Cooling and heating rate dependence of precipitation in an Al-Cu alloy

M. J. Starink and P. van Mourik

Laboratory of Metallurgy, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft (Netherlands)

(Received November 14, 1991; in revised form February 18, 1992)

Abstract

Differential scanning calorimetry and X-ray diffraction were used to study the cooling and heating rate dependence of precipitation in an Al-1.66 at% Cu alloy. After homogenizing, cooling at a rate of 22 K min^{-1} (SC22) is sufficient to retain all copper in solid solution. GP zone formation during subsequent heat treatment is hindered; this is ascribed to an insufficient number of (excess) vacancies. After a water quench (WQ) a large number of GP zones are formed during subsequent storage at room temperature for 1 h. The heat content of the GP zone dissolution effect can quantitatively be described in terms of the heat of precipitation of GP I zones and the solid solubilities as derived from the GP I zone solvus. The heat content of the combined θ' / θ phase precipitation effect appeared to be proportional to the number of copper atoms precipitated, yielding an average value for the heat of copper precipitation of 36 kJ mol^{-1} copper. The activation energy for θ' phase formation is 0.75 eV for SC22 specimens and $1.10 \pm 0.10 \text{ eV}$ for WQ specimens. The differences in reported activation energies for θ' phase formation are discussed in terms of mobility of dissolved atoms (related to the vacancy concentration), interfacial energy and direction of growth (normal or perpendicular to the θ' phase plate).

1. Introduction

Recently it has been shown that the heat of precipitation in a solid quenched Al-Cu alloy reinforced with silicon particles can quantitatively be described in terms of the heats of precipitation of both alloying elements and of solid solubilities of the constituting binary alloys [1]. Further, it appeared that copper precipitation was dependent on the heating rate: at low heating rates (20 K min^{-1} or less) copper precipitated mainly as the metastable θ' phase, whereas at high heating rates (40 K min^{-1} or more) copper precipitated mainly as the equilibrium θ -phase.

Although the precipitation from a supersaturated Al-rich phase in binary Al-Cu alloys during non-isothermal ageing has often been studied [2-4], the relation between precipitation effects and the heating rates applied has, to our knowledge, not been investigated until now. The full precipitation sequence in quenched Al-Cu alloys is usually given as follows:

where GP I/II stands for Guinier-Preston zones, θ' is a transition phase having a structure which is a tetragonal distortion of the CaF_2 structure and which has a composition Al_3Cu and θ is the equilibrium phase

having a body centred tetragonal structure with the same chemical composition as θ' [5]. (Until recent publications, discussion about the nature of GP I and GP II zones has persisted [6]. GP II zones are considered to be a slightly modified (multilayered) form of (predominantly monolayered) GP I zones, or to be a different phase (then the indication θ'' -phase instead of GP II zones is usually preferred). In this paper the indication GP II is used. In any case, GP II is subsequent to GP I.) According to Nakamura *et al.* the so-called X phase would occur between GP II and θ' . This phase should be responsible for the peak hardness during ageing of quenched Al-Cu alloys. The X phase has, however, not been identified by X-ray or transmission electron microscopy (TEM) analysis.

In this paper the results of a study on the influence of the heating rate on the precipitation effects in a conventionally cast Al-Cu alloy are presented. The quench sensitivity of the precipitation reactions was investigated by variation of the cooling conditions after the homogenizing treatment, which consisted of water quenching and cooling at a rate just fast enough to keep copper in solid solution. As copper precipitation from an Al-rich matrix is associated with enthalpy changes large enough to allow differential scanning calorimetry (DSC), this technique was applied. In addition, X-ray diffraction was used for the identification of DSC effects and to obtain, via the determination of the Al

rich phase lattice parameter, information about the average copper content of the Al-rich phase

2. Experimental procedures

2.1. Specimen preparation and heat treatment

A binary Al-1.66 at.%Cu alloy was produced by conventional casting. After casting, the Al-Cu alloy was homogenized at 773 ± 5 K for 48 h. Chemical analysis showed the following composition of the alloy: 1.66 at.%Cu, 0.01 at.%Si, 0.012 at.%Fe, 0.001 at.%Ti, 0.001 at.%Zn, 0.005 at.%Mg, balance aluminium.

After homogenizing, cylindrical specimens (height about 0.5 mm, diameter about 6 mm) were machined from the ingots. These specimens were subjected to a solution heat treatment, consisting of homogenizing at 793 ± 2 K for 10 min followed by a quench in water at room temperature. The specimens were stored at room temperature for 1 h before further investigation (mostly by DSC). These specimens will be referred to as WQ (water quenched) specimens. Some of the WQ specimens were reheated to 790 ± 3 K inside the DSC apparatus, kept at this temperature for 2 min and subsequently cooled to room temperature inside the DSC apparatus. For one set of specimens the cooling was free and hence determined by the heat conduction from the DSC cell to the surroundings; the cooling of each specimen in this set was identical and nearly exponential (the cooling rate on passing the copper solvus at 760 K was 22 K min^{-1} and on passing 550 K it was 6.5 K min^{-1}). These specimens will be referred to as the SC22 (slowly cooled at 22 K min^{-1}) specimens. For other specimens, the initial cooling rate was set at fixed values: 12, 8, 6, 5, 4, 2, 1 and 0.5 K min^{-1} . However, the heat conduction from the DSC cell to the surroundings was in all cases too low to maintain the set cooling rate over the whole temperature range. For each set value, it appeared that from a certain temperature downwards, the cooling was identical to the free cooling of the SC22 specimen. The specimens with a set initial cooling rate will be referred to as the SC12, SC8, etc., specimens.

