

## THE KINETICS OF INTERNAL NITRIDING OF AN Fe-7at.% Al ALLOY

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### ABSTRACT

The kinetics of the internal nitriding of an Fe-7at.% Al alloy was studied using mass-increase data obtained in a thermobalance, for specimens nitrided in a  $\text{NH}_3/\text{H}_2$  gas mixture at temperatures in the range of 803 - 848 K. Specimens were nitrided starting from both recrystallised and cold-rolled conditions. Contrary to expectations, the specimens did *not* exhibit strong nitriding interaction behaviour. Surprisingly, the recrystallised specimens displayed more tendency to strong interaction behaviour than the cold-rolled specimens. The nitriding behaviour of the latter varied from weak to intermediate.

### 1. INTRODUCTION

#### 1.1 SCOPE AND PURPOSE

The nitriding of ferritic steels is used for enhancing the fatigue resistance and improving the wear and corrosion properties. The nitriding behaviour of alloyed steels containing many elements is difficult to analyse. The nitriding behaviour of binary Fe-X alloys where X is a nitride forming element, is more amenable to detailed characterisation. While the response to nitriding of Fe-Cr, Fe-Ti and Fe-V alloys is relatively well known, the nitriding behaviour of Fe-Al has not been studied in detail [1,2]. The present paper deals with the kinetics of internal nitriding of thin foil Fe-7at.%Al specimens, either recrystallised (REC) or cold-rolled (CR). Thermogravimetric analysis (TGA), microhardness determination and Electron-Probe Microanalysis (EPMA) were used.

#### 1.2 NITRIDING INTERACTION BEHAVIOUR

The TGA method yields the nitrogen-mass uptake as a function of (nitriding) time. Each TGA data point represents the total nitrogen uptake of the specimen, averaged over all depths in the specimen. Therefore, straightforward analysis of the data is only possible in the case of *ideally weak nitriding interaction* or in the case of completely *strong nitriding* interaction behaviour [1,2]. In the first case nitrogen uptake is the same at all depths in the specimen. This situation occurs when the time required for nitrogen diffusion is short with respect to that necessary for nitride precipitation. *Ideally weak nitriding interaction* occurs when the free enthalpy of formation of the nitride is small or the energy barrier for nucleation is high. Strong interaction arises when the nitrogen arriving by diffusion at a certain depth in the specimen is immediately and completely bonded to the alloying element atoms. In this case a nitriding front progresses steadily inward. A sharp case/core transition occurs. The speed of the front depends on (i) the solubility and the diffusion coefficient of N in ferrite (ii) the concentration of the alloying element dissolved in the  $\alpha$ -Fe matrix. The magnitude of the free enthalpy of formation of AlN suggests that Fe-Al would exhibit *strong interaction* behaviour as has been found for Fe-Ti [3], Fe-V [4] and also Fe-Cr [5,6,7]. This was not observed in Fe-2at.%Al. The observed *weak* behaviour is attributed to a high energy barrier for nucleation of AlN. The literature

indicates that a change of the amount of alloying element content sometimes leads to changes in nitriding behaviour [5]. Therefore it was expected that Fe-7at.%Al would exhibit a different and stronger nitriding interaction.

## 2. KINETIC ANALYSIS

In the case of ideally weak interaction the precipitation of AlN progresses to completion at the same rate at each depth in the specimen. After nucleation particles grow by diffusion of Al while additional nucleation may still occur. The precipitation of AlN is carried to completion with *respect to time*. The kinetics of the process has been dealt with in the literature [2]. Precipitation of the nitride in the  $\alpha$ -Fe matrix is slow. Nitrogen bonded to the alloying element is immediately replenished and saturation of the matrix with N is restored. Then the kinetics of nitriding is only related to the activation energy for diffusion of the alloying element and not to that for diffusion of N [1,2].

In the case of strong interaction the situation is different. Precipitation of AlN progresses to completion with *respect to depth in the specimen*. It is taken that all dissolved Al atoms at a certain depth in the specimen are instantaneously bonded to N. Provided the supply of N is sufficient, the nitriding kinetics can be described using internal oxidation theory [8]. Then the kinetics of the total process is strongly determined by the activation energy for diffusion of N.

