Trapping of Nitrogen at the Fe-AlN Precipitate Interface Studied by the Positron Doppler Broadening Technique

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Abstract During internal gas nitriding of steels containing the alloying element Al this element reacts with the nitrogen to form small AlN precipitates. By applying the positron Doppler broadening technique using a monoenergetic positron beam it was possible to monitor the decoration and annealing of defects connected with the formation of AlN precipitates during the nitriding and denitriding of a cold rolled Fe-2at%Al alloy.

Introduction

The nitriding of steels containing alloying elements such as Al, Cr, V and Ti has been shown to improve the mechanical properties, e.g., resistance against fatigue and wear, due to the strengthening of the ferritic matrix [1]. Nitriding can be performed by heating the alloy in a NH_3/H_2 nitriding gas mixture at a temperature typically in the range from 800 to 850 K. By choosing suitable process conditions the formation of iron nitrides can be suppressed and in case no iron nitrides are formed on the surface the process is called "internal nitriding". Upon nitriding the alloying elements form nitride precipitates typically smaller than 5 nm.

Earlier thermogravimetric measurements on a nitrided Fe-2at%Al alloy showed that the total amount of nitrogen taken up in this system significantly exceeds the amount of nitrogen necessary to convert the aluminium into stoichiometric AlN, and the amount of nitrogen which would be dissolved in the iron matrix if it behaves as pure α -Fe. This surplus of nitrogen is defined as excess nitrogen. For cold rolled nitrided specimens the presence of excess nitrogen is ascribed to adsorption of nitrogen at the AlN precipitate/matrix interface $[\text{N}]_{\text{ads}}$, at dislocations $[\text{N}]_{\text{disl}}$, and to an enhanced solubility in the Fe matrix around the precipitate due to the elastic accommodation of the misfit $[\text{N}]_{\text{strain}}$. The amount of nitrogen associated with the formation of AlN follows directly from the aluminium contents in the specimen, i.e., 2 N /100 Fe. Using the same notation, the amount of nitrogen dissolved in the matrix of α -Fe at 833 K yields 0.13 N/100 Fe. Typical values for $[\text{N}]_{\text{ads}}$ and $[\text{N}]_{\text{disl}} + [\text{N}]_{\text{strain}}$ are 0.65 and 0.34 N/100 Fe, respectively. For the cold rolled specimens it was found that an appreciable part (90%) of the latter is due to the misfit strain [2,3].

Activation energy measurements at different nitriding temperatures show that the formation of precipitates in cold rolled specimens is governed by the diffusional growth of cubic AlN particles nucleated at the dislocations present at the very start of the nitriding process.

Heating the nitrided specimens in a hydrogen atmosphere at typically 700 K removes the nitrogen from the matrix, the dislocations and from the accommodated misfit [4,5,6]. In order to detect the presence of open volume associated with the misfit at the precipitates, we have performed positron beam Doppler Broadening S and W measurements on a Fe-Al alloy at several stages of the nitriding and denitriding process.

Experimental

Cold rolled Fe-2at%Al samples have been nitrided at a temperature of 803 K in a NH_3/H_2 gas mixture with a ratio of 3.3/96.7. The fraction of Al transformed into AlN is controlled by changing the nitriding time. The denitriding is performed in a H_2 atmosphere at a temperature of 723 K. The nitrogen uptake and release during the nitriding and denitriding steps, respectively, are given in table 1. From these values the fractions of Al transformed into AlN are derived where corrections are made for the amount of N dissolved in the iron matrix. In order to assess the effect of the heat treatment alone the cold rolled sample has been vacuum annealed for 15 min. at the nitriding temperature.