It appeared that for the SC22 specimens nearly all copper was kept in solid solution (see Section 4.1). In order to study possible GP zone or X-phase formation, the SC22 specimens were aged at temperatures between 423 and 523 K. Cooling of these specimens took place inside the DSC apparatus. Subsequently, these specimens were investigated by DSC.

WQ and SC22 specimens heated at a constant heating rate to the end temperature of the main precipitation peak (see Section 3.1.) were also prepared. For this, DSC scans at heating rates 0.5, 2, 5, 20 and 40 K min^{-1} were interrupted at the end temperatures of the

main precipitation peaks. After interruption of the scan, the specimens were immediately (within 10 s) removed from the DSC apparatus and quenched in water at room temperature. These specimens will be indicated as WQ_{DSC} and SC_{DSC} specimens, followed by the heating rate.

2.2. Differential scanning calorimetry

The DSC apparatus used was a Dupont type 910. A protective gas atmosphere of pure argon was employed. The calibration and baseline correction methods are described elsewhere [8]. For the WQ specimens the following heating rates were applied: 0.5, 2, 5, 20 and 40 K min^{-1} , for the SC22 specimens 0.5, 2, 5, 10, 20, 40, 60 and 80 K min^{-1} were applied. For the SC specimens cooled at rates lower than 22 K min^{-1} , only the heating rate 5 K min^{-1} was used. For the SC22 specimens aged at temperatures between 423 and 523 K, DSC runs were performed at 40 K min^{-1} . Runs were recorded between 298 and 791 K. Unless stated otherwise, the accuracy of the measurement of peak temperatures is within about ± 2 K, the accuracy of the measurement of other characteristic temperatures is within about ± 3 K, and the accuracy of the determination of heat contents is within about $\pm 5\%$.

2.3. X-ray diffraction

To study the composition of the Al-rich phase at the end temperature of the main precipitation peak (see Section 3.1.), the lattice parameters of WQ_{DSC} and SC_{DSC} specimens were determined by X-ray diffraction. These experiments were performed on filings of the DSC specimens by the Debye-Scherrer (DbS) method (see, for instance, ref. 9). X-ray diffraction started within 3 h after quenching of the original DSC specimen. Exposure time was 6 h. Copper radiation filtered by a nickel filter was used. The temperature inside the DbS camera at a point close to the specimen was measured and recorded. Temperatures were between 294 and 297 K. Temperature variations during single experiments were typically of the order of 0.5 K. Film type and film development procedures were identical for all experiments. The Al-rich phase lattice parameter was determined by using the so-called Nelson-Riley extrapolation (see ref. 9). The lattice parameters were corrected for the average temperature during the measurement, adopting the linear expansion coefficient of pure aluminium (23.5×10^{-6} ; see ref. 10). All lattice parameters presented in this work are corrected to 298 K.

To investigate the influence of filing on the Al-rich phase lattice parameter the following experiment was performed. Firstly, an SC22 specimen was heated to 673 K, kept isothermal for 2 min and then cooled very slowly (at rates between 0.1 and 0.5 K min^{-1} and inter-

rupted for isothermal ageing at 473 and 423 K for 10 h) down to room temperature. From filings of this specimen, the Al-rich phase lattice parameter was determined, yielding 0.40488 ± 0.00002 nm. These filings were then subjected to exactly the same heat treatment as described above, and again the lattice parameter was determined, now giving 0.40490 ± 0.00002 nm. In both cases only the Al-rich phase and the θ -phase were detected.

For phase identification, an additional X-ray diffraction experiment was performed on a WQ specimen using a high temperature Guinier camera. The diffraction pattern of Cu $K\alpha_1$ radiation transmitted through a thin (approximately 70 μm) specimen was recorded on a water cooled film during heating the specimen from 293 to 773 K at 0.5 K min^{-1} .

2.4. Optical microscopy

Jena Neophot optical microscopes were used to characterize the microstructures of WQ_{DSC} and SC_{DSC} specimens. Polished specimens were etched with a 1:1 mixture of Keller and Wilcox reagent and 5% Nital.

3. Results

3.1. Differential scanning calorimetry

Figure 1 shows a DSC run of a WQ specimen taken at 5 K min^{-1} . Five effects (two exothermic and three endothermic) are discerned. The effects are numbered I to V. In line with results from literature [2-4, 11, 12], the effects observed in the DSC curves of the WQ run of the Al-Cu alloy are attributed to the following reactions (see also Sections 3.2. and 4.2): (i) GP-zone formation, (ii) GP-zone dissolution, (iii) θ' / θ -phase precipitation (main precipitation effect), (iv) θ' -phase dissolution; (v) θ phase dissolution.

Fig. 1. DSC run of a WQ specimen.

In Fig. 2 a DSC curve of an SC22 specimen taken at 5 K min^{-1} is shown. The effects are interpreted analogously to the effects in the WQ specimen (Fig. 1) and are numbered accordingly. Comparison of Fig. 2 with Fig. 1 yields the following observations:

- (i) the GP zone formation effect (effect I in Fig. 1) is absent in the SC22 specimen,
- (ii) the GP-zone dissolution effect (effect II in Fig. 1) is very small for the SC22 specimen,
- (iii) the magnitude of the main precipitation effect (effect III) is smaller for the SC22 specimen than for the WQ specimen;
- (iv) the end temperature of the main precipitation effect is higher for the SC22 specimen than for the WQ specimen,
- (v) the θ' -dissolution effect (effect IV in Fig. 1) is less pronounced for the SC22 specimen than for the WQ specimen.

Table 1 summarizes the experimental data obtained for effects I and II (except for the SC specimens). All characteristic temperatures increase with increasing heating rate, whereas the heat contents generally decrease with increasing heating rate. From Fig. 1 it is observed that effect II seems to consist of two sub-

Fig. 2. DSC run of a SC22 specimen.