## 3. EXPERIMENTAL

### 3.1 SPECIMEN PREPARATION

The Fe-Al alloy used in this study was prepared by melting iron and aluminium powder under an H<sub>2</sub> flow in a sintered Al<sub>2</sub>O<sub>3</sub> crucible. Composition of the Fe-Al alloy has been determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy): [Al]=7.3at.% and a total content of Ti, Cu, Mg, Ca, V, Mn, P and Ni of less than 0.02at.%. The as-cast Fe-Al bar was cold rolled to a thickness of 0.32 mm, applying intermediate annealing treatments at 973K. In the final step, following annealing for 3h at 973K and pickling at 333K in a 50/50 mixture of HCl and water, the specimens were 60% cold rolled to a thickness of 0.13 mm. Specimens (8x14x0.13 mm<sup>3</sup>) were cut from the rolled strip. The specimens to be used in the REC condition were again annealed 3h at 973K. Just prior to nitriding the specimens were chemically polished in Kawamura's [9] reagent obtaining a final thickness of 100  $\mu$ m approx., etched 30 sec in 1% nital and ultrasonically cleaned in isopropanol. The hardness of the specimens prior to nitriding was 173 HV<sub>0.025</sub> for REC and 285 HV<sub>0.025</sub> for CR specimens.

### 3.2 NITRIDING

The CR and REC specimens were both fully and partially nitrided at 803, 818 and 848 K in a thermobalance (DuPont TGA 951) using an NH<sub>3</sub>/H<sub>2</sub> gas mixture with a nitriding potential  $r_N$  ( $= p(\text{NH}_3)/p(\text{H}_2)^{3/2}$ ) of  $2.45 \times 10^{-4} \text{ Pa}^{-1/2}$  and a linear gas velocity of  $15.0 \text{ mm}\cdot\text{s}^{-1}$ . The value of  $r_N$  was chosen such that no iron nitrides could develop during nitriding. Purification of the nitriding gases was performed as described earlier [10]. However, it was observed that the increased Al content of this alloy led to an extreme sensitivity to oxidation during nitriding. Traces of oxygen could lead to brown or even black specimen surface appearances. In these cases, the kinetics of nitriding was evidently disturbed and such specimens were discarded. The mass increase in the thermobalance was checked by weighing the specimens before and after the TGA experiments, using a Mettler mechanical microbalance. After nitriding, all specimens were annealed at 723 K in pure H<sub>2</sub> to remove the nitrogen not chemically bonded (denitriding).

### 3.3 METALLOGRAPHY AND COMPOSITIONAL ANALYSIS

The microhardness profiles of the cross-section of the specimens were determined using a Leitz Durimet Vickers hardness tester with a load of 5 g. Hardness values thus obtained were converted to typical hardness values for a 100g load, thereby eliminating the influence of elastic deformation. EPMA was employed for quantitative determination of nitrogen-concentration profiles across the specimens. Full details of the method are given in [1].

#### 4. RESULTS AND DISCUSSION

##### 4.1 THERMOGRAVIMETRIC ANALYSIS (TGA)

The TGA curves converted to fraction AlN precipitated are shown in figure 1a for the Fe-7at.%Al *REC* specimens. As in the case of internal nitriding Fe-2at.%Al [1,2] the TGA curves exhibited a plateau in the initial stage corresponding to saturation of the  $\alpha$ -Fe matrix with nitrogen. In the present case the plateau was not so clearly distinguishable since nitride precipitation already started before saturation of the  $\alpha$ -Fe matrix was completed. After an incubation period depending inversely on the nitriding temperature the nitrogen uptake increases rapidly until saturation is obtained. At saturation on average 8.8at.%N was adsorbed. Taking into account the initial Al content of the specimen and the amount of N required for matrix saturation (0.13at.%), an amount of 1.4at.% of *excess nitrogen* is obtained. This is by a factor of about 7 larger than found for Fe-2at.%Al [1]. After denitriding at 723 K still approximately 8at.%N remained. This indicates that the amount of *excess nitrogen* adsorbed at the AlN/matrix interfaces roughly equals the amount of nitrogen additionally dissolved in the strained matrix *plus* that adsorbed at dislocations [1].

The TGA curves of the *CR* specimens (figure 1b) also exhibited a behaviour similar to those obtained for the internal nitriding of Fe-2at.%Al alloy in the cold-rolled state [2]. Nitride precipitation starts at the beginning of the nitriding process, leading to *apparent* first order ('homogeneous') reaction kinetics. In contrast to the case of the Fe-2at.%Al alloys, almost the same amount of excess nitrogen was found in fully nitrided *CR* specimens as in the fully nitrided *REC* specimens.

