ATOMIC RESOLUTION OBSERVATIONS OF SOLUTE- ATOM SEGREGATION EFFECTS AND PHASE TRANSITIONS IN STACKING FAULTS IN DILUTE COBALT ALLOYS—I. EXPERIMENTAL RESULTS

R. HERSCHITZ† and D. N. SEIDMAN

Cornell University, Bard Hall, Department of Materials Science and Engineering and
The Materials Science Center, Ithaca, NY 14853-0121, U.S.A.

(Received 20 July 1983; in revised form 17 June 1984)

Abstract—Solute atom segregation effects to *individual* stacking faults in Co–0.96 at.% Nb and Co–0.98 at.% Fe alloys have been investigated using the atom-probe field-ion microscope. The composition of *individual* stacking faults has been *directly* measured in the range 450–575°C. The diameter of the analyzed cylinder of alloy was ~ 30 –50 Å. It is shown that the solute concentration profile falls off very quickly with distance—within less than 4 Å—from the plane of the fault in both alloys. And it is suggested that the Nb and Fe segregation effects are most likely confined to the plane of the fault. Very strong solute atom segregation effects to stacking faults have been observed in both alloys. After correction for the matrix contribution to the chemical analyses, the Nb concentration in the stacking faults in a Co–0.96 at.% Nb alloy is greater than the bulk composition by factors of 30, 12 and 7 at annealing temperatures of 450, 525 and 575°C. The corrected Fe concentration in the stacking faults in a Co–0.98 at.% Fe alloy is greater than the bulk composition by factors of 10, 6 and 4 at the annealing temperatures 450, 550 and 575°C. Small solute-rich fluctuations, (~ 5 –20 Å dia), whose compositions differ significantly from the average fault composition, have been observed in the plane of the stacking faults at 525 and 575°C in the Co–0.96 at.% Nb alloy. This, in combination with the experimental observation that at 450°C the stacking fault composition is close to that of Co₂Nb, suggests that in addition to solute atom segregation we have evidence for a disorder–order transformation within the plane of the fault with decreasing temperature. Small solute-rich fluctuations (~ 20 Å dia) have also been observed in the Co–0.98 at.% alloy at 550 and 575°C.

Résumé—Nous avons étudié les effets de la ségrégation d'atomes de soluté sur des défauts d'empilement individuels dans Co–0.96 at.% Nb et Co–0.98 at.% Fe à l'aide de la sonde atomique d'un microscope à émission de champ. Nous avons mesuré directement la composition des défauts d'empilement individuels entre 450 et 575°C. La diamètre du cylindre d'alliage analysé était de l'ordre de 30 à 50 Å. Nous montrons que le profil de concentration en soluté décroît très vite avec la distance moins de 4 Å—au plan du défaut dans les deux alliages. Nous pensons donc que les effets de ségrégation de Nb et Fe ne se produisent que dans le plan du défaut. Nous avons observé des effets de ségrégation atomique de soluté très forts dans les deux alliages. Après correction pour la contribution de la matrice aux analyses chimiques, la concentration en Nb des défauts d'empilement dans un alliage Co–0.96 at.% Nb est plus grande que la concentration dans la masse d'un facteur 30, 12 et 7 pour des températures de recuit de 450, 525 et 575°C. La concentration en Fe corrigée dans les défauts d'empilement d'un alliage Co–0.98 at.% Fe est supérieure à la concentration dans la masse d'un facteur 10, 6 et 4 pour des températures de recuit de 450, 550 et 575°C. Nous avons observé de petites fluctuations riches en soluté (diamètre compris entre 5 et 20 Å), dont la composition diffère notablement de la composition moyenne du défaut, dans le plan des défauts d'empilement à 525 et 575°C dans l'alliage Co–0.96 at.% Nb. Ajouté à l'observation expérimentale selon laquelle la composition du défaut d'empilement à 450°C est proche de celle de Co₂Nb, ceci donne à penser qu'en plus de la ségrégation d'atomes de soluté, il y a une transformation désordre-ordre dans le plan du défaut lorsqu'on abaisse la température. Nous avons également observé de petites fluctuations riches en soluté (diamètre de l'ordre de 20 Å) dans l'alliage Co–0.98 at.% Fe à 550 et 575°C.