TABLE 1. The end temperature (T_e), peak temperature (T_p) and heat content of effect I and the heat content of effect II for WQ specimens as a function of DSC heating rate.

Heating rate (K min^{-1})	Effect I		Effect II	
	T_p (K)	T_e (K)	Heat content (J mol^{-1})	Heat content (J mol^{-1})
0.5	— ^a	378 ± 5	— ^a	190 ± 40
2	347	388	— ^a	140 ± 30
5	363	393	17	130 ± 20
20	372	398	18	130 ± 15
40	389	415	17	100 ± 10

^a Could not be estimated due to low heat flow.

TABLE 2. The end temperature (T_e), peak temperature (T_p) and heat content of effect III for WQ and SC22 specimens as a function of DSC heating rate

Heating rate (K min ⁻¹)	Peak temperature (K)		End temperature (K)		Heat content (J mol ⁻¹)	
	WQ	SC22	WQ	SC22	WQ	SC22
0.5	546	563	578	600 ± 5	420 ± 40	430 ± 50
2	586	601	618	638	370 ± 30	300 ± 30
5	603	629	638	668	320 ± 15	200 ± 10
10		648		685		130 ± 6
20	638	660	673	698	170 ± 10	80 ± 4
40	658	670	693	707	80 ± 4	16 ± 1
60		— ^a		713 ± 5		4 ± 4
80		— ^a		718 ± 5		3 ± 3

^aCould not be estimated due to low heat flow

effects. For higher heating rates (20 K min⁻¹ or more), two endothermic peaks are discerned in the temperature range of effect II.

In Table 2 the experimental data obtained for effect III for the WQ and SC22 specimens are summarized. Clearly, all characteristic temperatures increase with increasing DSC heating rate, whereas the heat content of effect III decreases with increasing heating rate. Further, it is noted, that for a constant DSC heating rate, the characteristic temperatures for the SC22 specimens are always higher than those for the WQ specimens. For a constant heating rate the heat contents of effect III for the SC22 specimens are generally lower than those for the WQ specimens.

The temperature of minimum absolute heat flow between effect IV and effect V in the WQ specimens increases with increasing heating rate from 670 K at 0.5 K min⁻¹ to 745 K at 40 K min⁻¹. The peak temperature of effect V is almost identical for SC and WQ specimens. It appeared to be nearly insensitive to variations in the heating rate, although for high heating rates (20 K min⁻¹ or more) it shifted to slightly higher values.

DSC runs on the very slowly cooled specimens were performed at 5 K min⁻¹. The DSC curves obtained did not show any heat effects below 520 K. The DSC curves for the SC5, SC6, SC8 and SC12 specimens strongly resemble the DSC curve for the SC22 specimen (Fig. 2). Figure 3 shows the DSC curves of the SC4, SC2 and SC1 specimens; for comparison the curve of the SC22 specimen is also shown. It is observed that the heat content of effect III (the main precipitation effect) decreases with decreasing cooling rate. For a cooling rate of 0.5 K min⁻¹ no precipitation effect is observed during the subsequent DSC experiment at a heating rate of 5 K min⁻¹ (DSC curve of SC0.5 is not shown). The end temperature of effect III decreases with decreasing cooling rate.

Fig. 3. DSC curves of SC1, SC2, SC4 and SC22 specimens

For cooling rates 4 K min⁻¹ or less, the magnitude of effect V decreases with decreasing cooling rate. For these low cooling rates a new effect, situated in the temperature range 730–790 K, appears (see Fig. 3). The magnitude of this new effect, denoted effect VI, increases with decreasing cooling rate.

The total heat release during a DSC scan (*i.e.* the integral of the heat flow from room temperature to end temperature of the scan), is directly related to the number of copper atoms precipitated during the cooling before the scan. The total heat release during a DSC scan, ΔQ_{tot} , was obtained by integration of the DSC curves between 520 and 789 K (before 520 K no heat effect occurs). In Fig. 4, ΔQ_{tot} (which is always endothermic) is given as a function of the cooling rate. The accuracy of these measurements is within ± 30 J mol⁻¹. It is observed that ΔQ_{tot} increases slightly when the cooling rate is decreased from 20 to 2 K min⁻¹. When the cooling rate is decreased further, ΔQ_{tot} increases rapidly to about 500 J mol⁻¹. This is higher

than the values obtained for the heat release during the main precipitation effect (see Table 2).

SC22 specimens were isothermally aged at 423, 443, 463, 483, 503 and 523 K for fixed times. The

Fig. 4 Total heat consumed during the DSC run of SC specimens, ΔQ_{tot} , as a function of the cooling rate

Fig. 5 DSC run of a SC22 specimen aged for 2000 min at 423 K

DSC runs of SC22 specimens aged at 423 K for more than 480 min show an endothermic effect in the temperature range 460 to 570 K (see Fig. 5). After ageing for 2000 min the heat content of this effect equals $220 \pm 10 \text{ J mol}^{-1}$. DSC runs of SC22 specimens aged for up to 2000 min at temperatures between 443 and 523 K do not show any heat effect below 580 K. Above 580 K either the main precipitation effect (effect III), or the endothermic θ' -dissolution effect (effect IV) was observed.

3.2 X-ray diffraction

The results of the Al rich phase lattice parameter determinations are summarized in Table 3. The D₀S experiments on filings of specimens quenched from the end temperature of effect III (see Section 2.3) enabled the identification of phases present at this temperature. The phases detected are also given in Table 3. As a minimum amount of a diffracting phase should be present in order to cross the detection threshold, the absence of diffracted lines from a certain phase does not imply the absence of that phase.

