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Measurements of the Diffusion of Iron and Carbon in Single Crystal NiAl using Ion Implantation and Secondary Ion Mass Spectrometry

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ABSTRACT

Classical diffusion measurements in intermetallic compounds are often complicated by low diffusivities or low solubilities of the elements of interest. Using secondary ion mass spectrometry for measurements over a relatively shallow spatial range may be used to solve the problem of low diffusivity. In order to simultaneously obtain measurements on important impurity elements with low solubilities we have used ion implantation to supersaturate a narrow layer near the surface. Single crystal NiAl was implanted with either ^{12}C or both ^{56}Fe and ^{12}C in order to investigate the measurement of substitutional (Fe) versus interstitial (C) tracer diffusion and the cross effect of both substitutional and interstitial diffusion. When C alone was implanted negligible diffusion was observed over the range of times and temperatures investigated. When both Fe and C were implanted together significantly enhanced diffusion of the C was observed, which is apparently associated with the movement of Fe. This supports one theory of dynamic strain aging in Fe alloyed NiAl.

INTRODUCTION

Recent studies have shown that NiAl alloys may exhibit several manifestations of strain aging under deformation.[1, 2] In particular the Portevin-LeChatelier effect has been observed in single crystal NiAl alloyed with both Si and C, and less clearly, in NiAl alloyed with Fe and C [2]. In order for interstitial species to cause dynamic strain aging effects it is generally required that they diffuse through the material faster than the movement of dislocations. That the presence of substitutional solutes results in an enhanced strain aging effect suggests that the diffusion of the substitutional element (Si or Fe) enhances that of the interstitial. The solubility of C in NiAl is less than the normal impurity levels observed in NiAl (~100 ppm) hence diffusion measurements are extremely difficult using normal techniques. Using ion implantation however, it is possible to supersaturate a region just below the surface with nearly any element then measure the rate that it is transported away from the implanted region under thermal annealing by using secondary ion mass spectrometry. To determine if the simultaneous presence of a substitutional element enhances the transport of the interstitial, the second element of interest can be implanted in the same region. In this study we chose to investigate the effect of Fe on C in NiAl since the experimental evidence for the association of Si with enhanced C transport seems clear, but the effect of Fe has been more difficult to elucidate using mechanical techniques. [2]

EXPERIMENTAL

High purity single crystal NiAl was produced using a modified Bridgman technique as described elsewhere [3]. A round disk was cut from the crystal at the [100] orientation with

orientation checked with the Laue backscatter x-ray technique. The oriented crystal wafer was polished on both sides to a 1 micron diamond finish using standard metallographic technique then given a final 0.06 micron finish with colloidal silica. Ion implantation was performed using a Varian-Extrion implanter in the Surface Modification and Characterization Facility at Oak Ridge National Laboratory (SMAC-ORNL). Implantation parameters (dose and energy) were modeled using the PROFILE code [4]. The implantation energies were chosen so that the combined Fe-C implants would overlay as closely as possible within the available range of implantation energies (30-170 keV). One side of each wafer was implanted with C and the other side with both C and Fe. Carbon was implanted at an energy of 35 keV and iron was implanted at 160 keV at individual fluences of 5×10^{16} ions/cm². The resulting implanted distribution for the combined implant is shown in figure 1.

The implanted samples were then sectioned into 8 wedges. The wedges were given post implantation anneals of 3 to 10 hours at temperatures ranging from 400 to 800° C. All anneals were conducted in an atmosphere of Ar-6%H₂ to avoid oxidation, nonetheless some slight oxidation was observed on the Fe/C implanted side at 800 C, as evidenced by a light brown film on the surface. Temperature was monitored with a type S thermocouple located within the furnace atmosphere at the same position as the samples. Essentially no movement of the implanted species in NiAl could be observed at anneals below 600° C. Therefore, only results from anneals at 600, 700 and 800° are discussed here. Since the C and C/Fe implants were on opposite sides of the same sample, they each were exposed under exactly the same conditions.

