TRAPPING SITE LOCATION FOR Sb IN Fe-Ti-Sb-C ALLOYS*
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The lattice location of Sb trapped at TiC precipitates in Fe has been determined. Channeling analysis of ion-backscattering and ion-induced characteristic x-ray yields from Fe and Sb showed a substitutionality of $\geq 50\%$ for trapped Sb relative to the Fe lattice for ion beams incident along Fe $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$. In contrast, Ti x-ray yields showed channeling through the oriented TiC precipitates only along Fe $\langle 100 \rangle$. We conclude that Sb is trapped at interfacial Fe sites adjacent to TiC precipitates, rather than within the TiC.

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I. Introduction

Segregation of metalloid impurities to grain boundaries leads to a loss of toughness in low-alloy steels, an effect known as temper embrittlement.⁽²⁾ Previous work⁽¹⁾ at our laboratory has shown that TiC precipitates are effective traps for Sb in Fe, and that these traps could be important in controlling Sb segregation at grain boundaries. We have now determined that the trapping site for Sb in an Fe crystal is at the TiC-Fe precipitate interface using channeling techniques in ion-backscattering and ion-induced characteristic x-ray analysis of ion-implanted alloys. Although interfacial trapping was proposed in the interpretation of earlier experiments,⁽¹⁾ the specific configuration of trapped Sb could not be determined; that is, whether the Sb was incorporated into the precipitate or trapped at the TiC-Fe interface. The present identification of this trapping site increases our understanding of the trapping mechanism, and consequently the choice of other possibly beneficial alloying additions.

We believe this to be the first example of the use of channeling analysis to examine impurity location in or near oriented precipitates and expect that this technique may be useful in studying other impurity/precipitate systems as well. Specifically, we have taken advantage of the orientation of the TiC lattice with respect to the Fe lattice, which permits channeling through the precipitates for one axial direction but not for others. We then deduce that the trapped Sb occupies sites at the Fe-TiC interface, with an average substitutionality for the Sb of >50% on Fe lattice sites.

II. The Orientation of TiC Precipitates

By using TEM to examine the microstructure of Fe implanted with Ti and Sb and then annealed to 873-973 K, it was shown that the Ti getters C impurities and precipitates as TiC.⁽¹⁾ This precipitation is always observed, whether or not Sb is also implanted. For the implantation and annealing conditions used here, the fcc TiC precipitates were observed⁽³⁾ to be ~2 nm diameter, and oriented in the bcc Fe matrix with the Baker-Nutting orientation:⁽⁴⁾

$$[100]_{\text{TiC}} \quad [100]_{\text{Fe}} \quad (1a)$$

$$[011]_{\text{TiC}} \quad [001]_{\text{Fe}} \quad (1b)$$

That is, one fcc cubic axis of each TiC particle is aligned with an Fe [100] direction and the two remaining TiC cubic axes are aligned with Fe [011] axes. Figure 1 shows an electron diffraction pattern obtained from such a sample. In this particular sample, the implantation was done at elevated temperature to produce stronger reflections, but the orientation of the resulting TiC precipitates is the same as for the post-implantation annealing.

There are three distinct groups of TiC precipitates, each of which aligns with one of the Fe cubic axes. Reflections for each of the three variants are marked by the parallelograms in Fig. 1. The square parallelogram, with corners ending on (220) TiC reflections just inside (200) Fe reflections, marks reflections from the set of precipitates having a [100] axis aligned with the Fe $\langle 100 \rangle$ axis along which the electrons are incident. The fact that the TiC reflections are very close to the Fe reflections

shows that the lattices match very well in the Fe (100) plane for this variant, within ~7%. Thus we would expect an ion beam to channel through this variant of the TiC along the Fe $\langle 100 \rangle$ axis.