Zusammenfassung—Die Segregation gelöster Atome an einzelnen Stapelfehlern wurde in den Legierungen Co–0.96 At.-% Nb und Co–0.98 At.-% Fe mit der Atomsonde des Feldionenmikroskopes untersucht. Die Zusammensetzung der *einzelnen* Stapelfehler wurde *direkt* für den Temperaturbereich zwischen 450 und 575°C gemessen. Der Durchmesser des analysierten Zylinders betrug 30–50 Å. Das Konzentrationsprofil für die segregierten Atome fällt in beiden Legierungen sehr rasch mit dem Abstand von der Stapelfehlerebene ab (innerhalb von weniger als 4 Å). Es liegt nahe, daß die Nb- und Fe-Segregation sehr wahrscheinlich auf die Stapelfehlerebene beschränkt ist. In beiden Legierungen wurden sehr starke Segregationseffekte an Stapelfehlern beobachtet. Nach Korrektur der Matrixbeiträge zur chemischen Analyse ergibt sich, daß die Nb-Konzentration an den Stapelfehlern der Legierung Co–0.96 Nb bei den Auslagerungstemperaturen 450, 525 und 575°C um 30-, 12- und 7-mal höher ist als der Volumenwert. Für

†Present address: R.C.A., Astroelectronic Division, Princeton, NJ 08540, U.S.A.

das Eisen in der Legierung Co-0,98 Fe gelten die Faktoren 10, 6 und 4 bei den Auslagerungstemperaturen 450, 550 und 575°C. Kleine, an Lösungsatomen reiche Fluktuationsbereiche (~ 5 bis $20 \text{ \AA}$ Durchmesser), deren Zusammensetzung sich deutlich von der mittleren Konzentration am Stapelfehler unterscheidet, wurden in der Stapelfehlerebene bei 525 und 575°C im Co-0,96 Nb aufgefunden. Bei 450°C liegt die Zusammensetzung am Stapelfehler bei Co₂Nb, sodaß wahrscheinlich auch noch ein Ordnungs-Entordnungsübergang zusätzlich zur Segregation in der Stapelfehlerebene mit sinkender Temperatur auftritt. In der Legierung Co-0,98 Fe wurden bei den Temperaturen 550 und 575°C ebenfalls kleine ($\sim 20 \text{ \AA}$ Durchmesser), an Lösungsatomen reiche Fluktuationsbereiche beobachtet.

1. INTRODUCTION

The phenomenon of interfacial segregation plays an important role in determining many physical properties of materials [1]. Equilibrium segregation of alloying elements to internal boundaries affects processes such as corrosion, hydrogen and liquid metal embrittlement and fracture behavior of materials, while solute segregation to free surfaces has a strong influence on the processes of oxidation, catalysis and wetting. Most of the studies of interfacial segregation deal either with grain boundaries or free surfaces, while very little attention has been given to solute segregation to stacking faults—commonly called Suzuki segregation [2, 3]. Although there have been several studies to elucidate the effects of alloying elements and temperature on stacking fault energies in cobalt alloys [4, 5], there have been no *direct* measurements of the composition of stacking faults in any alloy. This is due to the fact that stacking faults are not readily accessible to analysis by the presently available conventional surface analytical tools.

In this paper we present the results of an atom-probe field-ion microscope (FIM)—hereafter called an atom probe—study of solute segregation to stacking faults in Co-0.96 at.% Nb and Co-0.98 at.% Fe alloys. The atom-probe allows us to determine the chemical identity of individual atoms with a mass (m) resolution of ($\Delta m/m$) $\sim 1/200$ [6–9]. In addition, the atom-probe has a lateral atomic resolution for composition (in the surface) of a few angstroms and therefore it is an ideal tool for studying Suzuki segregation. The depth resolution, for chemistry, is equal to the interplanar spacing of the crystallographic region analyzed.

