>0.95</td>
<td>0.30</td>
<td>0.6</td>
<td>0.063</td>
<td>1200</td>
<td>1.2</td>
</tr>
<tr>
<td>-50</td>
<td>0.01</td>
<td>0.034</td>
<td>+</td>
<td>0.95</td>
<td>0.65</td>
<td>2</td>
<td>0.34</td>
<td>1200</td>
<td>12</td>
</tr>
<tr>
<td>0</td>
<td>0.01</td>
<td>0.1</td>
<td>+</td>
<td>0.35</td>
<td>0.7</td>
<td>4</td>
<td>0.1</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>50</td>
<td>0.01</td>
<td>0.18</td>
<td>–</td>
<td>0.4</td>
<td>1.44</td>
<td>1.8</td>
<td>0.056</td>
<td>125</td>
<td>1.25</td>
</tr>
<tr>
<td>50</td>
<td>0.1</td>
<td>0.3</td>
<td>+</td>
<td>0.4</td>
<td>2.4</td>
<td>7</td>
<td>0.34</td>
<td>125</td>
<td>12.5</td>
</tr>
<tr>
<td>100</td>
<td>0.01</td>
<td>0.2</td>
<td>–</td>
<td>1.5</td>
<td>6</td>
<td>5</td>
<td>0.05</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>0.1</td>
<td>0.25</td>
<td>+</td>
<td>1.5</td>
<td>7.52</td>
<td>17</td>
<td>0.4</td>
<td>100</td>
<td>10</td>
</tr>
</tbody>
</table>

* the presence of secondary cracks is indicated using the symbol +

# value for $I_{\text{stat.}}$ as calculated by using equation 8.12

In table 8.1 it has also been indicated whether or not secondary cracks are formed. If no secondary cracks are formed, a reasonable agreement exists between the values for $I_{\text{stat.}}$ calculated by using equation 8.12 and the measured values for $I_{\text{stat.}}$. However, if secondary cracks are formed, the measured values for $I_{\text{stat.}}$ are considerably higher than the calculated values for $I_{\text{stat.}}$. This can be explained, since the secondary cracks also contribute to the current, whereas the calculated value for $I_{\text{stat.}}$ is only applicable for the situation where only one crack grows. Since the situation where secondary cracks grow is not well defined, the mass transport calculations are only performed for the situation where no secondary cracks are formed.

In order to investigate whether or not crack growth is restricted by diffusion limitations, three situations have been considered.

**Calculation of $\Delta c$ for the first situation**

In the first situation it is assumed that all current originates from the occurrence of reaction 8.1 and reaction 8.2, whereas neither reaction 8.3 nor reaction 8.4 occur. For this situation the $H^+$ concentration at $x = 0$, i.e. $c_{H^+}(x=0)$, is calculated using equation 8.17.

$$c_{H^+}(x=0) = c_{H^+}(x=L) + \Delta c_{H^+}$$ (8.17)
The value of $c_{H^+}(x=L)$ is equal to the bulk concentration which is $10^{-9}$ mol·l$^{-1}$ in the present work. The value for $\Delta c_{H^+}$ is calculated using equation 8.14, where $D_{H^+} = 10^{-8}$ m$^2$·s$^{-1}$, $L = 0.5$ mm, and where $n = 13/7$, the latter being based on the assumption that the oxidation of Zn and Cu occurs at a rate proportional to their concentrations in the bulk alloy.

For the first situation, the obtained values for $c_{H^+}(x=0)$ have been given in table 8.2. The $H^+$ concentration where reaction 8.2 is in equilibrium, i.e. $c_{H^+}^{eq}$, as calculated using equation 8.5, has been given in table 8.2 as well. Comparison of $c_{H^+}(x=0)$ and $c_{H^+}^{eq}$ shows that the values for $c_{H^+}(x=0)$ are two to four orders of magnitude higher than the values for $c_{H^+}^{eq}$. This leads to the conclusion that the transport of the $H^+$ ions as $H^+$ ions alone cannot occur at a sufficiently high rate in order to keep the $H^+$ ions in the crack tip region sufficiently low for the continued occurrence of reaction 8.2 at the rates measured.

Calculation of $\Delta c$ for the second situation
In the second situation it is assumed that all current originates from the occurrence of reaction 8.1 and reaction 8.3, and it is further assumed that reaction 8.3 occurs, but not reaction 8.4. It is further assumed that the amount of $H^+$ which diffuses in the form of $H^+$ is negligible compared to the amount of $H^+$ which diffuses in the form of HNO$_2$.

For this situation the HNO$_2$ and NO$_2$ concentrations at $x = 0$, i.e. $c_{HNO_2}(x=0)$ and $c_{NO_2}(x=0)$ respectively are calculated using equations 8.18 and 8.19.

\[
c_{HNO_2}(x=0) = c_{HNO_2}(x=L) + \Delta c_{HNO_2}
\]

\[
c_{NO_2}(x=0) = c_{NO_2}(x=L) - \Delta c_{NO_2}
\]

The value of $c_{HNO_2}(x=L)$ is considered to be equal to the bulk concentration which is calculated to be $2.2 \times 10^{-6}$ mol·l$^{-1}$ using equation 8.5 for a 1 M NaNO$_2$ solution of pH = 9. The value of $c_{NO_2}(x=L)$ is 1 mol·l$^{-1}$ in the present work. The values for $\Delta c_{HNO_2}$ and $\Delta c_{NO_2}$ are calculated using equation 8.14, where $D_{HNO_2}, D_{NO_2} = 10^{-9}$ m$^2$·s$^{-1}$, $L = 1$ mm, $L = 0.5$ mm, $n = 13/7$ for HNO$_2$ as well as for NO$_2$, the value for n being based on the assumption that the oxidation of Zn and Cu occurs at a rate proportional to their concentrations in the bulk alloy.

For the second situation, the results of the calculation of $c_{HNO_2}(x=0)$ and $c_{NO_2}(x=0)$ have been given in table 8.3. The HNO$_2$ concentration where both reaction 8.2 and reaction 8.3 are in equilibrium, i.e. $c_{HNO_2}^{eq}$, as calculated using equations 8.5 and 8.6 has been given in table 8.3 as well. For the calculation of $c_{HNO_2}^{eq}$ the value for the NO$_2$ concentration is taken to be equal to $c_{NO_2}(x=0)$.

Comparison of $c_{HNO_2}(x=0)$ with $c_{HNO_2}^{eq}$ shows that $c_{HNO_2}(x=0)$ is a factor of five higher than $c_{HNO_2}^{eq}$ at a potential of $-50$ mV SCE, which situation is impossible for the continued occurrence of reaction 8.2. At a potential of $+50$ mV SCE, $c_{HNO_2}(x=0)$ is a factor 1.5 lower than $c_{HNO_2}^{eq}$. Since the values of $c_{HNO_2}(x=0)$ and $c_{HNO_2}^{eq}$ are on the same order of magnitude for these potentials, it is concluded that diffusion limitations
Table 8.2 Calculated values for $\Delta c_{H^+}$, $c_{H^+}(x=0)$, and $c_{H^+}^{eq}$ for Cu30Zn in a 1 M NaNO₂ solution in the first situation, i.e. where all current originates from the occurrence of reaction 8.1 and reaction 8.2, whereas neither reaction 8.3 nor reaction 8.4 occur. $D_{H^+} = 10^{-8}$ m²·s⁻¹, $l = 1$ mm, $L = 0.5$ mm, $n = 13/7$

<table>
<thead>
<tr>
<th>potential (mV SCE)</th>
<th>$v_{crossh.}$ (µm·s⁻¹)</th>
<th>$v_{crack}$ (µm·s⁻¹)</th>
<th>$I_{stat.}$ (µA)</th>
<th>$\alpha$</th>
<th>$h_0$ (µm)</th>
<th>$\Delta c_{H^+}$ (mol·l⁻¹)</th>
<th>$c_{H^+}(x=0)$ (mol·l⁻¹)</th>
<th>$c_{H^+}^{eq}$ (mol·l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>− 50</td>
<td>0.001</td>
<td>0.016</td>
<td>0.6</td>
<td>0.063</td>
<td>1.2</td>
<td>0.018</td>
<td>0.018</td>
<td>1.8·10⁻⁵</td>
</tr>
<tr>
<td>50</td>
<td>0.01</td>
<td>0.18</td>
<td>1.8</td>
<td>0.056</td>
<td>1.25</td>
<td>0.057</td>
<td>0.057</td>
<td>9.0·10⁻⁴</td>
</tr>
<tr>
<td>100</td>
<td>0.01</td>
<td>0.2</td>
<td>5</td>
<td>0.05</td>
<td>1</td>
<td>0.182</td>
<td>0.182</td>
<td>6.3·10⁻³</td>
</tr>
</tbody>
</table>