From Table 3 it is observed that all measured Al rich phase lattice parameters are lower than the lattice parameter for pure aluminium (0.40496 nm, see ref. 13). For both the WQ and the SC specimens the Al rich phase lattice parameter increases with decreasing DSC heating rate.

During the initial part of the heating in the high temperature Guinier camera experiment on a WQ specimen only the Al-rich phase is detected. Lines related to the metastable θ' phase appear at 400 K and disappear at 640 K. Lines related to the θ -phase appear at 570 K and disappear at 750 K (the precision of these temperature determinations is within about $\pm 15 \text{ K}$).

3.3 Optical microscopy

Figures 6, 7 and 8 show optical micrographs of the SC_{DSC} 2, SC_{DSC} 20 and WQ_{DSC} 5 specimens respectively.

TABLE 3 The results of the X-ray diffraction analysis

Specimen	DSC end temperature (K)	Phases detected	Al lattice parameter (nm ± 0.00002)	χ_{Cu} (at % ± 0.04)
SC22		α	0.40421	1.57
SC _{DSC} 0.5	600	α , θ' , θ	0.40478	0.38
SC _{DSC} 2	638	α , θ' , θ	0.40464	0.67
SC _{DSC} 5	668	α , θ' , θ	0.40447	1.03
SC _{DSC} 20	698	α , θ' , θ	0.40430	1.38
SC _{DSC} 40	707	α	0.40422	1.55
WQ		α	0.40417	1.68
WQ _{DSC} 2	618	α , θ	0.40467	0.61
WQ _{DSC} 5	638	α , θ'	0.40455	0.86
WQ _{DSC} 20	673	α , θ' , θ	0.40436	1.26
WQ _{DSC} 40	693	α , θ	0.40426	1.47

Fig. 6. Optical micrograph of a SC22 specimen heated at 2 K min^{-1} to 638 K.

Fig. 7. Optical micrograph of a SC22 specimen heated at 20 K min^{-1} to 698 K.

All micrographs show the presence of θ' phase and θ -phase precipitates. The θ' phase precipitates can be distinguished by their characteristic plate-like structure. It is apparent that the density of precipitates is smallest in the $\text{SC}_{\text{DSC}} 20$ specimen. It is further observed, that the length of the θ' -phase plates is about $5 \mu\text{m}$ in the $\text{SC}_{\text{DSC}} 2$ and about $0.5 \mu\text{m}$ in the $\text{WQ}_{\text{DSC}} 5$ specimen. The grain size of the Al-rich phase in the $\text{SC}_{\text{DSC}} 2$, $\text{SC}_{\text{DSC}} 20$ and $\text{WQ}_{\text{DSC}} 5$ specimens is about $400 \mu\text{m}$.

4. Discussion

4.1. The fraction of dissolved Cu atoms of the Al-rich phase

The Al-rich phase lattice parameter of binary Al-Cu alloys shows a linear dependence on the copper fraction, v_{Cu} , of that phase [5]. Using data from refs. 14–16 the following relation between the Al-rich phase lattice parameter (at 298 K) and v_{Cu} is obtained

$$a_{\text{Al}} = a_{\text{Al}}^0 - v_{\text{Cu}} 0.0477 \text{ nm} \quad (2)$$

where a_{Al}^0 is the lattice parameter of pure aluminium. This equation is valid in cases where the average macrostress in a specimen is zero. Although filing causes broadening of diffracted lines, lattice parameters obtained from filings reflect in good approximation the “unstrained” lattice parameter [17]. The close correspondence between the Al-rich phase lattice parameter of the overaged and subsequently filed specimen and the Al-rich phase lattice parameter of the filed and subsequently overaged specimen (see Section 2.3) further evidences this. Thus, the Al-rich phase lattice parameters obtained from filings can be

Fig. 8. Optical micrograph of a WQ specimen heated at 5 K min^{-1} to 638 K.

safely used in eqn. (2) to obtain values of v_{Cu} , which are summarized in Table 3.

4.2. Identification of DSC effects

The identification of the heat effects occurring in DSC runs of WQ and SC22 specimens (see Section 3.1) has been discussed previously [8]. For most of the DbS experiments on WQ_{DSC} and SC_{DSC} specimens as well as for the high temperature Guinier experiment on a WQ specimen heated at 0.5 K min^{-1} , lines due to the θ' - and θ phase have been observed at the end temperature effect III (see Section 3.2.). These observations confirm that effect III is caused by the formation of θ' and θ phases. For the SC22 specimen heated at 40 K min^{-1} , a significant heat evolution ($16 \pm 1 \text{ J mol}^{-1}$ see Table 2) is observed during the main precipitation effect. However, the DbS X-ray diffraction on the $\text{SC}_{\text{DSC}} 40$ specimen detected only the Al-rich phase

Clearly DSC can detect smaller amounts of precipitating θ' / θ -phase than DbS experiments can. Hence, although for some WQ_{DBS} specimens no θ' - or θ -phase is detected (Table 3), the presence of these phases in these specimens cannot be ruled out. This is also indicated by the amount of copper dissolved in the Al-rich phase after completed precipitation (x_{Cu} in Table 3), which is lower than the Cu content of the alloy.

Except for effect VI, the heat effects observed in the DSC runs of the SC specimens cooled at rates lower than 22 K min^{-1} are attributed to the same reactions as those observed in the DSC run of the SC22 specimen. Effect VI is discussed in Section 4.3.