We have determined the temperature dependence of the solute concentration in stacking faults in Co(Nb) and Co(Fe) alloys and analyzed (see Part II) the thermodynamics of segregation in the light of the observations reported in this paper. We believe that this is the first time that the composition of individual stacking faults has ever been *directly* measured. These measurements show that the local concentration of solute atoms is extremely high and that solute-solvent atom interactions in the plane of the stacking fault can lead to the formation of ordered phases within the fault. In particular, we show that there are strong concentration fluctuations ($5\text{--}20 \text{ \AA}$ dia), whose compositions differ significantly from the average fault composition. This leads us to the sug-

gestion that in addition to solute-atom segregation, we have indirect evidence for a disorder-order transformation within the plane of the stacking fault with decreasing temperature. Our preliminary results on Nb segregation in Co-0.96 at.% Nb alloy were reported earlier [10].

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 (h.c.p.) to the face-centered cubic (f.c.c.) phase [11–14]. The transformation is believed to be martensitic (athermal) in character, although there is also a thermal component [12]. The similarity of the f.c.c. and h.c.p. structures is obvious as the atoms in the (111) planes of the f.c.c. structure are arranged in an hexagonal pattern just as the atoms in the (0002) planes of the h.c.p. structure. The only difference between the two phases is the way in which the close-packed layers are stacked. In an h.c.p. metal—the atoms in the second layer are positioned above one set of hollows in the first layer and the atoms in the third layer are directly above the atoms in the first layer; the stacking sequence can be denoted as AB-ABAB, where each letter stands for a close-packed layer. Using Frank's del-nabla notation for describing any stacking sequence [15, 16], the normal hexagonal close-packed structure is expressed as $\Delta\nabla\Delta\nabla\Delta$. The first two atom layers of an f.c.c. metal are arranged in the same way as in the h.c.p. structure, but the atoms of the third layer are placed in the hollows of the second layer in such a way that not until the fourth layer does the stacking sequence begin anew. The f.c.c. lattice, therefore, has the stacking sequence ABCABC, or in Frank's notation by $\Delta\Delta\Delta\Delta$.

A possible explanation of the high density of stacking faults that exists in cobalt-based alloys, lies with the fact that the difference in the Gibbs free energies (ΔG) between the h.c.p. and the f.c.c. phases is very small. Kaufman [17] has calculated the enthalpy (ΔH) and the entropy (ΔS) differences between the h.c.p. and the f.c.c. phases of a number of transition metals. For most of them ΔH and ΔS have different signs which leads to an appreciable value of ΔG — $\Delta G = \Delta H - T\Delta S$. For Co the quantities ΔH and ΔS have the same sign and thus the value of ΔG is small compared to other metals; e.g. at 450°C it is equal to $7.0 \times 10^{-4} \text{ eV atom}^{-1}$. Thus, the isothermal portion of the h.c.p. $\rightarrow$ f.c.c. phase transformation is extremely sluggish and it is difficult to obtain an absolutely pure h.c.p. or f.c.c. phase.

There are three types of stacking faults in the h.c.p. structure that do not disturb first and second nearest-neighbor packing. The stacking sequence for each type of fault and their corresponding Frank's notation is given below:

- (i) 1 Δ intrinsic—ABAB|CBC ($\Delta\nabla\Delta\Delta\nabla\Delta$)
- (ii) 2 Δ intrinsic—ABAB|CAC ($\Delta\nabla\Delta\Delta\Delta\nabla$)
- (iii) 3 Δ extrinsic—ABABCABA ($\Delta\nabla\Delta\Delta\Delta\Delta\nabla$).

It is expected that the stacking fault energy (γ) in h.c.p. metals follows the sequence $\gamma_{1\Delta} < \gamma_{2\Delta} < \gamma_{3\Delta}$ [18]. In the case of Co the stacking fault energy is in the range $15 \text{ erg cm}^{-2} = 15 \text{ mJ m}^{-2}$ ($5.2 \text{ meV atom}^{-1}$) to $27 \pm 4 \text{ mJ m}^{-2}$ ($9.4 \text{ meV atom}^{-1}$) [4].