Table 8.3 Calculated values for $\Delta c_{HNO₂}$, $c_{HNO₂}(x=0)$, $c_{HNO₂}^{eq}$, $\Delta c_{NO₂}$ and $c_{NO₂}(x=0)$ for Cu30Zn in a 1 M NaNO₂ solution in the second situation, i.e. where all current originates from the occurrence of reaction 8.1 and 8.2, and where reaction 8.3 occurs, but not reaction 8.4. $D_{HNO₂}$, $D_{NO₂} = 10^{-5}$ m²·s⁻¹, $l = 1$ mm, $L = 0.5$ mm, $n = 13/7$

<table>
<thead>
<tr>
<th>potential (mV SCE)</th>
<th>$v_{crossh.}$ (µm·s⁻¹)</th>
<th>$v_{crack}$ (µm·s⁻¹)</th>
<th>$I_{stat.}$ (µA)</th>
<th>$\alpha$</th>
<th>$h_0$ (µm)</th>
<th>$\Delta c_{HNO₂}$ (mol·l⁻¹)</th>
<th>$c_{HNO₂}(x=0)$ (mol·l⁻¹)</th>
<th>$c_{HNO₂}^{eq}$ (mol·l⁻¹)</th>
<th>$\Delta c_{NO₂}$ (mol·l⁻¹)</th>
<th>$c_{NO₂}(x=0)$ (mol·l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>− 50</td>
<td>0.001</td>
<td>0.016</td>
<td>0.6</td>
<td>0.063</td>
<td>1.2</td>
<td>0.18</td>
<td>0.034</td>
<td>0.18</td>
<td>0.82</td>
<td>0.82</td>
</tr>
<tr>
<td>50</td>
<td>0.01</td>
<td>0.18</td>
<td>1.8</td>
<td>0.056</td>
<td>1.25</td>
<td>0.57</td>
<td>0.57</td>
<td>0.86</td>
<td>0.43</td>
<td>0.43</td>
</tr>
<tr>
<td>100</td>
<td>0.01</td>
<td>0.2</td>
<td>5</td>
<td>0.05</td>
<td>1</td>
<td>1.82</td>
<td>-</td>
<td>1.82</td>
<td>−0.82</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 8.4 Calculated values for $\Delta c_{NO₂}$ and $c_{NO₂}(x=0)$ for Cu30Zn in a 1 M NaNO₂ solution in the third situation, i.e. where all current originates from the occurrence of reaction 8.1 and 8.2, and where reaction 8.3 and reaction 8.4 occur, where no net in such a way that not net production of $H^+$ and HNO₂ occurs. $D_{NO₂} = 10^{-9}$ m²·s⁻¹, $l = 1$ mm, $L = 0.5$ mm, $n = 13/10.5$

<table>
<thead>
<tr>
<th>potential (mV SCE)</th>
<th>$v_{crossh.}$ (µm·s⁻¹)</th>
<th>$v_{crack}$ (µm·s⁻¹)</th>
<th>$I_{stat.}$ (µA)</th>
<th>$\alpha$</th>
<th>$h_0$ (µm)</th>
<th>$\Delta c_{NO₂}$ (mol·l⁻¹)</th>
<th>$c_{NO₂}(x=0)$ (mol·l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>− 50</td>
<td>0.001</td>
<td>0.016</td>
<td>0.6</td>
<td>0.063</td>
<td>1.2</td>
<td>0.26</td>
<td>0.74</td>
</tr>
<tr>
<td>50</td>
<td>0.01</td>
<td>0.18</td>
<td>1.8</td>
<td>0.056</td>
<td>1.25</td>
<td>0.85</td>
<td>0.15</td>
</tr>
<tr>
<td>100</td>
<td>0.01</td>
<td>0.2</td>
<td>5</td>
<td>0.05</td>
<td>1</td>
<td>2.7</td>
<td>−1.7</td>
</tr>
</tbody>
</table>

Table 8.5 Calculated values for $\Delta \phi$ for Cu30Zn in a 1 M NaNO₂ solution. $\rho = 14 \Omega·cm$, $l = 1$ mm, $L = 0.5$ mm.

<table>
<thead>
<tr>
<th>potential (mV SCE)</th>
<th>$v_{crossh.}$ (µm·s⁻¹)</th>
<th>$v_{crack}$ (µm·s⁻¹)</th>
<th>$I_{stat.}$ (µA)</th>
<th>$\alpha$</th>
<th>$h_0$ (µm)</th>
<th>$\Delta \phi$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>− 50</td>
<td>0.001</td>
<td>0.016</td>
<td>0.6</td>
<td>0.063</td>
<td>1.2</td>
<td>4.4</td>
</tr>
<tr>
<td>50</td>
<td>0.01</td>
<td>0.18</td>
<td>1.8</td>
<td>0.056</td>
<td>1.25</td>
<td>14</td>
</tr>
<tr>
<td>100</td>
<td>0.01</td>
<td>0.2</td>
<td>5</td>
<td>0.05</td>
<td>1</td>
<td>45</td>
</tr>
</tbody>
</table>
are likely to restrict the crack propagation rate, if diffusion of H⁺ ions from the crack tip only occurs in the form of HNO₂ ions and H⁺ ions. This situation could explain that both the electrode potential and the conditions for solute transport influence the crack velocity, since a higher electrode potential results in a higher value for c^HNO₂ in the crack tip region and thus in a higher maximum possible transport rate and in a higher maximum crack propagation rate.

The calculations further show that c_{NO₂}(x=0) is significantly lower than the bulk concentration c_{NO₂}(x=L). At a potential of +100 mV SCE, the results of the calculations give an impossible picture since c_{NO₂}(x=0) has decreased below zero. This NO₂ depletion gives also rise to a diffusion limitation, since it results in a lower value for c^HNO₂ in the crack tip region. Further, the HNO₂ transport rate from the crack tip is maximal if the NO₂ transport rate to the crack tip is maximal. If c_{NO₂}(x=0) has dropped to zero, the crack velocity is expected to be independent of the potential, since no further decrease of c_{NO₂}(x=0) can occur.

**Calculation of Δc for the third situation**

In the third situation it is assumed that all current is used for the occurrence of reaction 8.1 and reaction 8.2, and it is further assumed that reaction 8.2 is followed by reactions 8.3 and 8.4 in such a way that no net production of H⁺ and HNO₂ occurs, so that the successive occurrence of reaction 8.2, 8.3 and 8.4 can be written as reaction 8.7. For this situation the NO₂ concentration at x=0, i.e. c_{NO₂}(x=0) is calculated using equation 8.19.

\[
c_{NO₂}(x=0) = c_{NO₂}(x=L) - Δc_{NO₂}
\]

The value of c_{NO₂}(x=L) is 1 mol·l⁻¹ in the present work. The value Δc_{NO₂} is calculated using equation 8.14, where D_{NO₂} = 10⁻⁹ m²·s⁻¹, l = 1 mm, L = 0.5 mm, n = 13/10.5 under the assumption that the oxidation of Zn and Cu occurs at a rate proportional to their concentrations in the bulk alloy.

For the third situation, the results of the calculation of c_{NO₂}(x=0) have been given in table 8.4. It is shown that c_{NO₂}(x=0) is significantly lower than c_{NO₂}(x=L) and that c_{NO₂}(x=0) decreases with increasing potential. At a potential of 100 mV SCE, c_{NO₂}(x=0) is calculated to be lower than zero, which situation is, obviously, impossible. These calculations show that diffusion limitations are certainly present for potentials above +50 mV SCE, where the NO₂ concentration in the crack tip region approach there minimum value, and where the rate of NO₂ diffusion to the crack tip and thus the rate of H⁺ removal from the crack tip is maximal. Like the second situation, the crack velocity is expected to be independent of the potential, c_{NO₂}(x=0) has dropped to zero, since then no further decrease of c_{NO₂}(x=0) can occur.

