ATOMIC RESOLUTION OBSERVATIONS OF SOLUTE ATOM SEGREGATION TO STACKING FAULTS
IN A Co-0.96 at.% Nb ALLOY

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Introduction

Alloying elements often segregate to external surfaces and solid-solid interfaces that
include grain boundaries, interphase boundaries and stacking faults (1). Many physical
properties of materials are strongly influenced by the presence of solute species which have
segregated to planar imperfections. Most of the studies of interfacial segregation deal with
either external surfaces or grain boundaries, while very little attention has been given to
solute segregation to stacking faults--frequently called Suzuki segregation (2,3). Although
there have been several studies to elucidate the effects of alloying elements and temperature
on stacking fault energies (e.g.,4,5), there have been no direct measurements of the
composition of stacking faults in alloys. This is due to the fact that stacking faults are not
readily accessible to analysis by presently available conventional surface analytical tools.

In this paper we present the results of an atom-probe field-ion microscope (FIM) study of
niobium segregation to stacking faults in a Co-0.96 at.% Nb alloy. Our atom-probe FIM allows
us to determine the chemical identity of individual atoms with a mass (m) resolution of (m/m)
\(\approx 1/200\) (6-9). In addition, the atom-probe FIM has a lateral atomic resolution, for
composition, of a few angstroms and therefore it is an ideal tool for studying
solute segregation to stacking faults.

Extensive studies of both cobalt and cobalt-based alloys abound in the literature as they
exhibit an allotropic phase transformation from the hexagonal close-packed (HCP) to the face-
centered cubic (FCC) phase (10-13). A high density of stacking faults exists in cobalt-based
alloys, because the difference in the Gibbs free energies of the FCC and HCP phases is very
small (14).

Experimental Details

Wire specimens with a diameter of 0.375 mm were fabricated with a nominal composition of
Co-0.96 at.% Nb; the Nb concentration was determined by atomic absorption spectroscopy. Heat
treatments were developed to: (a) produce a reasonable stacking fault density, i.e., a few
faults in the \(~10^{-10}\) cm\(^2\) field-of-view; and (b) produce an equilibrium concentration of Nb
atoms on each stacking fault. The thermal treatments which achieve these goals consist of
anneals at a temperature \((T_a)\) equal to 450°C for 21 days, 575°C for 14 days or 575°C for
two days. These specimens were encapsulated under vacuum, prior to their anneal, in quartz
capsules and quenched into water at 0°C at the end of the anneal. In the absence of diffusion
data or the Co(Nb) system we used the tracer diffusivity of Fe in Co (15) to estimate the
root-mean-square diffusion distance \((\langle x^2 \rangle)\) at 450, 525 and 575°C. At the lowest temperature
the value of \((\langle x^2 \rangle)\) is 8.0nm; this value is approximately equal to one-half the distance between
two stacking faults -- which suggests that an equilibrium concentration was most likely
achieved at all temperatures. An estimate of the integrated number of jumps during a quench
demonstrates that an upper limit to the corresponding value of \((\langle x^2 \rangle)\) is \(<1.0\)nm; therefore, there
was no redistribution of Nb during the quench. These first-order diffusion calculations
indicate that we are studying the equilibrium Nb concentration on the stacking faults, which is
characteristic of the annealing temperatures. FIN specimens were prepared by an
electropolishing technique. Next analyses were performed in our atom probe at a background
pressure of $6 \times 10^{-8}$ Pa and a specimen temperature ($T_s$) of 45 K. A pulse fraction ($f$) of 0.15 was used for all the analyses. The quantity $f$ is the ratio of the pulse voltage ($V_p$) to the standing voltage ($V_{dc}$). A constant pulse frequency of 60 Hz was employed. The average number of ions field evaporated per pulse was 0.02. Using these experimental conditions we are able to obtain good agreement between the nominal Nb composition and the Nb concentration as determined by the atom probe technique (see Results section). Further details concerning our atom probe have been published elsewhere (6-9).