Experimental observations also indicate the presence of both intrinsic and extrinsic stacking faults in Co and Co-based alloys; their relative frequency of occurrence depends on the specimen's thermal history [12, 14]. At temperatures close to the f.c.c. $\rightleftharpoons$ h.c.p. transformation the frequency of occurrence of 1 Δ intrinsic stacking faults is ~ 10 times greater than of 2 Δ intrinsic stacking faults and approximately the same as that of the 3 Δ extrinsic stacking faults. It was not found possible, in the FIM images, to distinguish among the contrast effects produced by different types of stacking faults. Hence we use the term stacking fault in a global sense.

We now briefly outline the material presented in this paper. First, the experimental details, i.e. specimen preparation, heat treatment of the alloys and the parameters used during the atom-probe analyses are presented. Then we describe the principle of the experiment. In particular, the contrast effects due to stacking faults and the basic ideas involved in chemically analyzing a stacking fault by the atom probe are considered. Finally, we present in great detail the experimental results on solute atom segregation effects to stacking faults.

2. EXPERIMENTAL

2.1. Specimen preparation

Wire specimens of Co–0.96 at.% Nb and Co–0.98 at.% Fe alloys with a diameter of 0.375 and 0.254 mm, respectively, were fabricated at the General Electric Research Laboratory (Schenectady, New York). Atomic absorption spectroscopy analysis was performed on these alloys and the nominal compositions were found to be Co–0.96 at.% Nb and Co–0.98 at.% Fe, respectively. The analyses were executed in the laboratory of Professor G. H. Morrison of the Chemistry Department at Cornell University. The wire was cut into 8.0 cm long specimens and these were encapsulated under vacuum (10^{-6} torr), prior to annealing treatments, in quartz capsules.

Sharply-pointed FIM specimens were prepared by a two-step polishing procedure. The first step consisted of electroetching 12 mm long wires of the original diameter in a chromic acid:water solution (3:10 by

volume) at 6 Vac, until the diameter was reduced to ~ 0.125 mm. Typically, it took 6 min of etching for a Co–0.96 at.% Nb and 4 min for a Co–0.98 at.% Fe alloy to reach this diameter; a stainless-steel counter-electrode was employed. Next the thinned wires were inserted in an FIM specimen holder and sharpened to a needle-like FIM tip (an initial radius of ~ 50 – $100 \text{ \AA}$) by electroetching in a freshly-made hydrochloric acid:water solution (1:10 by volume) at room temperature at a potential of 3.2 Vac—also employing a stainless steel counter-electrode. Normally a tip having the desired radius was obtained by dipping a 6 mm length of the specimen into the solution and then electroetching away 3 mm length of the specimen. Occasionally, certain specimens could not be polished to the desired radius by this technique. In order to overcome this problem the electroetching procedure was continued with the application of short (~ 0.5 s) voltage pulses of magnitude 1.0–5.0 Vac, until a satisfactory sharpness was achieved. A good specimen had the appearance of a well-sharpened pencil when examined with an optical microscope at a magnification of $400\times$. The initial end form of the electroetched tip was extremely rough on an atomic scale. An atomically smooth end form was obtained by a combination of dc and pulse field-evaporation.

2.2. Heat treatment of Co–0.96 at.% Nb and Co–0.98 at.% Fe alloys

The as-received wires were in a cold-worked state and FIM images of specimens prepared from these wires exhibited an extremely high stacking fault density ($> 10^{11} \text{ cm}^{-2}$); most of these stacking faults had been produced by the plastic deformation associated with the wire drawing process.

A heat treatment was 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 solute atoms on each stacking fault.