However, for a potential of ~50 mV SCE, it can not conclusively be shown that diffusion limitations are present. For this situation, the NO₂ in the crack tip region has certainly decreased, but not to zero. Since gas bubbles, which are indicative for the dissociation of HNO₂ according to reaction 8.4, no conclusive evidence can be provided
that diffusion limitations are present at this potential. However, the evidence that reaction 8.4 occurs, does not prove that it occurs to the extent that no net $H^+$ and $HNO_2$ production occurs, which is assumed in the third situation. Thus, diffusion limitations could still be present if the increase of the $H^+$ concentration in the crack tip region is sufficient to result in a considerable decrease of the overpotential for reaction 8.2. This would actually be a mixture of the second and third situation.

**Calculation of the potential drop, $\Delta \phi$**

Table 8.5 shows the calculated values for the potential drop as calculated using equation 8.16, where $\rho = 14 \, \Omega \cdot \text{cm}$, $l = 1 \, \text{mm}$, $L = 0.5 \, \text{mm}$. It is shown that the potential drop increases with increasing potential. At a potential of 100 mV SCE the potential drop has already a considerable value. This leads to the conclusion that at higher potentials the crack velocity is also expected to be restricted by the presence of a potential drop.

8.5 Conclusions

1. The experiments showing that an increase of the viscosity of the solution results in an decrease of the crack velocity indicate that the conditions for solute transport in the crack influence the crack velocity.

2. The calculations show that the diffusion of the $H^+$ ions as $H^+$ ions alone cannot occur at a sufficiently high rate in order to keep the $H^+$ ions in the crack tip region sufficiently low for the continued occurrence of the reaction in the crack tip region at the rates measured.

3. The calculations show that the crack propagation rate is certainly restricted by diffusion limitations at all potentials, if dissociation of $HNO_2$ does not occur.

4. Since the dissociation of $HNO_2$ does occur, the calculations do not provide conclusive evidence for the crack propagation rate being restricted by diffusion limitations in the lower potential region, i.e. at potentials of $-50 \, \text{mV SCE}$ and lower. However, despite the fact that the dissociation of $HNO_2$ does occur, the presence of diffusion limitations can be understood if the increase of the $H^+$ and $HNO_2$ concentration in the crack tip region is sufficient to result in a considerable decrease of the overpotential.

5. At potentials above $+50 \, \text{mV SCE}$, the crack propagation rate is restricted by a $NO_2$ depletion as well as by a potential drop. This can explain the observation that the crack velocity does not increase with increasing potential for potentials higher than $+50 \, \text{mV SCE}$. 
Comparison of the SCC behaviour of the Cu$_{30}$Zn/NaNO$_2$, Cu$_{30}$Zn/Cu(I)ammonia and Cu$_{25}$Au/NaCl systems

9.1 Outline discussion

In this chapter the SCC behaviour of Cu$_{30}$Zn in 1 M NaNO$_2$ solutions of pH = 9 (Cu$_{30}$Zn/NaNO$_2$ system) is compared with the SCC behaviour of disordered Cu$_{25}$Au in 0.6 M NaCl solutions (Cu$_{25}$Au/NaCl system) and Cu$_{30}$Zn in de-oxygenated 5 M NH$_3$, 0.16 M Cu$^+$ solutions containing excess of Cu powder (Cu$_{30}$Zn/Cu(I)ammonia system), the latter systems having been investigated by many workers in the group of Flanagan and Lichter [1-14,26,53]. The idea behind this comparison is that these systems show comparable mechanical behaviour, but different electrochemical behaviour. An overview of the observed differences between these systems is given in tables 9.1 and 9.2.

As the electrochemical behaviour is the variable, the differences in electrochemical behaviour will first be discussed in section 9.2. This will be followed by a comparison of the following SCC features:

- The relation between the specimen orientation and the fracture path
- Facets and steps
- Corrosion slots and secondary cracks
- Discontinuity of crack advance
- Crack velocity

The various models which have been proposed to explain these features will then be compared. Finally, it will be discussed if explanations for the observed differences can be given based on these models and on the differences in the electrochemical behaviour of these systems.
Table 9.1  Overview of differences between the electrochemical behaviour between the Cu30Zn/NaNO₂, Cu30Zn/Cu(I)ammonia and Cu25Au/NaCl system for a flat electrode

<table>
<thead>
<tr>
<th></th>
<th>Cu30Zn/NaNO₂</th>
<th>Cu30Zn/Cu(I)ammonia [53]</th>
<th>Cu25Au/NaCl [1-12]</th>
</tr>
</thead>
<tbody>
<tr>
<td>anodic reaction</td>
<td>oxidation of both elements (Cu, Zn)</td>
<td>selective dissolution of element forming smaller fraction in alloy (Zn)</td>
<td>selective dissolution of element forming larger fraction in alloy (Cu)</td>
</tr>
<tr>
<td>passivation</td>
<td>Cu₂O layer, only a thick layer is protective</td>
<td>Cu-enriched layer, only protective at rest potential</td>
<td>Au-enriched layer, a thin layers is already protective</td>
</tr>
<tr>
<td>anodic reaction rate at fresh surface</td>
<td>high, slightly higher, but comparable to Cu25Au/NaCl</td>
<td>unknown</td>
<td>high, slightly lower, but comparable to Cu30Zn/NaNO₂</td>
</tr>
<tr>
<td></td>
<td>Cu30Zn/NaNO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Cu30Zn/Cu(I)ammonia [53]</td>
<td>Cu25Au/NaCl [1-12]</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------------------------</td>
<td>--------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>average orientation fracture surface</td>
<td>type I primary {110}</td>
<td>primary {110}</td>
<td>primary {110}</td>
</tr>
<tr>
<td></td>
<td>type II Fracture surface not co-planar. Deviates from primary {110}</td>
<td>Fracture surface not co-planar. Deviates from primary {110}</td>
<td>primary {110}</td>
</tr>
<tr>
<td>orientation facets</td>
<td>type I primary {110}</td>
<td>primary {110}</td>
<td>primary {110}</td>
</tr>
<tr>
<td></td>
<td>type II secondary {110}</td>
<td>not determined</td>
<td>primary {110}</td>
</tr>
<tr>
<td>steps</td>
<td>type I not crystallographic in most cases</td>
<td>crystallographic, {111} (but <em>not</em> as pronounced as in &quot;classic&quot; examples [2,4,42])</td>
<td>crystallographic, {111}</td>
</tr>
<tr>
<td></td>
<td>type II not determined</td>
<td>crystallographic, {111} (but <em>not</em> as pronounced as in &quot;classic&quot; examples [2,4,42])</td>
<td>crystallographic, {111}</td>
</tr>
<tr>
<td>secondary cracks</td>
<td>type I+II tremendous secondary cracking at higher strain rates</td>
<td>secondary cracking at higher strain rates</td>
<td>not pronounced</td>
</tr>
<tr>
<td>crack propagation</td>
<td>type I macroscopically continuous</td>
<td>macroscopically continuous</td>
<td>macroscopically discontinuous (if Cu25Au is disordered)</td>
</tr>
<tr>
<td></td>
<td>type II macroscopically continuous</td>
<td>macroscopically continuous</td>
<td>macroscopically continuous</td>
</tr>
<tr>
<td></td>
<td>$v_{\text{crack, inst.}}$ possibly equal to $v_{\text{crack, av.}} = 0.005$-0.5 $\mu$m·s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>$\Delta x = &lt; 1$ µm</td>
<td>$\Delta x = 40$-200 µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Delta t_{\text{arrest}} = &lt; 7$ s</td>
<td>$\Delta t_{\text{arrest}} = 100$-500 s *)</td>
</tr>
<tr>
<td></td>
<td>$v_{\text{crack, inst.}} = \text{unknown}$</td>
<td>$v_{\text{crack, inst.}} = \text{unknown}$</td>
<td>$v_{\text{crack, inst.}} = 10$-100 µm·s&lt;sup&gt;-1&lt;/sup&gt; #</td>
</tr>
</tbody>
</table>

*) $\Delta t_{\text{arrest}}$ increases with decreasing potential.

#) $v_{\text{crack, inst.}}, v_{\text{crack, av.}}$ increases with increasing potential
Figure 9.1  Voltammogram for Cu30Zn measured at a scan rate of 0.2 mV·s⁻¹ in a deaerated 1 M NaNO₂ solution of pH = 9 and voltammogram for Cu25Au measured at a scan rate of 0.08 mV·s⁻¹ in a deaerated 0.6 M NaCl solution [8].