Secondary Ion Mass Spectrometry (SIMS) was performed using a Perkin Elmer-PHI 6600 SIMS system using a 7 keV Cs⁺ primary ion beam and positive secondary ion detection (CsX⁺ cluster ion spectrometry where X is the impurity element of interest). The primary ion beam current was set at 315 nA and the raster size was 500x500 μm² with a 65% gating (detected area 175x175 μm²)

Iron was monitored using ¹⁸⁹(CsFe)⁺. Carbon was monitored using ¹⁰⁹(NiAlC₂)⁺ and ¹⁴⁵CsC⁺. Mass ¹⁰⁹NiAlC₂ was found to provide a better detection limit for C. Masses ¹⁴⁹CsO⁺, and ¹⁶⁰CsAlO⁺ were monitored for oxygen since we had previously observed significant increases in the relative sensitivity factors (RSF) for the carbon in particular when oxygen was present.

Quantification of the SIMS profiles was accomplished by processing the raw data into concentration vs. depth using PHI-Matlab data processing software. The Relative Sensitivity factors for ¹²C and ⁵⁶Fe in the as-implanted samples were calculated with reference to a matrix ion. The depth of the craters sputtered into the samples was measured using a Dektak IIA profilometer after the SIMS analysis. An average of 5 measurements along the x-x and y-y directions was taken for each crater. Possible variations in sputter rate with depth were checked by sputtering craters for 5, 15, 30 and 60 minutes on several specimens.

RESULTS

The depth distribution of the implanted elements was measured in the as-implanted state and after anneals of 10 hours at 600° C, 3 hours at 700° C, and 3 hours at 800° C. In figure 2 the distribution of carbon in the as-implanted state and after the various anneals is shown. Very little movement of carbon from the implanted distribution can be detected. The height of the implanted carbon distribution does not decrease significantly until the 800° C anneal. Apparently the solubility of C in NiAl is below the background level since an inflection in the

curves would be expected at the solubility limit. [5] The C is therefore apparently being drained away from the implanted layer at a rate controlled by the diffusion of interstitial C in NiAl.

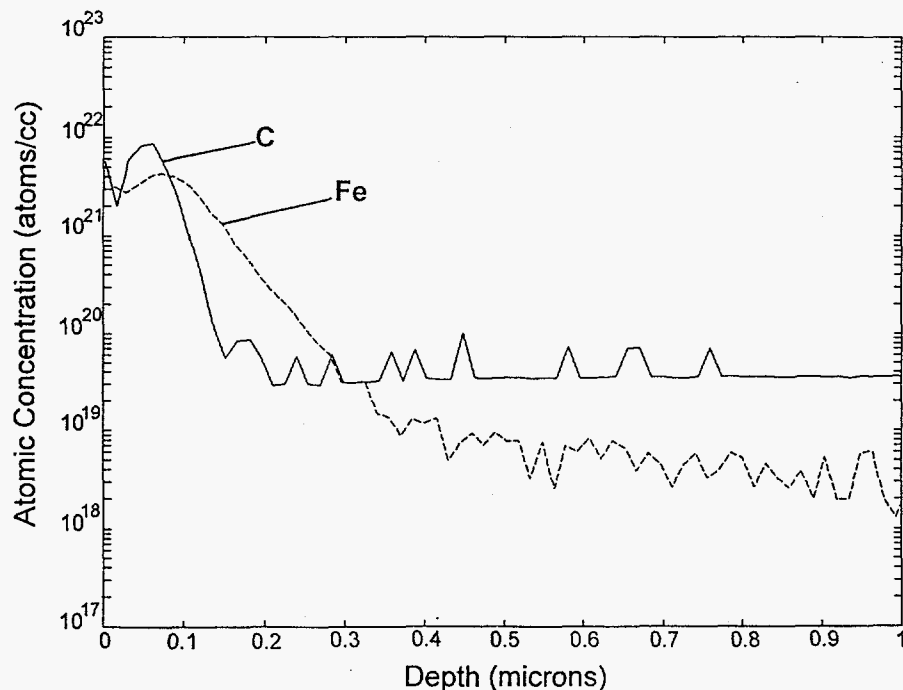


Figure 1. SIMS measurements of the as-implanted C and Fe distribution.