The thermal treatments which achieved these goals are summarized in Table 1. At the lowest temperature the value of the root-mean-square diffusion distance $(\bar{x}^2)^{1/2}$ was equal to one-half the distance between two stacking faults. An estimate of the integrated number of jumps during a quench (Appendix A) demonstrates that an *upper* limit to the corresponding value of $(\bar{x}^2)^{1/2}$ is $< 1 \text{ \AA}$; therefore, no redistribution of solute atoms occurred during the quench. Our specimens were *not* in a *global* thermodynamic equilibrium state, as we were unable to obtain h.c.p. stacking faults in the f.c.c. matrix for the annealing times at the T_a 's employed. That is, we studied solute atom segregation effects to stacking faults in an h.c.p. matrix. However, our diffusion calculations (Table 1) indicated that the stacking faults were probably in *local* thermodynamic equilibrium. The values of $(\bar{x}^2)^{1/2}$ were large enough for the stacking faults to

have come into thermodynamic equilibrium with the volume surrounding them; i.e. with their solute reservoirs†. It is important to note that the solute concentration in both alloys was below the solid solubility limit at all values of T_a [19].

2.3. Chemical analyses of the stacking faults

The atom-probe FIM was used to chemically analyze the stacking faults. This technique has been described in great detail elsewhere [6–9]. The analyses were performed at a background pressure of 4×10^{-10} torr 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 were able to obtain good agreement between the nominal solute composition, and the solute concentration as determined by the atom-probe technique for both alloys [20].

3. PRINCIPLE OF THE EXPERIMENT

3.1. FIM contrast effects due to stacking faults

The first-order contrast effects expected from stacking faults in FIM images can be understood using purely geometrical considerations. A schematic diagram of the region surrounding a pole of an FIM specimen from a perfect crystal is shown in Fig. 1(a). This region conforms to a smoothly curved surface. The size of the consecutive crystal planes constituting this region is limited by this surface. The pole is characterized by a unit normal $\mathbf{n}$. For the close-packed planes only the atoms at the plane ledges protrude enough to give rise to an image, therefore the projected image of this region consists of a series of concentric circles as shown in Fig. 1(b).

A schematic diagram of an FIM specimen which contains a single stacking fault is shown in Fig. 1(c) and (d). Figure 1(c) is a section through a pole of an FIM specimen, while Fig. 1(d) shows the contrast effect expected in the FIM image due to the presence of a stacking fault. The displacement in the stacking fault plane is characterized by the shear vector ($\mathbf{R}$). The magnitude of $|\mathbf{R}|$ is the same everywhere on the surface of the stacking fault. The intersection of the stacking fault with the surface of the tip produces an atomic step. The vertical height of this step is given by the dot product of $\mathbf{R}$ and the unit normal $\mathbf{n}$ to the crystallographic plane which the stacking fault intersects.

$$\mathbf{R} \cdot \mathbf{n} = qd_{HKL},$$

Table 1. A summary of the annealing temperatures (T_a), annealing times and of calculated values of the root-mean-square diffusion distances $(x^2)^{1/2}$ for the dilute cobalt alloys

Annealing temperature T_a (°C)	Annealing time (days)	Root-mean-square diffusion distance $(x^2)^{1/2}$ (Å)
575	2	530
550	9	650
525	14	450
500	14	245
450	21	80

where $q = HU + KV + LW$ and d_{HKL} is the interplanar distance of the plane which the stacking fault intersects; (HKL) and $[UVW]$ are the Miller indices of the plane and the direction in a three-axis hexagonal system. The index i is simply the sum of the first two indices, i.e. $i = -(H + K)$. In a four-axis hexagonal system the Miller–Bravais indices for the planes ($hkil$) are the same as in a three-axis system, i.e. $h = H$, $k = K$ and $l = L$, whereas for the directions the relationship between the two systems is given by $U = 2u + v$, $V = u + 2v$ and $W = w$. The various axial systems used to describe crystals with hexagonal symmetry are given by Otte and Crocker [21]. When the indices for planes and directions are specified with respect to the four-axis hexagonal system, the value of q is equal to $q = (2u + v)h + (u + 2v)k + lw$. Since u, v and w are not necessarily integers, the quantity q need not be an integer. If the vertical height of an atomic step 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 horseshoe-like appearance. The stacking fault is *invisible* when the