Reflections from the other two variants are marked by dashed and dot-dashed parallelograms in Fig. 1. For each of these precipitates, one cubic axis is aligned with either $\langle 010 \rangle$ or $\langle 001 \rangle$ Fe axes which are perpendicular to the electron beam while a TiC $[110]$ axis is aligned with the Fe $\langle 100 \rangle$ axis. The poor match between TiC and Fe reflections for these two variants in Fig. 1 demonstrates their poor lattice matching in the Fe(100) plane (~41% lattice mismatch). Thus we would expect very poor channeling through these two variants when the ion beam is incident along Fe $\langle 100 \rangle$.

The diagram of an Fe (011) plane in Fig. 2 contains a TiC precipitate from the first variant with a $[100]$ axis aligned with the vertical Fe $[100]$ axis. One-third of the precipitates share this orientation, and these are expected to channel well along $[100]$ Fe. Figure 2 also illustrates the poor lattice matching for the first variant in the $[110]$ and $[111]$ directions, for which poor channeling is thus expected. After examining the orientations of all three variants, we conclude that channeling through the small TiC precipitates should be appreciable only along Fe $[100]$, and then almost entirely through those of the first variant.

The situation illustrated in Fig. 2 allows a discrimination between Sb trapped inside the precipitate and Sb trapped at the interface between Fe and TiC. If the Sb is substitutional at Ti or

C sites inside the TiC precipitate, ion beam analysis would show channeling along Fe [100] for both Sb and Ti, while analysis along Fe [111] or Fe [110] would show little or no channeling effect for either Ti or Sb. If Sb were clustered or located randomly in the TiC precipitate or the interface, no channeling orientation effects would be observed for any direction. However, if Sb is trapped at or near Fe lattice sites at the interface, as shown in Fig. 2, then ion beam analysis would show channeling for Sb along all three axes, but only along [100] for Ti. Geometric considerations show that C (or Sb on C sites) would exhibit the same channeling effect as that of Ti.

III. Ion-Beam Analysis

In order to test this hypothesis, we performed channeling analysis on implanted and annealed high-purity Fe single crystals cut in [100] orientation. Two samples were used, one implanted at room temperature with 1×10^{17} atoms/cm² of Ti at 180 keV and then with 2×10^{16} atoms/cm² of Sb at 180 keV. The second sample was prepared with 6×10^{16} atoms/cm² of Ti and 1×10^{16} atoms/cm² of Sb implanted at the same energies. Both samples were annealed for one hour at 873 K, which is known to produce precipitates of ~ 2 nm size.⁽³⁾ The experimental results were the same for the two samples, but we will present data taken from the second sample, whose lower concentrations of TiC and Sb gave stronger channeling effects.

Backscattering analyses before and after the anneal showed that the Sb profile moved during the anneal to conform with the

Ti profile, reflective of the trapping of Sb in or near the TiC precipitates. This effect is illustrated by Fig. 3, where the Sb profile before and after the anneal is shown, along with the Ti profile estimated from that determined in an earlier experiment by 6 MeV He⁺ backscattering.⁽⁵⁾ The Ti concentration has been scaled x 1/3 to facilitate comparison with the Sb profile. The Sb profiles were measured using a 1.8 MeV He⁺ ion beam. The peak concentration of Sb after the anneal is 2.4 atomic percent at ~ 40 nm below the surface.

A. Backscattering Channeling Analysis

The pair of backscattering spectra in Fig. 4 illustrate the channeling effect for the annealed sample. These were collected with the ion beam incident first along the <100> axis and then along a random direction. The dip in the random Fe yield corresponds to the region of decreased Fe content, while direct backscattering from Ti increases the yield at energies just below the dip. Examination of the aligned spectrum shows that the presence of the precipitates has a strong dechanneling effect on the ion beam in the region below the surface down to ~ 120 nm. However, channeling is still sufficient along the major axes to be able to infer lattice location information for the Sb impurity. For example, the [100] spectrum of Fig. 4 shows a channeling reduction at the peak concentration of Sb which corresponds to ~ 65% substitutionality relative to the Fe lattice. This is calculated by $(1-X_{\text{Sb}})/(1-X_{\text{Fe}}) \times 100\%$, where X_{Sb} and X_{Fe} are the channeling yields normalized to random yield. A similar result