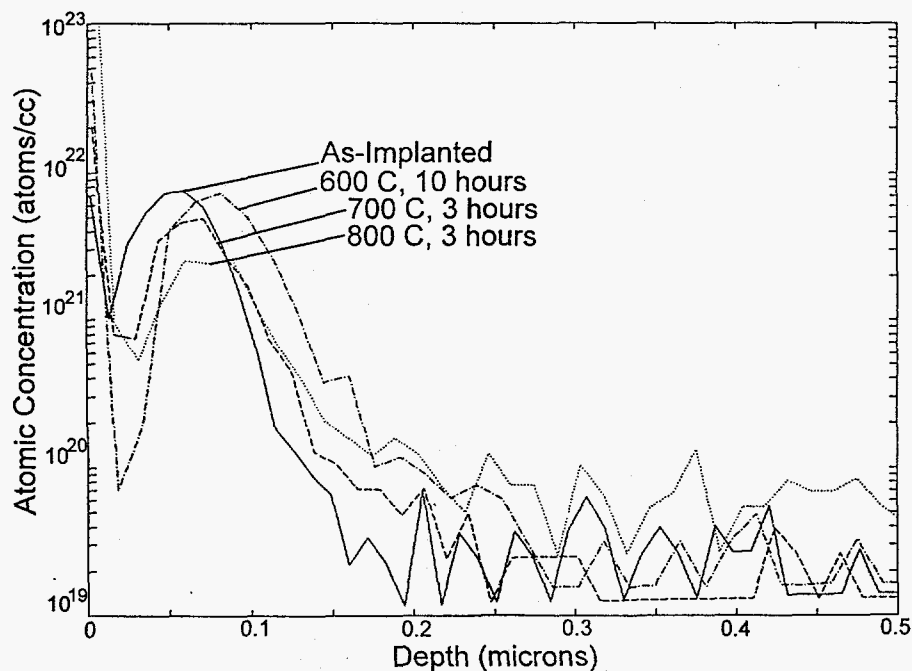


Figure 2. Carbon distribution in as-implanted and annealed NiAl implanted with C alone.

Figure 3 shows the C distribution measured in the samples on the side implanted with C and Fe simultaneously. The C distribution is significantly different than observed on the side implanted with carbon alone. There is clearly enhanced diffusion of C into the substrate, which

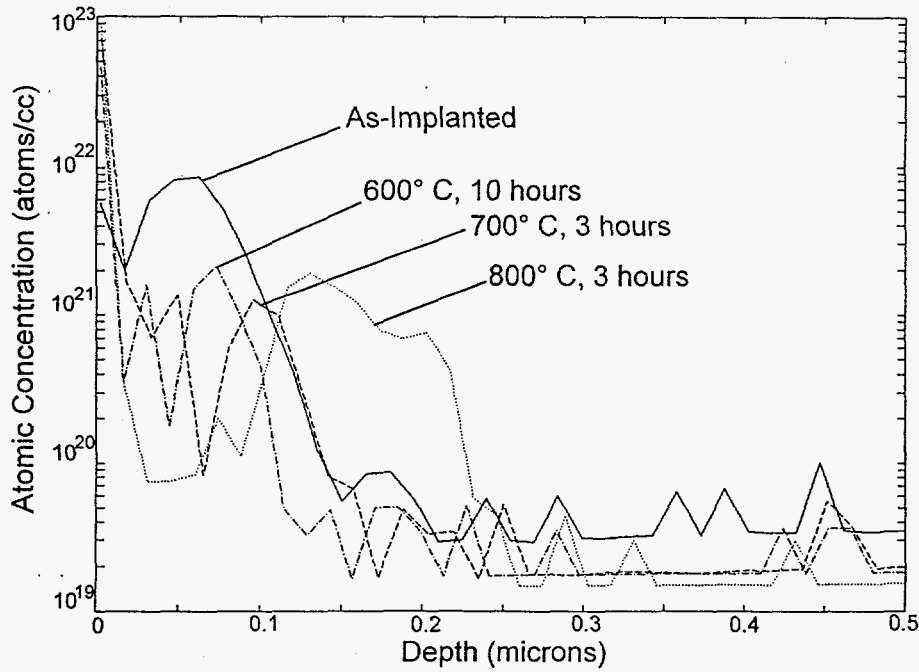


Figure 3. Carbon distribution in as-implanted and annealed specimens of NiAl implanted with C and Fe.