**Principle of the Experiment**

The basic ideas involved in this experiment are embodied in fig. 1. In this figure an FIM specimen is exhibited which contains a single stacking fault parallel to the axis of the tip. The intersection of the stacking fault with the surface of the tip produces an atomic step (fig. 1a). The vertical height of this step is given by the dot product of the shear vector characterizing the stacking fault and the unit normal to the crystallographic plane which it intersects (16). If the vertical height is equal to a non-integral value of the interplanar spacing of the plane which the stacking fault intersects, then it is readily discernible in the FIM image. The planes have a horse-shoe like appearance -- see figs. 1b and 2, and Bowkett and Smith (16). When the vertical height of a step is equal to an integral number of interplanar spacings the stacking fault is invisible.

The stacking fault is shown with a number of Nb atoms residing in its plane (fig. 1a). Each atomic plane is dissected by the application of a series of field evaporation pulses (8,9). Typically $5 \times 10^3$ pulses are employed to evaporate a plane containing 100 atoms. The field evaporated ions which have trajectories that take them into the probe hole, in the image intensification system, are focused onto the Chevron detector with the aid of an Einzel lens (8,9). The distance of the image intensification system from the FIM tip is adjusted so that the diameter of the cylinder analyzed is $\approx 3.0-6.0$nm. The mass-to-charge ratios of all the atoms -- both Co and Nb -- in this cylinder are determined by the time-of-flight atom probe technique. To obtain the composition of the analyzed cylinder of alloy the cumulative number of Nb events is plotted versus the cumulative number of Nb plus Co events -- such a plot is called an integral profile. The average slope of this plot corresponds to the average Nb composition ($<C_{Nb}>_u$) of the volume analyzed; where the subscript $u$ on the bracket means an uncorrected value. The value of $<C_{Nb}>_u$ is a lower limit to the actual Nb concentration in the stacking fault ($<C_{Nb}*>$). The relationship between $<C_{Nb}>_u$ and $<C_{Nb}>*$ is considered in the Discussion section.

**Results**

A typical FIM micrograph, exhibiting several stacking faults, is shown in fig. 2. This micrograph was recorded with $T_s$ equal to 45 K employing neon as the imaging gas ($6 \times 10^{-6}$ Pa gauge pressure). The stacking fault is FCC in an HCP matrix and lies on a {111} plane. The characteristic horseshoe-like contrast effect is readily discernible and two of the faults are clearly decorated with a large number of bright spots. In general, solute atoms can give rise to either a bright spot or a dark spot contrast effect (e.g.,17,18). We have not yet established unambiguously that the contrast effect produced by a niobium atom is indeed a bright spot. However, it is interesting to note that even though the composition measured for different faults is approximately the same -- some faults are decorated with a large number of bright spots along their traces, while others are not decorated at all (see fig. 2). This observation indicates that the mechanism for imaging Nb atoms on stacking faults is a function of the crystallographic plane(s) which the fault intersects.

A typical mass spectrum -- number of events versus the mass-to-charge ratio -- for a Co-0.96 at. % Nb alloy is exhibited in fig. 3; both Co and Nb are single isotope metals. Cobalt appears only in the plus-two ionization state ($^{59}$Co$^{+2}$) and 93% of the niobium events appear in the plus-three ionization state ($^{93}$Nb$^{+3}$) with the remaining 7% appearing in the plus-two ionization state (not shown). We discovered during a series of detailed control
experiments that the measured Nb concentration is a function of f and T_s for a fixed pulse frequency, with the average number of ions per pulse in the range 0.01 to 0.05. At temperatures less than 60 K the measured Nb concentrations are in good agreement with the nominal value at all values of f.

Fig. 2. An FIM micrograph of a Co-0.96 at. % Nb alloy annealed at T_a=450°C for 21 days. At least four stacking faults are seen in the field-of-view. Note the presence of a large number of bright spots along stacking faults (1) and (2). The arrow points to the characteristic horseshoe-like contrast effect produced by a stacking fault when it intersects the surface of the tip. The solid black circle is the image of the probe hole.

Fig. 3. The Co^{+2} and Nb^{+3} spectrum of the Co-0.96 at. % Nb alloy. The spectrum was recorded at a specimen temperature of T_s = 45 K with f = 0.15, in a vacuum of 6x10^{-8} Pa.