Figure 9.2  Current response for Cu30Zn in a deaerated 1 M NaNO₂ solution of pH = 9 following stepping from the rest potential to E = 0 mV SCE and current response for Cu25Au in a deaerated 0.6 M NaCl solution following stepping from the rest potential to E = + 400 mV SCE [9].
9.2 Electrochemical behaviour as determined at a flat electrode

The differences between the electrochemical behaviour of the systems in their potential domain for SCC cracking concern the nature as well as the rate of the anodic reaction. These differences, which are indicated in table 9.1, will now be discussed.

In the Cu25Au/NaCl system, only the least noble element, i.e. Cu, becomes oxidised and enters the solution as a dissolved ion [4,5,7-9]. In this case, the selectively dissolved element forms the larger atomic fraction in the alloy. At potentials below the critical potential, passivity is achieved by an ennobled, Au-rich, layer which is left behind following the dissolution of a few monolayers of Cu. In the Cu30Zn/Cu(I)ammonia system [26,53], it is also the least noble element, i.e. Zn, which becomes oxidised, but the element which becomes oxidised forms the smaller atomic fraction in the alloy. Passivity is achieved by the formation of a copper enriched layer. In the Cu30Zn/NaNO₂ system, both elements become oxidised, where Cu is oxidised to form Cu₂O, which remains on the surface as a grain-like oxide, and where oxidised zinc enters the solution. In this system the formation of the grain-like Cu₂O film can result in passivation after it has reached a sufficient thickness.

For the Cu25Au/NaCl system as well as for the Cu30Zn/NaNO₂ system, the rates of the anodic reaction in the potential domain for SCC cracking can be compared using polarisation studies. Data for the rate of selective dissolution in the Cu30Zn/Cu(I)ammonia system can not easily be obtained, as the potential for SCC is the rest potential, at which the selective dissolution of Zn is balanced by the reduction of Cu⁺ ions.

In figure 9.1 the anodic branches of the voltammograms for the Cu25Au/NaCl system and the Cu30Zn/NaNO₂ system have been plotted. In this figure it can be seen that the current density in the SCC domain for the Cu30Zn/NaNO₂ system is approximately two orders of magnitude higher than the current density in the SCC domain for the Cu25Au/NaCl system below the critical potential. Since a surface layer is being formed in the anodic domain of both systems, a surface layer is continuously present during both measurements. From the higher current densities in the Cu30Zn/NaNO₂ system it can, therefore, be concluded that the Cu₂O film in the Cu30Zn/NaNO₂ system is less protective than the ennobled Au-layer in the Cu25Au/NaCl system. This is also demonstrated in figure 9.2, where the current responses have been compared for both systems after stepping the potential from the rest potential to a value in the potential domain for SCC cracking. In this figure it can be seen that the current density decreases more rapidly in the Cu25Au/NaCl system than in the Cu30Zn/NaNO₂ system. Calculating the charge density which needs to pass before the current density has reached a passive value, reveals that passivity is only achieved following the dissolution of hundreds to a few thousands of monolayers in the case of the Cu30Zn/NaNO₂ system. In contrast, only a few monolayers need to dissolve to obtain passivity in the Cu25Au/NaCl system.

Since the initial values for current responses in figure 9.2 increase with increasing potential for both systems, the results of a comparison of both systems based on the
initial current densities depend on the applied potentials. However, at the potentials which have most frequently been studied in the SCC experiments, the initial current densities are several factors higher for the Cu30Zn/NaNO₂ system than for the Cu25Au/NaCl system, but they are still within the same order of magnitude.

9.3 The relation between the specimen orientation and the fracture path

A difference between the systems which was unexpected before the onset of this work concerns the relation between the fracture path and the specimen orientation, i.e. \{110\}<001> or \{110\}<110>. Here the sign convention previously given in figure 6.1 is used. In the Cu25Au/NaCl system, the fracture paths are reported to be orthogonal to the [110] tensile axis for \{110\}[001] as well as for \{110\}[110] specimens, and both specimen types exhibited fracture on primary [110] facets, which are orthogonal to the [110] tensile axis. The Cu30Zn/(I)ammonia system as well as the Cu30Zn/NaNO₂ system exhibit a fracture surface which is perpendicular to the [110] tensile axis and which consists of primary [110] facets for \{110\}[001] specimens. However, in contrast to the Cu25Au/NaCl system, this is not the case for \{110\}[110] specimens in the Cu30Zn/Cu(I)ammonia and the Cu30Zn/NaNO₂ system, in which case the average fracture surface is found to deviate strongly from the [110] plane perpendicular to the [110] tensile axis. For the Cu30Zn/NaNO₂ system it has been shown that the fracture surface then consists of a combination of various secondary \{110\} type facets which make an angle of 30° with the [110] tensile axis. This has been illustrated in figure 6.7, showing a Cu30Zn, \{110\}[110] type specimen in a NaNO₂ solution which exhibits fracture on secondary (011) and (011) facets. For Cu30Zn, \{110\}[110] type specimens in Cu(I)ammonia solutions, the deviation of the average fracture surface from [110] may also be the result of fracture on various secondary \{110\} type planes, but this has not been verified experimentally. Summarising, while the fracture surface of all systems show comparable features for \{110\}[001] specimens, a major difference exists between the fracture path's found for \{110\}[110] specimens in the Cu30Zn/NaNO₂ and Cu30Zn/Cu(I)ammonia system on one hand and the Cu25Au/NaCl system on the other hand.

Since the most important difference between the specimen orientation seems to involve the orientation relation between the intended crack growth direction and the slip planes which are bisected by the fracture plane, theories which describe a role of the orientation of the slip planes will be discussed in relation with this phenomenon. These theories comprise the Corrosion-Enhanced Plasticity model, the Corrosion-Assisted Cleavage model, and a theory not related to a particular model.

The Corrosion-Enhanced Plasticity model postulates that a crack, which appears to be a \{110\} crack, actually propagates by a process, where, in an alternating way, \{111\} and \{111\} facets are formed, see figure 2.2b. As has been pointed out by Magnin et al., it is then required that the crack front contains the \{111\} and \{111\} slip planes [31]. In
figure 2.2b and figure 2.3 it can be seen that the crack front must then coincide with the [110] intersection of these (111) and (111) facets and that the crack propagation direction is expected to be [001], i.e. orthogonal to the crack front and in the (110) plane. Magnin et al. have proposed that a different fracture path in the case of (110)(110) specimens can be explained as being the result of the crack front not containing the (111) and (111) slip planes [31]. According to the Corrosion-Assisted Cleavage model, re-nucleation of an arrested (110) crack involves the formation of a corrosion slot along a (111) or (111) slip plane, which is followed by a transition of the crack from the (110) or (111) slip plane to the (110) plane. Such a transition seems to require that the intersection of the initial (111) or (111) plane with the (110) plane coincides with the crack front. In figure 2.3 it can be seen that this intersection is [110]. Thus, the initial crack front is expected to be [110], while the initial crack propagation direction is expected to be [001], i.e. orthogonal to the crack front and in the (110) plane. A third possible reason for the crack front preferably being [110] and the crack propagation direction preferably being [001] involves a possible necessity for the occurrence of slip to open up the crack to allow the solution to reach the crack tip. As has been illustrated in figure 2.3, slip on primary (111) or (111) slip planes only results in crack tip opening if the crack front coincides with the intersection of the (111) or (111) slip planes, which is the case if the crack front is [110]. If the crack propagation direction is orthogonal to the crack front, the preferred crack growth direction is [001] for a (110) fracture surface.

Thus, based on the three theories, it can be argued that it may be that crack growth occurs preferably in a [110] type direction. If this would indeed be the case, it can be imagined that it may be difficult to force a crack to grow in a [110] type direction, which is the intended crack growth direction in (110)<110> specimens. This may then be the cause of an alternative fracture path, such as the fracture on secondary (011) and (011) facets in (110)(110) type specimens which has been illustrated in figure 6.7.

Thus, explanations for the difference between the fracture path's for the different specimen orientations have been offered. However, no explanation has been given for the observation that this difference between the fracture paths does exist for the Cu30Zn/NaNO₂ and Cu30Zn/Cu(1)ammonia system, but does not exist for the Cu25Au/NaCl system. It is also uncertain whether or not this difference between the systems are related to differences in their electrochemical behaviour or if other differences which are related to the mechanical properties of the materials play a role. Therefore, it will must be concluded that, as long as the difference between the systems is not understood, the proposed explanations for the relation between the fracture path and the specimen orientation are certainly incomplete.