Table 1. Summary of nitriding and denitriding data and results of VEPFIT analysis.

sample	after nitriding				after denitriding		
	Δm (at%)	fr. Al transformed	S/Sref	W/Wref	Δm (at%)	S/Sref	W/Wref
1	0.6	0.20	1.0666	0.7522	0.44	1.0726	0.7737
2	0.94	0.33	1.0729	0.7352	0.84	1.0862	0.7386
3	1.21	0.43	1.0699	0.7379	0.98	1.0848	0.7409
4	1.68	0.61	1.0737	0.7295	1.41	1.0848	0.7347
5	2.44	0.90	1.0880	0.7025	2.28	1.0947	0.7138
6	2.6	0.96	1.0785	0.7179	2.26	1.0890	0.7220
7	2.64	0.98	1.0781	0.7198	2.15	1.0924	0.7220
cold rolled	-	-	1.0792	0.7841	-	-	-
annealed ref	-	-	1	1	-	1	1

The Doppler broadening measurements were carried out using the Delft variable energy positron beam [7]. For each sample annihilation spectra were recorded at selected positron implantation energies ranging from 100 eV to 25 keV. The 511 keV photo-peaks were characterised by the S(hape) and W(ing) parameters. The VEPFIT program [8] was used to derive relative bulk S and W parameter values (see Table 1) and the positron diffusion lengths. In Fig. 2 we show the data in a S-W map, with the fraction Al transformed into AlN as the running parameter. For both the cold rolled and nitrided samples the positron diffusion length is of the order of 50 nm. Annealing the cold rolled sample increases the diffusion length to 160 nm. The latter can be compared with the value of 150 nm derived from $L_b = (D\tau)^{1/2}$, with L_b the positron diffusion, $\tau = 110$ ps the positron lifetime in defect free α -Fe and $D = 2 \text{ cm}^2 \text{ s}^{-1}$, the value for the positron diffusion coefficient.

Discussion

Starting from the point in the S-W plot for the cold rolled sample a *vacuum* anneal at the nitriding temperature yields a lower S-parameter and a higher W-parameter. In addition, the effective diffusion length increases from 50 nm to 160 nm. Both results are indicative for the removal of defects such as vacancies and dislocations. By applying the relation between the effective diffusion length (L_{eff}), and the positron trapping rate at defects ($n\nu$) given by

$$\frac{n\nu}{\lambda} = \left[\frac{L_b}{L_{\text{eff}}} \right]^2 - 1$$

the short diffusion length for the cold rolled sample translates into 8 times higher rate for positron trapping compared to the rate of "bulk" annihilation. Inserting typical values for the annihilation rate $\lambda = 9 \times 10^9 \text{ s}^{-1}$ and the specific trapping rate at vacancies $\nu = 10 \times 10^{14} \text{ s}^{-1}$ yields a defect density in the order of 80 ppm. Trapping at dislocations with a trapping rate of the order of $1 \text{ cm}^2 \text{ s}^{-1}$ yields a dislocation density of 10^{10} cm^{-2} equivalent to an average separation distance in the order of

Figure 1. S-W map of the nitrided (o) and denitrided (o), cold rolled and annealed reference sample.

dependence on the fraction Al transformed is therefore ascribed positron trapping in defects in the interface regions and is to be associated with the elastic accommodation of the misfit between Fe matrix and cubic AlN precipitate. Further support for this is given by the observed decrease of S (triangle in Fig. 1) when the precipitates are transformed into a hexagonal structure, releasing the misfit strain.

Conclusions

By combining the Doppler Broadening S and W techniques four positron states have been identified in the FeAl(N) system: 1) deformation defects, 2) nitrogen decorated defects, 3) cubic AlN with and 4) without excess nitrogen. The relative position of the specific states in an (S,W) map are understood in terms of open volume at interfaces and decoration by light atoms.

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the measured positron diffusion length. Annealing in a *nitriding* atmosphere results in a lowering of both S and W whereas the diffusion length remains unchanged. This behaviour is a result of the competition between removal of the defects (as in case of a vacuum anneal), the decoration of the defects and dislocations with nitrogen and the formation of small AlN nitride precipitates. This competition is clearly seen for the low fraction (20%) of Al transformed. Further nitriding increases S and lowers W. This effect is ascribed to the larger area of the precipitate/matrix interface surface and therewith increased fraction of positrons trapping in this region. The fact that the diffusion length does not change agrees with the precipitation mechanism mentioned in the introduction. Upon *denitriding* S increases while W remains practically unchanged. (see Table 1) The latter indicates that the annihilation is still related to the *precipitates* and not to defects or dislocations. The increase of S upon removal of N from the matrix and its