The temperature range of the endothermic effect between 460 and 570 K in DSC runs of the SC22 specimen aged for 2000 min at 423 K (see Fig. 5) corresponds well with the endothermic GP II-zone dissolution effect for a GP II-zone containing, Al-1.7 at.% Cu specimen [18]. The temperature range for the dissolution of GP I zones is about 50 K lower than the temperature range for GP II-zone dissolution [2, 18]. This indicates that the observed endothermic effect is caused by the dissolution of GP II zones. In addition it is noted that in water quenched Al-1.7 at.% Cu specimens aged for 2000 min at 423 K the formation of GP II zones and the dissolution of GP I zones are both close to being completed, while the amount of θ' -phase formed is still negligible [19].

According to the metastable solvus of the X-phase (see ref. 7), X phase dissolution should occur in a temperature range about 50 K higher than GP II-zone dissolution. The endothermic effect between 460 and 570 K in the SC22 specimen aged for 2000 min at 423 K is attributed to GP II zone dissolution. SC22 specimens aged for up to 2000 min at temperatures between 443 and 523 K did not show any dissolution effects below 580 K. Thus it is concluded that no X-phase formation had occurred in the isothermally aged SC22 specimens. During the X-ray diffraction experiments no Cu-containing phases except for the θ' and θ -phases were observed. So the occurrence of the X-phase, which was reported by Nakamura *et al* [7], cannot be confirmed.

4.3 The influence of cooling rate on copper supersaturation and on copper precipitation/dissolution

Since precipitation during cooling involves θ -phase formation (see, for instance, TTT diagrams of quenched Al-Cu in ref. 2), the amount of copper precipitated during cooling, Δx , can be estimated from (see also next section):

$$\Delta Q_{\text{tot}} = \Delta x \Delta H_{\theta} \quad (3)$$

in which ΔH_{θ} is the heat of precipitation of θ phase, 44 kJ mol^{-1} copper in the θ -phase. The amount of

copper atoms precipitated during cooling at a rate of 22 K min^{-1} can be estimated from either ΔQ_{tot} (using eqn (3)) or from the Al-rich phase lattice parameter (using eqn (2)). The two determinations agree within experimental error, and it follows that about 3% of all copper atoms had precipitated. So all or nearly all copper remains in solid solution. At cooling rates below 22 K min^{-1} , the proportion of copper atoms remaining in solid solution decreases with decreasing cooling rate. At cooling rates below 2 K min^{-1} the proportion of copper atoms precipitated during cooling increases strongly. With eqn (3) it follows that during cooling at 0.5 K min^{-1} , about 70% of the copper atoms precipitate.

The endothermic effect VI is present after cooling at very low rates, for which the amount of θ -phase strongly increases (see above). Thus the effect VI is attributed to dissolution of θ -phase precipitates formed during the slow cooling prior to the DSC analysis. The θ -phase formed during slow cooling (at low undercoolings) will be coarser than the θ phase formed in effect III during heating (at large undercoolings). Since, due to longer diffusion paths, dissolution of coarse precipitates takes more time, dissolution of the coarse θ -phase precipitates formed during cooling will proceed beyond effect V (dissolution of θ phase precipitates formed during effect III). This is indeed observed (see Fig. 3).

For cooling rates of 22 K min^{-1} or less, virtually no traces of GP zone formation or dissolution are observed in the subsequent DSC runs. This is explained as follows. Slow cooling from the homogenizing temperature results in a reduction of the excess vacancy concentration. Since vacancies are needed for a quick start of GP-zone formation, GP zone formation during subsequent heat treatment is retarded. For very low cooling rates (1 K min^{-1} or less) the reduced supersaturation due to θ phase precipitation during cooling might prevent GP-zone formation.

4.4 Heat contents of precipitation/dissolution effects

4.4.1 Introduction

The heat produced during the precipitation of a certain phase can quantitatively be described in terms of the (metastable) solid solubility after precipitation and the heat of precipitation of the phase involved [1]. It is here assumed that the end of precipitation is reached when the driving force, the difference between the average proportion of atoms dissolved in the Al-rich phase and the (metastable) solubility, becomes zero. The total heat of precipitation per mole alloy, ΔQ , is then given by (see ref. 1):

$$\Delta Q = \Delta H \frac{x_{Cu}^0 - x_{Cu}'}{1 - 3x_{Cu}'} \quad (4)$$

where ΔH is the heat of precipitation per mole copper, x_{Cu}^0 is the atomic fraction of copper initially dissolved in the Al-rich phase (in our case the gross copper content), x_{Cu}^* is the (metastable) solid solubility at the end temperature of the precipitation effect. As $x_{Cu}^* \ll x_{Cu}^0 \ll 1$, the $\{1 - 3x_{Cu}^*\}$ term can be ignored.

The values of the heats of precipitation of GP I zones, GP II zones, θ' -phase and θ phase can be obtained from the slope of the straight line through the data points of the plot of the logarithm of the (metastable) solid solubility vs. the reciprocal temperature [1, 20]. Table 4 summarizes values for the heat of precipitation obtained from the literature.

For GP zones, the interfacial energy and the energy related to elastic strains around the zones can have a significant influence on the total energy of the formation of the zones [21]. Since both the creation of strains and interfaces require an energy input to the specimen, both strain and interfacial energy reduce the total amount of energy associated with the formation of zones. The importance of these contributions is determined by the average size of the zones: the total formation energy of small zones contains relatively large strain and interfacial energy contributions. For GP zones formed at room temperature (the average diameter of these zones is about 3 nm; see ref. 21) the total energy of the zones and elastically deformed matrix around them, is about 13 kJ mol⁻¹ copper in the zones [21].