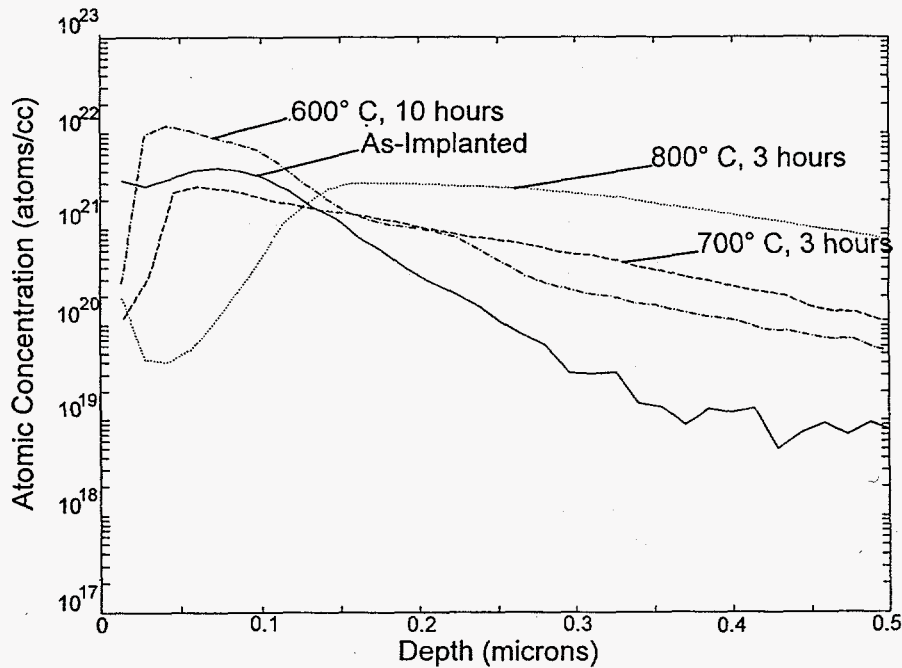


Figure 4. Iron distribution in as implanted and annealed samples of NiAl implanted with both ^{56}Fe and ^{12}C .

is associated with the simultaneous diffusion of iron. The Fe distribution in the same experiments is shown in figure 4. While there is some apparent matrix effect in the sample annealed at 600° C, resulting in an increase in the measured peak height, the Fe clearly is diffusing into the substrate as the sample is annealed. FeAl and NiAl form a continuous solid solution. [6]

Therefore, the peak shape is determined solely by the initial implanted distribution and the rate of tracer diffusion of Fe in NiAl.

The C distribution itself is now split into two peaks. As shown in figure 5, a local minimum in the C signal in the annealed samples corresponds to the maximum in the iron signal. The association of a minimum in the C with the Fe maximum suggests that at a critical