9.4 Facets and steps

For {110}<001> oriented specimens all systems show comparable features, i.e. fracture on primary {110} type facets, separated by steps which are undercut. Differences are
present in the appearance of the steps. The Cu25Au/NaCl system shows always \{111\} steps which are orthogonal to the primary facets and which intersections with the primary facets form <112> directions. Steps of this type are similar to the "classic" examples of crystallographic steps which are found in brass in cupric ammonia solutions [35,42,76]. Though the steps in the Cu30Zn/Cu(I)ammonia system have been reported to be crystallographic [53], their appearance is not as pronounced as in the "classic" examples and their presence seems to be restricted to large river lines. In the Cu30Zn/NaNO₂ system which is presently studied, crystallographic steps have been found in certain cases, but in most cases they are not crystallographic or they are crystallographic at a scale which can not be resolved.

It has been argued by Pugh [33] that crystallographic steps are to be expected if a low energy shearing process is available, which is speculated to be the case in materials showing restricted cross-slip, such as Cu30Zn and Cu25Au, but that the steps are expected to be non-crystallographic if a low energy shearing process is not available, which is speculated to be the case in materials showing cross-slip, such as copper. This argument was used to explain the crystallographic steps in Cu30Zn and the non-crystallographic steps in copper. The present work shows that the steps can be non-crystallographic in Cu30Zn and that systems which have restricted cross slip do not necessarily show crystallographic steps. The present work further confirms the picture which has come forward from the literature study described in section 2.1 that the occurrence of the crystallographic steps in Cu30Zn is not as general and that the appearance of the steps is dependent on the mechanical conditions as well as on the electrochemical conditions. Since Cu30Zn can show crystallographic steps, the absence of the crystallographic steps in the present work on Cu30Zn seems not to be attributed to the material. As crystallographic steps are found in Cu25Au under the present loading conditions, the absence of crystallographic steps in the Cu30Zn in not likely to be attributed to the present loading conditions. Therefore, the differences in the appearance of the steps in Cu30Zn and Cu25Au may originate from differences in electrochemical behaviour.

9.5 Corrosion slots and secondary cracks

In the Cu30Zn/NaNO₂ system the tendency for secondary cracking is strongly dependent on the strain rate. For relatively low strain rates, no secondary cracks are observed, and the fracture surfaces are relatively smooth. For relatively high strain rates numerous secondary cracks are found, and new cracks are found to emanate from these secondary cracks. The secondary cracks are often not flat, but if they are flat, they are usually secondary \{110\} type facets making an angle of 30° with the tensile axis. In exceptional cases \{111\} type cracks are found which are parallel to the primary slip planes. The combination of the primary with the numerous secondary cracks results in a rough and irregular appearance of the fracture surface. For the Cu25Au/NaCl system, no significant tendency for secondary cracking has been reported. For the
Comparison of the SCC behaviour of the Cu30Zn/NaNO₂, Cu30Zn/Cu(I)ammonia and Cu25Au/NaCl systems

Cu30Zn/Cu(I)ammonia system, secondary cracks are found, and, like the Cu30Zn/NaNO₂ system, the tendency for their formation is increases with increasing strain rate [53]. However, the tendency for secondary cracking is less than in the Cu30Zn/NaNO₂ system, and the fracture surface becomes less irregular. Thus, amongst the compared systems, the Cu30Zn/NaNO₂ system shows the strongest presence of secondary cracks at high strain rates, which indicates that secondary cracks can be nucleated the most easily in this system.

Among the models discussed in section 2.2, only the CAC model describes a theory on the role of secondary cracks. The theory of CAC model relates to the growth of a "dog-leg" crack along a \{111\} shear plane and to the formation of \{111\} corrosion slots by a process which the authors define as "slip-plane dissolution". If such a slip-plane dissolution process were to envisaged as a "classic" slip dissolution process, it could be understood that the Cu30Zn/NaNO₂ system shows the strongest tendency for slip-plane dissolution. This is believed to be the case, since electrochemical features of this system correspond to the electrochemical features which are claimed to be optimal for slip-dissolution, i.e. the combination of an high initial reaction rate at a fresh surface, which is followed by a decrease of the reaction rate which is neither too fast, nor too slow [22,56]. The electrochemical features of the other systems do not correspond to the features just mentioned. However, this explanation for the pronounced occurrence of the secondary cracking in the Cu30Zn/NaNO₂ system is not convincing, since the secondary cracks of which the orientation can be determined, are \{110\} and not \{111\} which would be the expected plane for slip-plane dissolution. The evidence for \{111\} cracks is very scarce. Therefore, it is concluded that, though a correlation is found between the high reaction rates and the strong tendency for secondary cracking, no evidence is present that these secondary cracks are the result of slip-plane dissolution.

9.6 Discontinuity of crack advance

This section deals with the macroscopically discontinuous cracking as has been observed in ordered \{110\}\{001\} Cu25Au single crystals in NaCl solutions. In this system a crack advance event shows a period of a second in which the crack velocity increases from zero to a value on the order of 100 \mu m\textit{s}^{-1} which is followed by a period of a few seconds in which the crack velocity decreases again to zero. The subsequent period of crack arrest lasts 100 to 500 seconds, this duration being dependent on the potential. The present work shows that no evidence for discontinuous cracking is found in the Cu30Zn/NaNO₂ system. The Cu30Zn/Cu(I)ammonia system does not show macroscopically discontinuous cracking either, but in this system microscopically discontinuous cracking has been reported, where the crack advance distances are smaller than a micrometer. The duration of a period of crack arrest and the velocity during an event of crack propagation are unknown for this system. Since this microscopically discontinuous cracking is not as well documented as the macroscopically discontinuous cracking, only the latter type of discontinuous cracking will be discussed.
The models of section 2.2 in which the role of crack arrests are treated explain the occurrence of crack arrest as being caused by mechanical blunting of the crack tip by slip. For instance, according to the corrosion assisted cleavage model, the arrest of a crack is caused by blunting, which is believed to occur after the increase of the stress intensity due to the increasing crack length has resulted in the activation of a major shear band. An alternative explanation by van der Wekken has been discussed in section 2.2. He describes the discontinuous cracking for \( [110] <001> \) specimens in the Cu25Au/NaCl system as the following repetitive process. Following nucleation of the crack, Cu\(^{2+} \) ions enter the crack solution, and during the growth of the crack the Cu\(^{2+} \) concentration rises. This rise proceeds until the solubility product of CuCl\(_2\) salt has been reached, after which precipitation of this salt occurs. This precipitation of the salt is expected to retard or block further dissolution in the crack tip region, which results in a decrease of the crack propagation rate, since the dissolution is necessary for crack propagation. This decrease of crack propagation rate is expected to increase the probability of crack blunting, if the slip planes have the appropriate orientation with respect to the crack front. According to this theory the crack can re-nucleate after the salt has dissolved to a sufficient extent.

It is obvious that models which attribute the occurrence of crack arrests only to mechanical factors, such as the occurrence of crack tip blunting by slip, can not explain why macroscopically discontinuous cracking does occur in the Cu25Au/NaCl system, whereas it does not occur in the Cu30Zn/NaNO\(_2\) system, if the only difference between these systems concerns differences in the electrochemical behaviour. However, the theory proposed by van der Wekken could in principle be suitable to provide such an explanation, since this theory deals with the chemistry of the system. When this theory is to be applied on the Cu30Zn/NaNO\(_2\) system, it has to be evaluated if salts are expected to precipitate in this system. The existence of zinc nitrite salts is not reported in the literature available to the author. As the Cu is oxidised to form Cu\(_2\)O and since the Cu ion concentration which can be formed at the present potentials is low, the precipitation of copper nitrite salts is considered to be unlikely. Since the macroscopically discontinuous cracking in the Cu25Au/NaCl system is attributed to the precipitation of a salt according to van der Wekken, the unlikelihood of the precipitation of salts in the Cu30Zn/NaNO\(_2\) system is considered as a possible explanation for the absence of this type of discontinuous cracking in this system.

9.7 Crack velocity

In this section differences between the crack velocities measured in the different systems will be discussed. Since crack propagation can be discontinuous, it is necessary to distinguish between the average crack velocity, \( v_{crack, av.} \), and the instantaneous crack velocity, \( v_{crack, inst.} \), during a period of crack advance. In the case of discontinuous crack growth a comparison of the different values of the instantaneous crack velocity is likely to provide more mechanistic information that a comparison of the values of the average
crack velocity, since the latter is dependent on more processes, such as the crack re-
nucleation time, the instantaneous crack velocity and the crack propagation distance
during a period of crack advance.