From the above it follows that after formation of GP zones during a DSC run has been completed, at least two reactions can occur on continued heating: GP zone dissolution and GP zone coarsening, resulting in endothermic and exothermic effects respectively. Further, it is expected that coarser GP zones dissolve at higher temperatures and produce an increased heat effect as compared to the finer zones. Thus, effect II in DSC runs on WQ specimens is dominated by dissolution of GP zones but it also comprises GP-zone coarsening. This explains the complicated, heating rate dependent shape of effect II (see also ref. 21).

4.4.2 Heat content of effect I and II

For the WQ specimens, the heat evolution during the DSC run caused by the formation of GP zones (about

17 J mol⁻¹ alloy; see Table 1) is one order of magnitude lower than the heat of dissolution of the zones (about 100–190 J mol⁻¹ alloy). This indicates that about 90% of the GP zones are formed during the storage for 1 h at room temperature between quenching and the start of the DSC run. It is therefore justified to approximate the heat of formation of the zones by the heat of GP zone formation at room temperature: 13 kJ mol⁻¹ copper in the zones (see Section 4.4.1). Since the heat evolution during the room temperature storage was not measured, it is not possible to obtain the total heat evolved during the formation of the zones. However, since reversion of GP zones in Al-Cu is complete [21], the heat dissipation during the GP-zone dissolution effect (heat effect II) equals the total heat evolved during the formation of the zones. It is now possible to apply eqn (4) to the heat dissipation during the dissolution of GP zones. For the solvus of GP I zones the formula given by Nakamura *et al.* [7] is used. The results of the calculations are given in Table 5. A good agreement between calculated and measured values is observed.

The endothermic heat effect in the SC22 specimen aged for 2000 min at 423 K (see Fig. 5) is attributed to the dissolution of GP II zones (see Section 4.2.). Since GP II zones form by coarsening of previously formed GP I zones (see ref. 22), the proportion of copper atoms in GP II zones is determined by the GP I solvus. In applying eqn (4), we must thus take x_{Cu}^* equal to the solvus of GP I zones at 423 K (about 0.91 at %). This leads to a value of 230 ± 40 J mol⁻¹ for the dissolution of the GP II zones, which corresponds well with the measured value (220 ± 10 J mol⁻¹).

4.4.3 Heat content of effect III

On the basis of the assumptions given in Section 4.1.1., the heat content of effect III can be calculated. In this case two possible modes of precipitation should be considered, and two values are obtained for the heat evolution during precipitation: one for θ' -phase

TABLE 4 Heats of precipitation of GP zones, stable and metastable phases in Al-Cu alloys

Phase/zone	ΔH (kJ mol ⁻¹)	References
GP I	22 ± 3	7, 21
GP II	31 ± 5	7
θ'	34 ± 4	1
θ	44 ± 1	1, 7

TABLE 5 Comparison of the measured and theoretical heat content (ΔQ_{meas} and ΔQ_{theor} respectively) of the GP zone dissolution effect (effect II) as observed in the DSC runs of the WQ Al-Cu alloy as a function of DSC heating rate, the copper solubility at the end temperature of the GP zone formation peak (x_{Cu}^*) as obtained from the GP I zone solvus is also given

Heating rate (K min ⁻¹)	x_{Cu}^* at %	ΔQ_{theor} (J mol ⁻¹)	ΔQ_{meas} (J mol ⁻¹)
0.5	0.43	160	190 ± 40
2	0.51	150	140 ± 30
5	0.56	140	130 ± 20
20	0.61	140	130 ± 15
40	0.81	110	100 ± 10

precipitation ($\Delta Q''$) and one for θ phase precipitation ($\Delta Q''$). The respective values of v_{Cu}^0 are derived from the θ' and θ phase solvus lines as given by Murray [5]. From eqn. (4) it follows that the end temperature can be regarded as the determining variable for the heat content of effect III. Hence, Fig. 9 gives the theoretical estimates for $\Delta Q''$ and $\Delta Q''$, as well as the experimental values for the heat content of effect III, ΔQ , as a function of the experimental end temperature of effect III. The values of ΔQ are always intermediate between $\Delta Q''$ and $\Delta Q''$. This again confirms that effect III is caused by the combined θ' / θ phase precipitation. All data points in Fig. 9 are well represented by a single line, i.e. the end temperature of effect III is, in this case, solely related to the experimentally observed heat content of effect III.

In Fig. 10 the average composition of the matrix at the end temperature of the main precipitation effect is given as a function of that end temperature. Again, as was also observed for the heat evolved during the main precipitation effect, there is virtually no difference between the average matrix composition after the main precipitation effect for the SC and the WQ specimens at a fixed end temperature of the precipitation effect.

From the value of the atomic copper fraction of the Al rich phase at the end temperature, $v_{Cu}^{T_{end}}$, and the atomic copper fraction of the Al rich phase at the start of the DSC run, v_{Cu}^0 , the amount of copper atoms precipitated, Δx , can be calculated as $\Delta x = v_{Cu}^0 - v_{Cu}^{T_{end}}$. In Fig. 11, the experimentally observed heat content of effect III is given as a function of Δx . It is observed that all the data points, both for WQ and SC22 specimens, are well represented by a single straight line through the origin, the slope of which gives the average heat of precipitation of the copper atoms which are present in

a precipitate at the end of effect III, $\Delta \bar{H}$: $\Delta \bar{H} = 36 \pm 1$ kJ mol⁻¹ copper. This value is intermediate between the heats of precipitation for θ' and θ -phase (34 and 44 kJ mol⁻¹ respectively), and thus in agreement with the attribution of effect III to θ' and θ -phase precipitation.