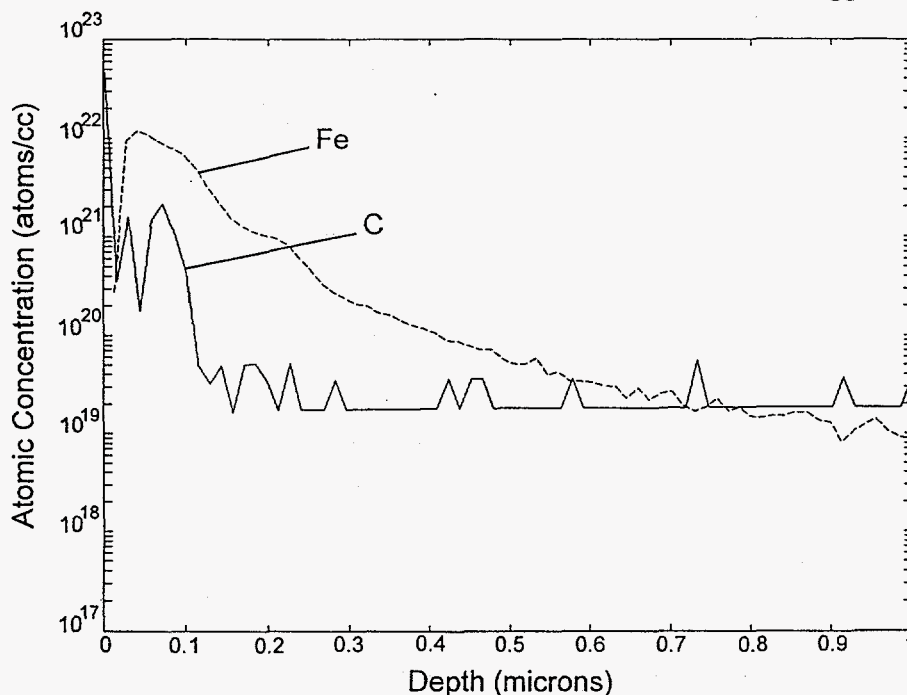


Figure 5. Fe and C distribution measured in a sample of NiAl annealed at 600° C for 10 hours. Note that the local minimum in the C distribution corresponds to the maximum in the Fe distribution.

concentration Fe and C form a compound (Fe_3C ?) which results in a decrease in the C emission. Alternatively, it might be taken as evidence that the excess iron causes carbon to rapidly move toward the surface and into the bulk. This view is harder to rationalize given the high affinity of iron for carbon.

DISCUSSION

The approach taken here (II/SIMS) is sufficiently sensitive to demonstrate the cross effect in Fe/C diffusion in NiAl, an effect that would be extremely difficult to observe using classical diffusion techniques. The measured iron distributions are sufficiently well defined that it should be possible to calculate an effective Fe tracer diffusion coefficient using the methods of Hirvonen [7]. In this case however, because of the presence of the C we felt that such a calculation would be difficult to interpret. The low rate of thermal diffusion of C observed when C is implanted alone suggests that the interstitial mechanism is limited by the solubility of C in Fe. Radiation enhanced diffusion would only result in transport to the surface since the tendency must be for excess vacancies to move toward the surface rather than into the bulk of stoichiometric NiAl. When Fe is implanted with the carbon, the rate of interstitial diffusion is significantly enhanced. Double peaks are observed in all of the C profiles when C is implanted with Fe. The carbon which moves toward the surface might be associated with the relaxation of the radiation damage

associated with the Fe implant, but there is clear evidence that C is also moving into the substrate. Furthermore, the fact that the Fe, although the more mobile species, does not move toward the surface suggests that the C movement is not due to radiation damage. Although some surface oxidation was present at 800 C resulting in an apparent overall shift of the C into the sample, this effect is due simply to the lower sputtering rate through the oxide rather than the metal. Nonetheless, apparently both peaks are moving together, which suggests that the carbon closer to the surface is also starting to diffuse in at 800 C. Furthermore, this oxidation effect does not explain the clear shifts in the C observed at 700 and 800° C Irregularities in the Fe distribution are associated with peaks and valleys in the C distribution., for example the local minimum in the C distribution at 600 C is associated with the maximum in the Fe distribution, which suggests that the C is bound to Fe above a critical concentration, resulting in an apparent decrease in the C signal monitored.

CONCLUSIONS

- 1) The combination of ion implantation and SIMS has been shown to be an effective technique for observing the diffusion of low solubility elements over a very short range. This type of measurement would be extremely difficult and time consuming. using classical diffusion techniques.
- 2) When no other alloying elements are present, the diffusion of C away from the implanted layer is limited by the low solubility of C in NiAl.
- 3) The presence of Fe clearly enhances the diffusion of C in binary NiAl. This effect supports the hypothesis that iron causes dynamic strain aging effects in NiAl by increasing the rate of diffusion of C sufficiently to keep up with moving dislocations.
- 4) The enhanced diffusion of C is probably the result of complex interaction between C and Fe, since no evidence of enhanced diffusion due to radiation damage is observed.

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