Unfortunately, only for the Cu25Au/NaCl system, the instantaneous crack velocity
is known with certainty. In this system the instantaneous crack velocity increases with
increasing potential, and the maximum observed values, which have been found for
\{110\}<001> specimens, are on the order of several tens to a few hundreds micrometers
per second. For the Cu30Zn/Cu(I)ammonia system, for which there are indications that
crack growth occurs discontinuously on a micro-scale, it has not been possible to
determine the instantaneous crack velocity. For this system it can only be stated that
the instantaneous crack velocity must be higher than 0.1 to 0.2 micrometers per
second, which is the value of the average crack velocity. For the Cu30Zn/NaNO₂
system, there is no evidence for discontinuous crack growth, but the possibility can not
be excluded that discrete crack advance events occur which are too small to be detected
separately. Despite the fact that it is not certain that crack propagation in the
Cu30Zn/NaNO₂ system is indeed continuous, an attempt will be made to explain the
difference between the instantaneous crack velocity in the Cu25Au/NaCl system and the
average crack velocity in the Cu30Zn/NaNO₂ system under the assumption that the
latter is equal to the instantaneous crack velocity. As has been indicated in figure 5.7,
the crack velocity in the Cu30Zn/NaNO₂ system increases with increasing potential up
to a potential above which it is independent on the potential. The maximum observed
value for the crack velocity is on the order of several tenth's of micrometers per second,
which is two orders of magnitude lower than the maximum observed value in the
Cu25Au/NaCl system. It has to be explained why the maximum observed crack
velocity in the Cu25Au/NaCl system is two orders of magnitude higher than in the
Cu30Zn/NaNO₂ system.

When it is to be evaluated if such an explanation can be given on the basis of one
or more of the models described in section 2.2, it is necessary to evaluate how the
various models predict the magnitude of the instantaneous crack velocity. Among the
models described in section 2.2, only the slip-dissolution model and the surface
mobility model predict the instantaneous crack velocity quantitatively. However, the
slip-dissolution model is not expected to be operative in the present systems, because
the fracture surfaces in the present systems can not be explained based on this model.
The surface mobility model does predict a value for the instantaneous crack velocity,
but it does not seem to include the electrode potential as a parameter influencing the
instantaneous crack velocity. Therefore, it is unclear how this model can predict values
for the instantaneous crack velocity if the latter is strongly dependent on the potential,
which is the case in the present systems. Further, it has been argued in section 4.4.4,
that there are strong doubts if the electrochemical circumstances are present which are
required for this model to be operative. The film-induced cleavage model discards the
concept of an instantaneous crack velocities which values are on the order of the values
which are presently being compared, as it postulates that the instantaneous crack
velocity is on the order of the speed of sound. The other models described in section
2.2, i.e. the corrosion-enhanced plasticity model and the corrosion-assisted cleavage model, describe qualitatively that a higher anodic reaction rate at the crack tip is expected to result in higher instantaneous crack velocities, e.g. due to higher rates of corrosion-enhanced plasticity, ligament dissolution or stress-enhanced dissolution. However, the possible role of other electrochemical parameters than the rate of the reaction at the crack tip, like the nature of the reaction, remains unclear. As long as models only describe in a quantitative way that a higher crack tip reaction rate results in a higher instantaneous crack velocity, there is no possibility to verify if the measured instantaneous crack velocities obey one model more than the other. Therefore, based on the general concept that a higher crack tip reaction rate results in a higher instantaneous crack velocity, but not based on a particular model, it will now be investigated if the measured differences in the crack velocity between Cu25Au/NaCl system and Cu30Zn/NaNO₂ can be correlated with differences in the reaction rates expected to be present at the crack tip.

As it is impossible to measure the crack tip reaction rate, the differences between the crack tip reaction rates of the two systems need to be estimated. This will be done by comparing the initial values of the current responses which have been measured following a potential step from the rest potential to a value in the SCC domain. The initial values are compared since these are expected to correspond to the reaction rates at a fresh surface and since the conditions at the crack tip are believed to be best represented by the reaction rates at a fresh surface. Figure 9.2 shows the results of stepping experiments, where the initial reaction rate is higher for the Cu30Zn/NaNO₂ system than for the Cu25Au/NaCl system. However, at these potentials the instantaneous crack velocity for the Cu25Au/NaCl system is two orders of magnitude higher than the, presumably, instantaneous crack velocity for the Cu30Zn/NaNO₂ system. Thus, it has to be explained why a higher reaction rate at a fresh surface in the Cu30Zn/NaNO₂ system corresponds to a crack velocity which is two orders of magnitude lower than in the Cu25Au/NaCl system. This is especially remarkable, because in both systems the crack velocity increases with increasing crack tip reaction rate, which is indicated by an increasing crack velocity with increasing potential.

In chapter 8 it has been argued that the conditions for solute transport presumably influence the composition of the crack tip solution and, thereby, decrease the rate of the anodic reaction at the crack tip. It has further be concluded that certainly the maximum observed crack velocity, but most likely also the lower crack velocities in this system are found to be restricted by the conditions for solute transport in the crack. In this respect it is noted that the high reaction rates at the crack walls due to the poor passivation in the Cu30Zn/NaNO₂ system are an important factor which makes the role of solute transport already pronounced at relatively low crack velocities. Mass transport calculations for the Cu25Au/NaCl system by van der Wekken have confirmed that the maximum possible values for the crack velocities are indeed on the order of several tens to several hundreds of micrometers per second. Therefore, it is concluded that the differences in crack velocities between the two systems can be attributed to differences in the conditions for solute transport. The conclusion that the lower crack velocities in
the Cu30Zn/NaNO₂ system can be attributed to the conditions for solute transport in this system reveals that the lower crack velocities can not be used as evidence for other phenomena which retard the crack velocity, such as, e.g. the occurrence of small crack arrests.

9.8 Conclusions

1. Explanations for the observed difference in fracture path between {110}<001> and {110}<110> specimens can be based on the Corrosion Enhanced Plasticity model, the Corrosion-Assisted Cleavage model or on a general theory not related to a particular model. However the proposed explanations can not explain why this phenomenon is observed in the Cu30Zn/NaNO₂ and the Cu30Zn/Cu(I)ammonia system, but not in the Cu25Au/NaCl system.

2. The difference in the extent to which the steps are crystallographic can not be explained based on the existing models for SCC. The results of the present work show that the occurrence of crystallographic steps is not a general feature in SCC.

3. The observation that the Cu30Zn/NaNO₂ system shows the strongest tendency for secondary cracking could be explained if these secondary cracks are the result of slip plane dissolution. However, no experimental evidence is available that the secondary cracks are the result of slip plane dissolution, since {111} secondary cracks are rarely observed.

4. The absence of macroscopically discontinuous cracking in the Cu30Zn/NaNO₂ system, whereas it is present in the Cu25Au/NaCl system, can be explained based on van der Wekkens theory that the crack arrests in the Cu25Au/NaCl system are actually caused by the precipitation of a salt, whereas the occurrence of a salt precipitation is unlikely in the Cu30Zn/NaNO₂ system. The absence of evidence for discontinuous cracking in the Cu30Zn/NaNO₂ system confirms the picture that the evidence for discontinuous cracking is not as general as has been thought earlier.

5. The difference in maximum observed crack velocity which is found to be two orders of magnitude higher in the Cu25Au/NaCl system than in the Cu30Zn/NaNO₂ system can be explained as being caused by differences in the conditions for solute transport in these systems. This explanation shows that it is not necessary to explain the lower crack velocity in the Cu30Zn/NaNO₂ system as being caused by the occurrence of microscopic crack arrests, too small to be detected separately.
Literature


Summary

The subject of this thesis is the electrochemistry and the transgranular stress-corrosion cracking (T-SCC) behaviour of oriented Cu30Zn single crystals in NaNO₂ solutions. This material/environment combination, which is a model system, was investigated as a part of a collaborative effort between Vanderbilt University, Nashville, TN, USA, and Delft University of Technology, The Netherlands. During this collaboration the T-SCC behaviour of oriented single crystals is being studied for different material/environment combinations which display comparable mechanical, but different electrochemical behaviour. These systems comprise, besides the Cu30Zn/NaNO₂ system, Cu25Au in NaCl solutions, Cu30Zn in de-oxygenated cuprous ammonia solutions and stainless steels in chloride-containing solutions. The aim of the project is to obtain understanding of the mechanism(s) of T-SCC and to develop a theory which can explain and predict the SCC behaviour of the above mentioned model systems as well as that of material/environment combinations which are more relevant in practice.