4.5 Activation energy analysis

The activation energy of a reaction occurring during heating at a constant heating rate can in some cases be obtained by a Kissinger analysis or variants thereof [23]. Such an analysis can only be performed in cases where heat effects are caused by a single precipitation process. For non-isothermal annealing with a constant heating rate, Φ , (i.e. the case of DSC experiments) it can be shown, that in good approximation the follow-

Fig. 10. Average matrix composition at the end temperature of the main precipitation effect as a function of the end temperature of the main precipitation effect. Solid solubilities for θ and for θ' phases (obtained from ref. [5]) and measured values for the main precipitation peak in SC and WQ specimens are given.

Fig. 9. The heat evolved during the main precipitation effect as a function of its end temperature. Calculated values (using eqn. (4)) for the case of θ precipitation and for the case of θ' precipitation and measured values for the main precipitation effect in SC and WQ specimens are given.

Fig. 11. The heat evolved during the main precipitation effect as a function of the amount of copper precipitated.

ing relation between the temperature for a fixed stage of transformation, T_1 , and the heating rate, Φ , holds [23]

$$\ln \frac{T_1}{\Phi} = \frac{E_A}{k_B T_1} + \ln \beta_1 \quad (5)$$

where β_1 is the state variable fully determining that fixed state of transformation, E_A is the activation energy of the process and k_B is Boltzmann's constant. Thus, the activation energy can be obtained from the slope of straight lines through the data points of $\ln(T_1/\Phi)$ vs. $1/T_1$.

It was decided to obtain effective values for the activation energy only for the early stages of effect III, where it can safely be assumed that only θ' phase formation is taking place (see results of the X ray diffraction experiments, Section 3.2). It follows from eqn. (3) that a fixed amount of heat developed, Q_1 , corresponds to a fixed amount of precipitated θ' phase. Two transformation stages were chosen, for $Q_1 = 28 \text{ J mol}^{-1}$ and $Q_1 = 55 \text{ J mol}^{-1}$. In order to ensure that the temperature of the fixed stage of transformation, T_1 , was always lower than the peak temperature of effect III, only values of T_1 equal to or below 656 K were considered. The lowest temperature included in the analysis was 526 K. The values thus obtained do not depend significantly on the stage chosen. The average values for the apparent activation energy of θ' phase formation are for the WQ specimen, $1.10 \pm 0.10 \text{ eV}$; for the SC22 specimen: $0.75 \pm 0.15 \text{ eV}$.

In Table 6 activation energies for θ' phase formation obtained from literature are summarized. Most of the data concern the overall kinetics of θ' phase formation. Only Aaronson and Laird [24] observed differences in the kinetics of thickening and lengthening of θ' phase plates in a solid quenched and aged Al-1.7 at.% Cu. For the thickening, the rate dependent step appeared to

be ledge formation of the broad surface of the θ' phase plates, whereas for the lengthening, the rate dependent step was found to be pipe diffusion. The thickening was described by a linear time dependency, whereas the lengthening was described by a square root time dependency. The activation energy for thickening was found to be $1.20 \pm 0.13 \text{ eV}$, and the activation energy for lengthening was found to be $1.02 \pm 0.02 \text{ eV}$. Chen and Doherty [25] also studied the rate of thickening. They proposed a square root time dependency of the thickening during isothermal ageing. Combining their data (as presented in Figs. 1 and 2(a) of ref. [25]) and the data by Aaronson and Laird, and using this square root dependency, results in an activation energy for thickening of $1.25 \pm 0.09 \text{ eV}$.

The activation energy for θ' phase precipitation in the SC22 specimen is significantly lower than activation energies reported in the quoted studies (see Table 6). It is also much lower than the activation energy for θ' phase formation in the WQ specimens. This can be accounted for by: (i) difference in lengthening and thickening kinetics, (ii) excess vacancies, (iii) interfacial energy. These will be discussed below.

4.5.1 Lengthening and thickening kinetics

The optical micrographs of precipitate structures (Figs. 6, 7 and 8) show that the θ' phase plates in the SC_{DSC} specimens are generally much longer than those in the WQ_{DSC} specimens (about 5 and 0.5 μm respectively). This strongly suggests that lengthening is relatively more important for θ' phase formation in SC22 specimens than for θ' phase formation in WQ specimens. Since the activation energy for lengthening is about 0.2 eV lower than the activation energy for thickening (see above), this can, at least partly, explain the observed difference between the activation energy for θ' phase precipitation in SC22 specimens and the activation energy for θ' phase precipitation in the WQ specimens.

TABLE 6. Activation energies for θ' phase formation (WQ = water quench, IWQ = ice water quench, I = isothermal, NI = non isothermal)

Homogenizing temperature (K)	Cooling	Heat treatment		Cu content (at.%)	E_A (eV)	Kinetics studied	Reference
		I/NI	Temp. range (K)				
798	WQ ^a	I	473-548	1.7	1.1	Overall	26
821	WQ	I	473-573	1.7	1.02	Lengthening	24
					1.20	Thickening	24
813	IWQ	I	543-683	1.3	0.89	Overall	27
793	WQ	NI	526-644	1.7	1.10	Overall	This study
790	SC22	NI	527-656	1.7	0.75	Overall	This study

^aFollowed by a reversion treatment

4.5.2 Excess vacancies

All apparent activation energies for the θ' -phase precipitation (see Table 6) are lower than the activation energy for copper diffusion in aluminium and self diffusion in aluminium (both about 1.4 eV; see ref. [10]). As copper diffusion can only proceed via a vacancy mechanism, this indicates that in all these specimens significant amounts of excess vacancies are present.

4.5.3 Interfacial energy

Interfacial energy acts to increase apparent activation energies obtained from Arrhenius analysis [28]. According to Berkenpas [28], this effect increases with decreasing temperature. This can explain why the activation energies obtained from studies at relatively low temperatures (around 530 K) are higher than the ones obtained from studies at higher temperatures (around 600 K) (see Table 6).