The data for a typical experiment during our study of Nb atom segregation to stacking faults were recorded at a T_s of 45±0.01 K. An atom probe analysis of a region which was far from any stacking faults was performed to obtain the concentration of Nb in the matrix (<C_{Nb}>). The Nb integral profile for this case is exhibited in fig. 4.; the smallest vertical step corresponds to the detection of one Nb event. The average slope of this plot yields <C_{Nb}> = 0.94±0.24 at. % Nb; where the uncertainty is the ratio of the square root of the number of Nb events to the total number of Nb plus Co events detected. This value of <C_{Nb}> is in good agreement with the atom probe determinations of this same quantity for specimens which did not contain any stacking faults in the field-of-view.

Figure 5 exhibits an integral Nb profile for a cylinder of alloy which contains a stacking fault; the radius of the cylinder is 2.4nm. The average slope of this plot corresponds to <C_{Nb}>. For this case <C_{Nb}> = 2.65±0.17 at. % Nb. An examination of the FIM image after the atom-probe analysis indicated that the stacking fault was still positioned in the center of the probe hole. Hence <C_{Nb}> is for a cylinder of alloy which contained a stacking fault throughout the entire analysis.

The fact that <C_{Nb}> is a factor of 3.0 greater than the <C_{Nb}> clearly indicates that Nb atoms segregate to stacking faults in this alloy. It is emphasized strongly that the measured
value of \( \langle C_{Nb}^b \rangle_u \) is an average concentration for the cylinder of alloy analyzed. Hence, it is clear that the value of \( \langle C_{Nb}^b \rangle_u \) reported here represents a lower limit to the actual concentration of Nb atoms in the stacking fault.

**Analysis**

The result obtained for \( \langle C_{Nb}^b \rangle_u \) is a lower limit and to find the actual Nb concentration in the stacking fault (\( \langle C_{Nb}^b \rangle^* \)) it is necessary to correct for the matrix contribution to the \( \langle C_{Nb}^b \rangle_u \). An expression for the relationship between \( \langle C_{Nb}^b \rangle_u \) and \( \langle C_{Nb}^b \rangle^* \) based on conservation of mass is

\[
\langle C_{Nb}^b \rangle_u = \langle C_{Nb}^b \rangle^* v_f + \langle C_{Nb} \rangle v_m ;
\]

where \( v_f \) is the volume fraction of the cylinder occupied by the stacking fault and \( v_m \) is the remaining volume fraction of the cylinder analyzed -- \( v_f + v_m \) must, of course, be equal to unity. For the case of a cylinder containing a planar defect, which is parallel to the axis of a cylinder, and where the width of the solute distribution is equal to the diameter of the cylinder the quantities \( v_f \) and \( v_m \) are exactly equal to their corresponding areal fractions. The expression for \( \langle C_{Nb}^b \rangle^* \) is, therefore,

\[
\langle C_{Nb}^b \rangle^* = \left[ \frac{\langle C_{Nb}^b \rangle u A_f}{A_f} - \langle C_{Nb} \rangle \right] \frac{(D/t)^2}{4} \bigg/ \pi D / 4 t ;
\]

where \( A_f \) is the cross-sectional area of the stacking fault and \( A_p \) is the cross-sectional area of the cylinder of alloy analyzed. The ratio \( A_p/A_f \) is given by

\[
\frac{A_p}{A_f} \sim \frac{(D/t)^2}{\pi D / 4 t} \equiv A_D / D ;
\]

where \( D \) is the diameter of the cylinder analyzed and \( t \) is the full width of the solute distribution. Therefore, the value of \( \langle C_{Nb}^b \rangle^* \) is sensitive to the ratio \( (D/t) \).