Comparison of the present nitriding curves with those for Fe-2at.%Al showed a strong similarity in the shape of the curves but a reduction in the nitriding times for corresponding initial specimen conditions of a factor  $6 \pm 1$ . This reduction is larger than the reduction in the nitriding times predicted from a simple diffusion model taking into account the shorter distance between neighbouring Al atoms with increasing Al concentration:  $2.54 (= (7.3/2.0)^{2/3})$ . The TGA curves did generally not reproduce very well: on repeating experiments significantly different nitriding rates could be found. In all these cases the specimens did not show any sign of visible oxidation after nitriding. However, applying ESCA analysis it was found that detectable amounts of Al<sub>2</sub>O<sub>3</sub> were present on the surface of the specimen after nitriding. The corresponding signal vanished after sputtering off 15 nm of the top surface layer of the specimen. Nitriding kinetics may have been influenced.

##### 4.2 NITRIDING INTERACTION BEHAVIOUR

The type of nitriding interaction behaviour can be determined by measuring N concentrations across the thickness for partially nitrided samples. The results are shown in figures 2a and 2b for *CR* samples nitrided at 803 and 848 K, respectively. At each temperature three specimens were used: 20% nitrided (curve a), 50% nitrided (curve b) and fully nitrided (curve c). Surprisingly, comparison of figures 2a and 2b shows that the nitriding interaction behaviour depends on the nitriding temperature. At a nitriding temperature of 803 K (figure 2a) the interaction behaviour can be classified as 'weak to intermediate'. At a nitriding temperature of 848 K (figure 2b) the nitriding interaction behaviour can almost be classified as strong.

This dependence of strength of interaction behaviour on nitriding temperature can also be deduced from microhardness measurements on the same *CR* samples (figures 3a and 3b). Good qualitative agreement between figures 2 and 3 is obtained. The hardness profiles for *CR* samples nitrided at 818 K (not shown) displayed an *intermediate interaction behaviour*, indicating that there is a continuous change in nitriding interaction behaviour with nitriding temperature.

The microhardness profiles for nitrided *REC* specimens are shown in figures 4a and 4b for nitriding temperatures of 803 and 848 K respectively. Again, at the lower nitriding temperature the nitriding interaction behaviour can be classified as weak, while the nitriding behaviour at 848 K is strong. The nitriding behaviour at 818 K (not shown) can also be classified as intermediate. At each nitriding temperature the degree of interaction is somewhat stronger for the *REC* specimens than for the *CR* specimens.

#### 4.3 KINETIC ANALYSIS

Regarding the observed changes in nitriding interaction behaviour with nitriding temperature, no kinetic analysis can be performed since the nitriding mechanism changes with temperature. Essential for a kinetic analysis is that identical situations, but obtained at different temperatures, are compared. However, for those conditions where strong interaction is observed (at the highest nitriding temperature of 848 K), the observed nitriding kinetics can be compared to that predicted by the internal oxidation theory. Ignoring the effect of Al on the diffusion of N and assuming the nucleation barrier for precipitate formation to be zero, the kinetics of nitriding can be calculated. The nitriding kinetics determined experimentally is about a factor of 2 slower than the kinetics predicted. The discrepancy is attributed to the decelerating effects of the concurrent oxidation at the surface and the fact that some nucleation barrier for nitride formation still exists.

#### 5. CONCLUSIONS

- The strength of the interaction behaviour in Fe-7at.%Al alloys depends on the nitriding temperature.
- For both recrystallised and cold-rolled specimens the degree of interaction increases from weak to almost strong with increasing nitriding temperature.
- At the same nitriding temperature recrystallised samples showed a slightly stronger interaction behaviour than the cold-rolled samples.
- The nitriding kinetics of CR and REC Fe-7at.%Al samples is rather different. The differences are similar to those observed in Fe-2at.%Al specimens.

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FIGURES

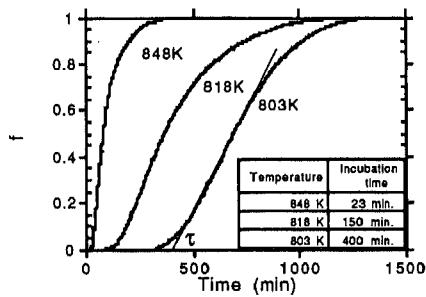


Figure 1a: Fraction AlN precipitated (f) for REC specimens as a function of nitriding time. The value of the incubation time  $\tau$  is taken as the part cut from the abscissa by the tangent in the point of inflection.