5. Conclusions

For an Al-1.66 at % Cu alloy it is found that

(i) During cooling from the homogenizing temperature at rates lower than 22 K min^{-1} , significant numbers of copper atoms precipitate. For cooling rates higher than 22 K min^{-1} , all copper atoms remain in solid solution.

(ii) After cooling at a rate of 22 K min^{-1} , the copper atoms are virtually completely retained in solid solution. GP-zone formation during subsequent heat treatment is hindered. This is thought to be due to an inefficient number of (excess) vacancies.

(iii) After a water quench (*i.e.* in the presence of a large number of excess vacancies) many GP zones are formed during subsequent storage at room temperature for 1 h.

(iv) The heat content of the dissolution of GP zones (effect II) can quantitatively be described in terms of the heat of precipitation of GP I zones and the solid solubilities as derived from the GP I zone solvus.

(v) The heat content of the combined θ'/θ phase precipitation effect appeared to be proportional to the number of copper atoms precipitated, yielding an average value for the heat of copper precipitation of 36 kJ mol^{-1} copper.

(vi) The apparent activation energies for θ' -phase formation are much smaller after slow cooling than after water quenching. Three factors can influence this apparent activation energy: mobility of dissolved atoms, interfacial energy; direction of growth (normal or perpendicular to the θ' phase plate). The relative importance of these factors may depend on temperature and cooling rate.

Acknowledgments

The authors are indebted to Mr. H. Kleinjan for preparing the alloy, to Ing. N. M. van der Pers and Mr. J. F. van Lent for assistance with and discussions concerning the X-ray diffraction experiments, and to Mr. P. J. van der Schaaf for experimental assistance. Stimulating discussions with Professor B. M. Korevaar are gratefully acknowledged.

The financial support of the Foundation for Fundamental Research of Matter and for Technological Sciences (FOM/STW) is gratefully acknowledged.

References

1. M. J. Starink and P. van Mourik, *Metall. Trans. A*, **22** (1991) 665-674.
2. K. Hirano and H. Iwasaki, *Trans. Jpn. Inst. Met.*, **5** (1964) 162-170.
3. A. M. Zahra, C. Y. Zahra and M. Laffitte, *Scr. Metall.*, **9** (1975) 879-886.
4. I. L. Polmear and H. K. Hardy, *J. Inst. Met.*, **83** (1954) 393-394.
5. I. L. Murray, *Int. Metall. Rev.*, **30** (1985) 211-233.
6. V. Gerold, *Scr. Metall.*, **22** (1988) 927-932 and subsequent papers in Viewpoint Set.
7. F. Nakamura, F. Furukawa, M. Yanai and J. Takamura, *Philos. Mag. A*, **54** (1986) 67-78.
8. M. J. Starink and P. van Mourik, in T. Khan and G. Effenberg (eds.), *Proc. of the Int. Conf. on Adv. Al and Mg Alloys*, June 20-22, 1990, Amsterdam, ASH Europe, Brussels, 1991, pp. 695-704.
9. B. D. Cullity, *Elements of X-ray Diffraction*, Addison Wesley Reading, MA, 2nd edn., 1978.
10. C. J. Smithells (ed.), *Metals Reference Book*, Butterworths, London, 5th edn., 1976.
11. C. Garcia Cordovilla and E. Louis, *Metall. Trans. A*, **15A** (1984) 389-391.
12. J. M. Papazian, *Metall. Trans. A*, **12A** (1981) 269-280.
13. E. J. Mittemeijer, P. van Mourik and Th. H. de Keijser, *Philos. Mag. A*, **43** (1981) 1157-1164.
14. H. J. Axon and W. Hume Rothery, *Proc. R. Soc. London*, **A193** (1948) 1-24.
15. J. E. Dorn, P. Pietrowsky and T. E. Tietz, *Trans. AIME*, **188** (1950) 933-943.
16. E. C. Ellwood and J. M. Silcock, *J. Inst. Met.*, **74** (1948) 457-467.
17. I. C. Noyan and J. B. Cohen, *Residual Stress Measurement by Diffraction and Interpretation*, Springer Verlag, New York, 1987, pp. 126-130.
18. A. Zahra, K. M. Laffitte, P. Vigier and M. Winterberger, *Aluminium*, **52** (1976) 357-360.
19. T. Sato and T. Takahashi, *Scr. Metall.*, **22** (1988) 941-946.
20. M. van Rooyen and E. J. Mittemeijer, *Metall. Trans. A*, **20A** (1989) 1207-1214.
21. A. M. Zahra, M. Laffitte, P. Vigier and M. Winterberger, *Mem. Sci. Rev. Metall.*, **74** (1977) 561-567.
22. J. B. Cohen, *Scr. Metall.*, **22** (1988) 933-936.
23. E. J. Mittemeijer, Liu Cheng, P. J. van der Schaaf, C. M. Brakman and B. M. Korevaar, *Metall. Trans. A*, **19A** (1988) 925-932.

- 24 H. I. Aaronson and C. Laird, *Trans. AIME*, **242** (1968) 1437-1448
- 25 Y. H. Chen and R. H. Doherty, *Scr. Metall.*, **11** (1977) 725-729
- 26 P. Merle, F. Fouquet and J. Merlin, *Scr. Metall.*, **15** (1981) 373-378
- 27 I. Karov and W. V. Youdelis, *Mater. Sci. Technol.*, **2** (1986) 1183-1188
- 28 M. B. Berkenpas, J. A. Barnard, R. V. Ramanujan and H. I. Aaronson, *Scr. Metall.*, **20** (1986) 323-328