The specific goal of the present work was to obtain a systematic knowledge of the influence of the mechanical and electrochemical conditions on the SCC behaviour of Cu30Zn single crystals in NaNO₂ solutions and to find explanations for the observations. It was a further goal to compare the observations with those which have been done on the other systems and to investigate which theories can explain the observed differences between the systems.

In chapter 2 a literature overview is presented on features which are often observed in T-SCC. In particular, the appearance of the fracture surface and the evidence for discontinuous crack advance is reviewed extensively. Based on this review, it was concluded that the fractographic details and the evidence for discontinuous crack propagation are strongly dependent on the mechanical and electrochemical conditions. However, the precise influence of these conditions is not known in a systematic way. In the review, special attention is paid to the experimental work by Flanagan, Lichter and co-workers who performed systematic studies on oriented single crystals with an emphasis on Cu25Au single crystals in NaCl solutions. Following the review of the observations on T-SCC, various models which have been proposed to explain T-SCC are reviewed, including especially the Corrosion-Assisted Cleavage model originally proposed to account for the T-SCC behaviour of Cu25Au in NaCl solutions. The review illustrates that the various models often describe the role of the mechanical and electrochemical conditions on the SCC process in terms which are so general that it is difficult to discriminate between models based on experiments.
In chapter 3 the experimental set-up used for the SCC testing is described. Oriented Cu30Zn single crystals with a <110> tensile axis were tested in slow-strain rate tests. By coating the specimens except for a notch at one side, a nominal crack propagation direction was imposed. The experiments were performed while the specimens were anodically polarised. The applied potential, the crosshead speed and the imposed nominal crack propagation direction were varied. During the experiments, information on crack propagation was obtained by measuring the load, the current, and the position of the crack front, the latter being monitored using a high resolution video camera. The fracture surfaces were investigated using scanning electron microscopy (SEM).

In chapter 4 the results of studies on the electrochemistry of flat Cu and Cu30Zn electrodes in NaNO₂ solutions are described. The electrochemical behaviour was studied using linear sweep voltammetry, chronoamperometric experiments, analysis of the electrode surface using SEM and X-ray photoelectron spectroscopy (XPS), as well as analysis of the solution using atomic absorption spectroscopy (AAS). It was found that a porous Cu₂O layer formed in the potential domain for SCC cracking. This oxide had poor protective properties which was indicated by relatively high current densities in voltammograms in the domain for SCC cracking as well as by high initial current densities and slow repassivation rates in potential stepping experiments. Based on experiments as well as on mass transport calculations it was further found that the NO₂ ions play an essential role in promoting high reaction rates as well as in promoting the eventual formation of a film. It has been proposed that the combination of high reaction rates and possibilities for fast solute transport in the crack is a general factor promoting SCC, and it has been shown that this combination of factors is present in the Cu/NaNO₂ and Cu30Zn/NaNO₂ systems.

The results of the study of the SCC behaviour of the Cu30Zn/NaNO₂ system are described in chapters 5-8. In chapter 5 a general description of SCC behaviour is given as a function of the potential and the crosshead speed. In contrast to the Cu25Au/NaCl system, no evidence for discontinuous crack growth could be found for {110}<001> specimens in the Cu30Zn/NaNO₂ system. The crack velocity was found to increase with increasing potential and crosshead speed. The maximum crack velocity was several orders of magnitude lower than the maximum "instantaneous" crack velocity in the Cu25Au/NaCl system. It was further found that the combination of the crosshead speed and the potential influences the appearance of the fracture surface strongly, i.e. a stronger tendency for secondary cracking was found if the crosshead speed increased for a constant potential and if the potential decreased for a constant crosshead speed.

In Chapter 6 the study of the fractography is described. It was unexpectedly found that there is a relation between the crack propagation direction and the fracture path. For {110}<001> specimens crack growth occurred on primary {110} planes perpendicular to the tensile axis, whereas for {110}<110> specimens crack growth occurred on secondary {110} type planes which make an angle of 30° with the tensile axis. The orientation studies in chapter 6 further showed that the facets on which SCC fracture occurs in the Cu30Zn/NaNO₂ system are {110}. No evidence was found for alternating {111} microfacets which form an average {110} plane.
In chapter 7, a detailed investigation of possible occurrence of discontinuous crack propagation is presented. This is based on an analysis of the load and current data. This analysis confirmed the findings of chapter 5 in that no evidence for discontinuous crack propagation was obtained for the Cu30Zn/NaNO₂ system.

In chapter 8 the influence of the conditions for solute transport on the crack propagation rate has been investigated by calculation and by performing experiment in solutions of which the viscosity was increased by additions of glycerol. The calculations as well as the experiments showed that crack propagation in the Cu30Zn/NaNO₂ system is restricted by the conditions for solute transport in the crack, certainly in the higher potential domain, but possibly also at lower potentials.

In chapter 9 the observed electrochemistry and SCC behaviour in the Cu30Zn/NaNO₂ system and that of the Cu25Au/NaCl and Cu30Zn/Cu(I)ammonia systems have been compared. It appeared to be difficult to use the proposed models for SCC to explain all of the observed differences between these systems. However, differences in the discontinuity of crack propagation and in the maximum observed crack velocities were explained as being caused by differences in the conditions for solute transport in the crack.
Samenvatting

Het onderwerp van dit proefschrift is de elektrochemie en het transkristallijn spanningscorrosiegедrag (T-SCC) van georiënteerde Cu30Zn éénkristallen in NaNO₂ oplossingen. Deze combinatie van materiaal en milieu is als modelsysteem bestudeerd binnen een samenwerkingsverband tussen de Vanderbilt University, Nashville, TN, USA, en de Technische Universiteit Delft. Binnen dit samenwerkingsverband wordt het transkristallijn spanningscorrosiegédrag van georiënteerde éénkristallen onderzocht voor verschillende combinaties van materiaal en milieu, die zodanig worden gekozen dat de systemen een vergelijkbaar mechanisch, maar een verschillend elektrochemisch gedrag vertonen. Systemen die op deze wijze worden onderzocht, zijn Cu25Au in NaCl oplossingen, Cu30Zn in ontluichte ammoniaoplossingen die éénwaardige koperionen bevatten, Cu30Zn in NaNO₂ oplossingen en roestvast staal in chloridebevattende oplossingen. Het doel van het samenwerkingsproject is het verkrijgen van inzicht in het mechanisme van T-SCC en het ontwikkelen van een theorie die het spanningscorrosiegédrag verklaart van bovengenoemde modelsystemen, almede dat van systemen die voor de praktijk van meer belang zijn.

Het doel van het onderhavige werk is het verkrijgen van inzicht in de invloed van de mechanische en elektrochemische omstandigheden op het spanningscorrosiegédrag van Cu30Zn éénkristallen in NaNO₂ oplossingen en het verklaren van de waarnemingen. Het werk heeft tevens als doel de waarnemingen aan het Cu30Zn/NaNO₂ systeem te vergelijken met die aan de andere modelsystemen en te onderzoeken welke theorieën de waargenomen verschillen kunnen verklaren.

In hoofdstuk 2 wordt een literatuuroverzicht gegeven over waarnemingen die vaak als kenmerkend voor T-SCC worden gezien. In dit overzicht wordt bijzondere aandacht geschonken aan het uiterlijk van de breukoppervlakken en aan waarnemingen die als bewijs voor discontinue scheurgroei worden aangevoerd. Uit dit literatuuroverzicht wordt geconcludeerd dat het uiterlijk van het breukoppervlak en de waarnemingen die de continuïteit van de scheurgroei betreffen, sterk beïnvloed worden door mechanische en elektrochemische omstandigheden. Er blijkt echter dat geen systematiek bekend is in de invloed van deze factoren. In het overzicht wordt bijzondere aandacht geschonken aan het experimentele werk van de onderzoeksgroep van Flanagan en Lichter, waarin systematisch onderzoek is verricht naar het spanningscorrosiegédrag van georiënteerde éénkristallen en met name naar dat van Cu25Au in NaCl oplossingen. In aansluiting op het overzicht van de waarnemingen op het gebied van T-SCC, volgt een overzicht van theorieën die zijn voorgesteld om T-SCC te verklaren. Hierbij wordt uitgebreid
ingegaan op het zogenaamde "Corrosion-Assisted Cleavage" (CAC) model van Flanagan en Lichter dat oorspronkelijk is voorgesteld om het spanningscorrosiegredrag van georiënteerde Cu25Au éénkristallen in NaCl oplossingen te verklaren. Het overzicht van de verschillende modellen laat zien dat de modellen de rol van de mechanische en electrochemische omstandigheden vaak op een zeer algemene wijze beschrijven, waardoor het moeilijk is een uitspraak te doen over de toepasbaarheid van deze modellen op basis van experimenten waarbij deze omstandigheden worden gevarieerd.