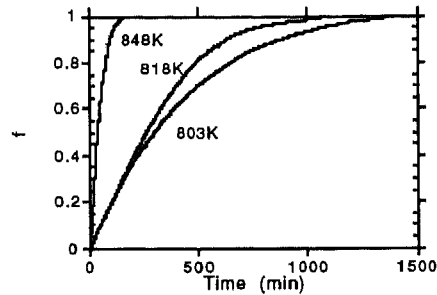


Figure 1b: Fraction AlN precipitated (f) for CR specimens as a function of nitriding time.

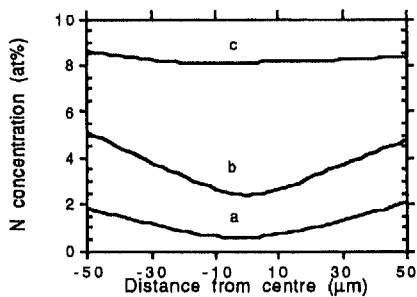


Figure 2a: Nitrogen-concentration (EPMA) depth profiles of CR specimens nitrided at 803 K. Symbols a, b and c: approx. 20% nitrided, approx. 50% nitrided and fully nitrided. All specimens denitrided at 723 K before EPMA measurements.

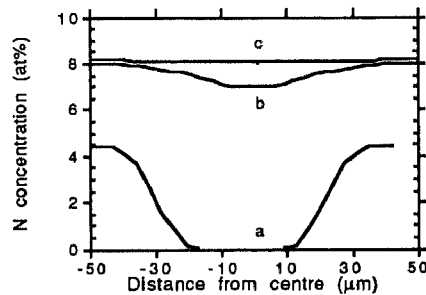


Figure 2b: Nitrogen-concentration (EPMA) depth profiles of CR specimens nitrided at 848 K. Symbols a, b and c: as in figure 2a. All specimens denitrided at 723 K before EPMA measurements.

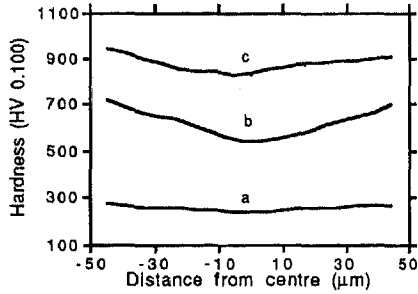


Figure 3a: Hardness-depth profiles of CR specimens nitrided at 803 K. Symbols a, b and c: as in figure 2a. All specimens denitrided at 723 K before hardness measurements.

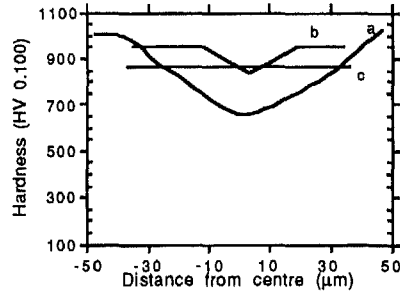


Figure 3b: Hardness-depth profiles of CR specimens nitrided at 848 K. Symbols a, b and c: as in figure 2a. All specimens denitrided at 723 K before hardness measurements.

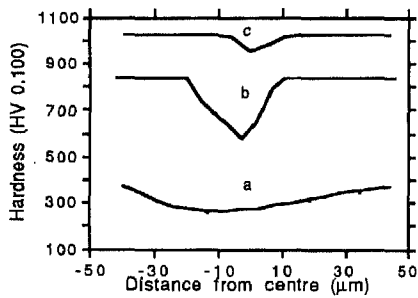


Figure 4a: Hardness-depth profiles of REC specimens nitrided at 803 K. Symbols a, b and c: as in figure 2a. All specimens denitrided at 723 K before hardness measurements.

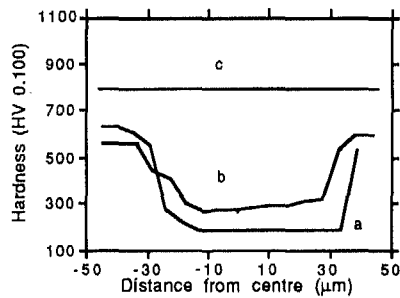


Figure 4b: Hardness-depth profiles of REC specimens nitrided at 848 K. Symbols a, b and c: as in figure 2a. All specimens denitrided at 723 K before hardness measurements.