is obtained from backscattering for the [111] and [110] axes, as well as from the higher fluence sample. Figure 5a shows the angular dependence of the channeling for Sb along Fe $\langle 100 \rangle$. The peak backscattering yield from Sb, normalized to the random Fe yield at that depth ($\sim 50\text{nm}$) is plotted versus tilt angle across the channel, along with the Fe yield. The half-angle $\psi_{1/2}$ of the backscattered channeling dip for Sb is essentially identical to $\psi_{1/2}$ for Fe. This result was also common to channeling along the other major axes.

If the TiC precipitates are not channeling along [111] or [110], as expected from the orientation considerations of Figs. 1 and 2, then these backscattering results indicate that the Sb is in fact at the interface, rather than inside the TiC. Unfortunately, it is impracticable to experimentally monitor the channeling effect for Ti or C with backscattering, since their weaker yields are superimposed on the Fe yield.

B. X-Ray Channeling Analysis

A more suitable monitor for the channeling of Ti is the yield of ion-induced characteristic x-rays produced by the same 1.8 MeV He^+ beam used in backscattering analysis. Use of a liquid nitrogen cooled Si(Li) detector showed well-separated peaks due to the K x-rays from Ti and Fe, and to the L x-rays from Sb. By summing the counts in each set of x-ray peaks, we were able to simultaneously monitor the x-ray yield from all three elements as a function of the angle of the probing ion beam. That this qualitatively monitors the same channeling effect is confirmed

by Fig. 5b, where we show the x-ray yield for Sb and Fe along the same angular scan as in Fig. 5a. The small differences in shape and $\psi_{1/2}$ are believed due to the size of the cross-sections for characteristic x-ray production, since the cross-section radius can be of the same order as the critical distance of approach for channeling. No depth information is conveyed with x-rays, but in this application that is not important, since the depth profiles of the Sb and Ti are known.

The results of scanning the ion beam across each of the three major axes are shown in Fig. 6. We have plotted the total ion-induced characteristic x-ray yields for Fe, Sb, and Ti, normalized to the random yield from Fe, versus the tilt angle relative to the center of each major axial channel. It is immediately apparent from Fig. 6 that the ion beam is channeling through some of the TiC precipitates when incident along [100], but not when incident along [111] or [110], as expected. The Sb yield, on the other hand, shows channeling dips along all three axis, in agreement with the backscattering results. This channeling behavior agrees with that expected for Sb trapped at interfacial Fe sites, as discussed in Section II. Table I shows the normalized backscattering yields of Sb and Fe and the x-ray yield for Ti for each of the three axes. The Sb and Fe values correspond to the yield from ~40 nm depth, where the peak concentrations of TiC and trapped Sb lie.

IV. Conclusions

The channeling yields in Table I can be used to quantify the Sb substitutionality in both Fe and TiC. A simple calculation using the observed yields allows an upper limit to be placed on the amount of Sb which can be substitutional inside the TiC. If we let F_{Fe} equal the fraction of Sb trapped in Fe substitutional sites, F_{TiC} the fraction of Sb in TiC substitutional sites, F_s the fraction of untrapped Sb remaining in solution, and F_r the fraction in random sites, then the total channeling effect for Sb may be expressed as

$$(1 - X_{Sb}) = (1 - X_{Fe})(F_{Fe} + F_s) + (1 - X_{Ti})(F_{TiC}) . \quad (2)$$