In hoofdstuk 3 zijn de proefopstelling en de meetmethoden beschreven die zijn gebruikt voor de spanningscorrosieproeven. Georiënteerde Cu30Zn éénkristallen met een <110> trekas werden beproefd met behulp van de zogenaamde langzame reksnelheidsmethode. Door in één zijde van het proefstuk een kerf aan te brengen en door op de rest van het proefstuk op de proefstukken een afsluitende, rubberachtige laag aan te brengen, kon een nominale scheurgroeirichting worden opgelegd. Gedurende de proef bevond het proefstuk zich in een NaNO2-oplossing, waarbij een anodische potentiaal was opgelegd. De opgelegde potentiaal, de reksnelheid en de opgelegde nominale scheurgroeirichting werden gevarieerd. Gedurende de experimenten werd de scheurgroei gevolgd door het meten van de kracht en de stroom. Tevens werd de positie van het scheurfront aan één zijde van het proefstuk gevolgd met behulp van een camera met een hoge resolutie. De breukoppervlakken werden onderzocht met behulp van een elektronenmicroscoop (SEM).

In hoofdstuk 4 zijn de resultaten van het onderzoek naar het electrochemisch gedrag van vlakke Cu en Cu30Zn elektrodes in NaNO2 oplossingen beschreven. Voor dit onderzoek werd gebruik gemaakt van lineaire sweep voltammetrie, potentiaalstapmetingen, analyses van de elektrodeoppervlak met behulp van de SEM en X-ray Photoelectron Spectroscopy (XPS) en analyses van de elektrolytoplossing met behulp van Atomic Absorption Spectroscopy (AAS). Er is gevonden dat zich een poreuze Cu2O laag vormt in het potentiaal domein waarin spanningscorrosie optreedt. De beschermende eigenschappen van dit oxide zijn slecht, hetgeen zich uit in relatief hoge stroomdichtheden in de voltammogrammen. In de stapmetingen uiten de slechte beschermende eigenschappen van dit oxide zich in een hoge stroomdichtheid direct volgend op de potentiaalstap, en in een lage repassiveringssnelheid. Op basis van de experimenten en op basis van berekeningen van massatransport is geconcludeerd dat de NO2 ionen hoge reactiesnelheden bevorderen. De NO2 ionen bevorderen echter eveneens dat zich uiteindelijk een beschermende film vormt. Uiteindelijk is het idee voorgesteld dat de combinatie van een hoge reactiesnelheid en mogelijkheden voor snel massatransport in de scheur een algemene omstandigheid is die spanningscorrosie bevordert, waarbij is aangetoond dat deze combinatie van factoren aanwezig is in de Cu/NaNO2 en Cu30Zn/NaNO2 systemen.

De resultaten van het onderzoek naar spanningscorrosie in het Cu30Zn/NaNO2 systeem zijn beschreven in de hoofdstukken 5 tot en met 8. In hoofdstuk 5 is een algemene beschrijving gegeven van het spanningscorrosiegredrag van dit systeem als functie van de potentiaal en de reksnelheid. In tegenstelling tot het Cu25Au/NaCl
systeem is geen aanwijzing gevonden dat scheurgroei discontinu is voor \{110\}<001> proefstukken in het Cu30Zn/NaNO₂ systeem. De scheurgroeisnelheid neemt toe met toenemende potentiaal en reksnelheid. De hoogst gevonden waarde voor de scheurgroeisnelheid is verscheidene ordes van grootte lager dan de hoogst gevonden waarde voor de scheurgroeisnelheid in het Cu25Au/NaCl systeem. Er is verder gevonden dat de combinatie van de reksnelheid en de potentiaal het uiterlijk van het breukoppervlak sterk beïnvloedt: De mate van secundaire scheurgroei neemt sterk toe, indien de reksnelheid toeneemt bij een constante potentiaal en indien de potentiaal afneemt bij een constante reksnelheid.

In hoofdstuk 6 is het onderzoek van de breukoppervlakken beschreven. Verassenderwijze is gevonden dat er een relatie bestaat tussen de scheurgroeirichting en het breukoppervlak. In het geval van \{110\}<001> proefstukken vindt scheurgroei plaats op primaire \{110\} vlakken. In het geval van \{110\}<110> proefstukken vindt scheurgroei echter plaats op secundaire \{110\} vlakken die een hoek van 30° met de trekas maken. Het onderzoek naar de oriëntatie liet verder zien dat breuk in het geval van het Cu30Zn/NaNO₂ systeem plaatsvindt op \{110\} vlakken en dat geen aanwijzing is gevonden voor alternerende \{111\} micro-facetten die tezamen een gemiddeld \{110\} vlak vormen.

In hoofdstuk 7 is een gedetailleerd onderzoek naar het mogelijke optreden van discontinue scheurgroei beschreven. Dit onderzoek is gebaseerd op een analyse van de kracht- en stroommetingen. Deze analyse bevestigt het beeld van hoofdstuk 5 dat geen aanwijzingen voor discontinue scheurgroei aanwezig zijn in het Cu30Zn/NaNO₂ systeem.

In hoofdstuk 8 is de invloed van transport van opgeloste stof in de scheur op de scheurgroeisnelheid onderzocht met behulp van experimenten en berekeningen. De experimenten werden uitgevoerd door langzame reksnelheidsproeven uit te voeren, waarbij de viscositeit van de NaNO₂ oplossing werd vergroot door glycerol toe te voegen. Zowel de experimenten als de berekeningen hebben aangetoond dat de scheurgroeisnelheid zeker voor de hogere potentialen, maar mogelijk ook voor de lagere potentialen wordt beperkt door beperkte mogelijkheden voor massatransport in de scheur.

In hoofdstuk 9 zijn het voor het Cu30Zn/NaNO₂ systeem waargenomen elektrochemisch gedrag en spanningscorrosiegedrag vergeleken met de waarnemingen voor de Cu25Au/NaCl en Cu30Zn/Cu(I)ammonia systemen. Het is gebleken dat het moeilijk is om de voorgestelde modellen voor spanningscorrosie te gebruiken voor het verklaren van alle waargenomen verschillen tussen de systemen. De verschillen in discontinuïteit van de scheuruitbreiding en in de maximum scheurgroeisnelheden zijn echter verklaard op basis van verschillen in mogelijkheden voor massatransport in de scheur.
Samenvatting
Curriculum Vitae

The author was born in Rotterdam on August 20th, 1968. Between 1980 and 1986 he attended secondary school at Gymnasium Erasmianum, Rotterdam. Subsequently he went to Delft University of Technology to attend the Materials Science program. As a part of this program, he did a work placement at DSM Research in 1991, where he studied the possibility to use electrochemical noise measurements to detect corrosion. In 1993 he completed the MSc (ingenieurs) program with a study in the field of pitting corrosion of stainless steels, which was performed within the Division of Corrosion Technology and Electrochemistry of the Faculty of Chemical Engineering and Materials Science at Delft University of Technology. In the same year he started his PhD research within the same division. A part of this research was carried out within the corrosion group of the Department of Mechanical Engineering at Vanderbilt University, Nashville, TN, USA. The author is currently employed as a trainee at the patent department of DSM Research, Geleen, the Netherlands.
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During the course of my work I had numerous discussions with Kees van der Wekken and Bill Flanagan. I wish to thank them for their interest in my work, their critical comments and their helpful ideas.

Michiel van Hunen studied the electrochemistry of Cu and Cu30Zn in NaNO2 solutions for his MSc research. The results of his valuable work have been described in chapter 4 of this thesis, and his contribution is highly acknowledged. I highly appreciate the collaboration with my colleague student Yong Ling at Vanderbilt University as well. We worked together in growing Cu30Zn single crystals, exchanged equipment and specimens, and discussed our results.

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