The value of \( t \) is essentially unmeasured at present since we have not yet determined the composition profile perpendicular to the plane of a stacking fault on an atomic layer-by-layer basis. However, in all the FIM images of stacking faults in this Co-0.96 at. % Nb alloy, that we have observed, only the trace of the fault plane is observed to be decorated with bright spots. No evidence has been found for a high concentration of bright spots in the matrix immediately adjacent to the trace of the fault plane. Also recent calculations by Simon et al. (19) on the interaction energies between transition element solute atoms and stacking faults.
faults, in compact transition metals, indicate that the interaction is very short ranged -- it is typically zero at two to three (111) interplanar spacings. Niobium was not considered, nevertheless a long-range interaction between a low-energy stacking fault and a solute atom, such as Nb, does not seem physically realistic. Williams and Nason (20) have shown that the surface composition of an alloy approaches the bulk composition within a few atomic layers. Therefore, we conjecture that the value of \( t \) is much less than the value of \( D \) employed and the ratio \( \frac{D}{t} \) is greater than unity. An upper bound to \( C_{\text{Nb}}^* \) is determined by taking \( t \) equal to the atomic diameter of a solvent atom (Co) -- that is, the Nb atoms substitutionally replace the Co atoms in an extrinsic stacking fault.*

Three different methods were employed to determine the value of \( A_p \). The first two methods are based on geometrical considerations, while the third approach involves counting the number of atoms in each plane field evaporated. The third method can only be used when the trace of a stacking fault passes through the center of the plane being analyzed. We have compared these methods and find that the calculated radii of the areas analyzed are the same to within \( \pm 20 \)%. Figure 6 shows \( C_{\text{Nb}}^* \) versus \( t \). For a value of \( t \) equal to the diameter of a Co solvent atom (0.277 nm) the concentration in the fault can be as high as 30 at.\% Nb -- this corresponds to an enhancement factor of \( \sim 32 \). Note that the corrected Nb concentration approaches \( C_{\text{Nb}}^* \) within a few (0002) atomic planes on either side of a stacking fault.

**Fig. 6** Corrected Nb concentration vs. different assumed values of the full width of the solute distribution (\( t \)).

**Discussion**

The adsorption isotherm equation for Suzuki segregation has been derived by a number of authors (3, 23-26). This equation is of the same form as the Langmuir or McLean (27,28) adsorption isotherm equation. For a stacking fault it is given by

\[
\frac{C_{\text{Nb}}^*}{1-C_{\text{Nb}}^*} = \frac{C_{\text{Nb}}}{1-C_{\text{Nb}}} \exp(\frac{\Delta S_{\text{Nb},f}}{k}) \exp(\frac{-\Delta H_{\text{Nb},f}}{kT});
\]

where \( \Delta S_{\text{Nb},f} \) and \( \Delta H_{\text{Nb},f} \) are the partial molar entropy and enthalpy of segregation, respectively, of niobium atoms to a stacking fault, \( kT \) has its usual significance. We have determined the value of \( \Delta H_{\text{Nb},f} \) from the temperature dependence of \( C_{\text{Nb}}^* \) in the range 450 to 575°C. The upper limit to \( \Delta H_{\text{Nb},f} \) is \( \sim -0.6 \) eV atom\(^{-1}\). This is for the case where all the Nb atoms are assumed to sit substitutionally in the plane of the stacking fault. The lower limit to \( \Delta H_{\text{Nb},f} \) it is \( \sim -0.4 \) eV atom\(^{-1}\); physically this corresponds to the very unrealistic case where all the Nb atoms are distributed uniformly in the cylinder analyzed--diameter of 3.0 to 6.0 nm.

* For an FCC fault in an HCP matrix this is described by the sequence ABABACCRAB where we have used the standard notation (21,22) to describe the nature of an extrinsic stacking fault.
It is interesting that although the values of $<C_{Nb}^*>$ calculated by the two different methods described in the analysis section are the same within ~16%, the value of $\Delta H_{f,b}$ is independent of the method of evaluating $<C_{Nb}^*>$ -- for a fixed width of the solute distribution. This is due to the nature of exponential function in Eq. (4).

The fact that we have observed an enhanced Nb concentration on stacking faults indicates the existence of a strong driving force for segregation of Nb atoms to a stacking fault. It is not clear that the presently available theories of surface segregation (29,30) can be used to explain the magnitude of the effect we have observed. For example, even though the atomic volume of Nb is ~62% greater than that of a Co atom -- as a result large strains are produced in the matrix -- it is not clear how the solute strain energy can be relaxed by simply exchanging a Nb atom from the bulk with a smaller Co atom at a stacking fault. Experiments in progress on a Co-1 at. % Fe alloy, where the strain energy is very small, should be useful in sorting out the importance of the strain energy term as a driving force for solute segregation to stacking faults.

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References