Here X_{Sb} , X_{Fe} , and X_{Ti} are the channeling yields for Sb, Fe, and Ti, respectively, along any one axis. We have assumed here that solutionized Sb is 100% substitutional in Fe, and that substitutional Sb exhibits channeling identical to the host, whether Fe or TiC. Substituting the observed yields for the three axes and solving for the F's, we find $F_{TiC} \sim .09$ and $F_r \sim .25$. The uncertainty in F_{TiC} is large enough to include 0. We also obtain $F_{Fe} + F_s \sim .66$. From previous trapping analysis⁽¹⁾, we estimate F_s as $.30 \pm .10$, which leaves the fraction of Sb trapped at Fe substitutional interfacial sites as $\sim .36$. Thus we conclude that the trapped Sb ($F_{Fe} + F_{TiC} + F_r = .70$) has an average substitutionality of $\sim 50\%$ with respect to the Fe host and has very little substitutionality with respect to TiC.

If a single type of trapping site were assumed, the results might suggest a position somewhat displaced from an ideal Fe position. However, such a position would result in a narrowing of the channeling half-angle $\psi_{1/2}$ for Sb compared to Fe, an effect we do not observe. A more likely explanation is that ~50% of the trapped Sb occupies ideal Fe interfacial sites, with the remainder at random interstitial sites or highly distorted Fe sites. The random sites are unlikely to be within the TiC, in view of the large size of Sb.

The experimental results clearly indicate that the primary trapping site for Sb by TiC precipitates is at Fe interfacial sites, as previously suggested⁽¹⁾. The number of interfacial sites which would be expected for precipitates of this size and density is ~ 4 times the number of Sb atoms in the present experiment⁽³⁾. Furthermore, interfacial trapping is consistent with more recent observations of Sb trapping in Fe by both TaC and Cu precipitates,⁽⁶⁾ since the latter have a completely different chemical nature.

VI. Acknowledgments

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References

1. S. M. Myers, D. M. Follstaedt, and H. J. Rack, Appl. Phys. Lett. 33, 396 (1978); a more complete account will be published in Met. Trans.
2. I. Olefjord, Inter. Metals Rev., No. 4, 1978, pp. 149-163.
3. D. M. Follstaedt J. Appl. Phys. 51, 1001 (1980).
4. R. G. Baker and J. Nutting, ISI Special Report, No. 64, 1959.
5. D. M. Follstaedt, J. A. Knapp, and S. T. Picraux, to be published in Applied Physics Letters.
6. S. M. Myers, D. M. Follstaedt, to be published.

TABLE I. Normalized Channeling Yields

AXIS	Sb [†]	Ti [*]	Fe [†]
<100>	.65	.78	.50
<111>	.71	.98	.55
<110>	.76	.99	.65

[†] Backscattering

^{*} Characteristic x-ray

FIGURE CAPTIONS

FIGURE 1 - Electron diffraction pattern obtained along a [100] axis of Fe containing TiC precipitates, which formed during implantation of 6×10^{16} Ti/cm² at 60 keV with the sample at 700°C. The three parallelograms mark reflections from the three TiC precipitate orientations.

FIGURE 2 - Diagram of an Fe (110) plane containing a TiC precipitate and trapped Sb. The lines represent ion beams channeling along the three major Fe axes.

FIGURE 3 - Antimony depth profile before and after annealing, measured by backscattering of 1.8 MeV He⁺ ions. The dashed line is an approximate Ti profile estimated from previous work.⁽⁵⁾

FIGURE 4 - Aligned and random backscattering spectra obtained from an Fe crystal containing TiC precipitates and Sb. The depth scales shown correspond to the density of pure Fe. The backscattering angle was 162.5°.

FIGURE 5a- Backscattering channeling dips for Sb and Fe along Fe <100>.

FIGURE 5b- Ion-induced characteristic x-ray channeling dips for Sb and Fe along Fe <100>.

FIGURE 6 - Ion-induced characteristic x-ray yield channeling dips for Fe, Ti, and Sb along the three major Fe axes. Ti and Fe are plotted together in the upper portion, and Sb and Fe in the lower.