Fig. 1. (a) A cross-sectional view of a single pole on the surface of a perfect FIM tip which is characterized by a unit normal $\mathbf{n}$. (b) A projected FIM image of the pole shown in Fig. 1(a). Since for close-packed planes only the atoms at the plane ledges give rise to an image, it consists of a series of concentric rings. (c) A cross-sectional view of a single pole on the surface of an FIM tip which is intersected by a stacking fault; the fault is characterized by a constant shear vector $\mathbf{R}$. An atomic step is formed on the surface as a result of the presence of the stacking fault. (d) Contrast effect produced in the FIM image by a stacking fault when it intersects the surface of the tip. Note the horse-shoe like appearance of the atomic planes.

†In the case of the Co–0.98 at. % Fe annealed at 450 °C this may not be correct.

vertical height of a step is equal to an integral number of interplanar spacings. Consider an f.c.c. stacking fault in the h.c.p. matrix lying on an (0002) plane with $R = \frac{1}{3}$ [01 $\bar{1}$ 0] and intersecting the (01 $\bar{1}$ 0) plane. The value of $q = \frac{2}{3}$ and, therefore, step heights of $\frac{2}{3}d_{01\bar{1}0}$ and $\frac{1}{3}d_{01\bar{1}0}$ are expected during the field-evaporation dissection of a specimen. When, on the other hand, the same fault intersects the ($\bar{1}$ 2 $\bar{1}$ 0) plane the value of $q = 1$, which means that the step height is equal to $d_{\bar{1}2\bar{1}0}$. Therefore, the stacking fault should be visible in the FIM image when it intersects the (01 $\bar{1}$ 0) plane, but it should be invisible when it intersects the ($\bar{1}$ 2 $\bar{1}$ 0) plane.

When the stacking fault is inclined to the tip axis its trace shifts during the field-evaporation process. Whereas when the stacking fault is perpendicular to the tip axis the trace is always a circle that is concentric with this axis.

3.2. Atom-probe FIM analyses of stacking faults

A schematic diagram illustrating the basic ideas involved in chemically analyzing a stacking fault by the atom probe is shown in Fig. 2(a) and (b). The stacking fault, which is parallel to the axis of the tip, is shown with a number of solute atoms residing in its plane. The specimen was rotated, employing the goniometer stage, in such a way that the center of the probe hole in the image intensification system was aligned over the stacking fault. Each atomic plane was dissected by the application of a series of field-evaporation pulses. Typically 5×10^3 pulses were employed to evaporate a plane containing approx

100 atoms. The field evaporated ions which had trajectories that took them through the probe hole, in the image intensification system, were focused onto the Chevron detector with the aid of an Einzel lens. The distance of the image intensification system from the FIM tip (δ) was adjusted so that the diameter of the cylinder analyzed (D_a) was ~ 30 – 50 Å. The mass-to-charge ratios of all the atoms—both Co and Nb, or Co and Fe—in this cylinder were determined by the atom-probe technique.

To obtain the composition of the analyzed cylinder of alloy the cumulative number of Nb or Fe events is plotted vs the cumulative number of either Nb plus Co or Fe plus Co events—such a plot is called an *integral profile*. The *average* slope of this plot corresponds to the *average* solute composition $\langle c_s' \rangle_u$ of the volume analyzed, where the superscript and subscript f and s , stand for stacking fault and solute species (Nb or Fe), respectively, and the subscript u on the bracket means an uncorrected value. The value of $\langle c_s' \rangle_u$ is a *lower limit* to the *actual* solute concentration in the stacking fault $\langle c_s' \rangle^*$. The detailed relationship between $\langle c_s' \rangle$ and $\langle c_s' \rangle^*$ is discussed in the following paper [22]. In order to determine the solute composition in a region adjacent to a stacking fault plane the FIM tip was rotated in such a way that the edge of the analyzed cylinder was at a small distance λ (Å) away from the fault—see the schematic diagrams shown in Fig. 2(c) and (d).

The basic limitation on the value of D_a is due to the fact that the acceptance angle of the probe hole is determined by the physical dimensions of the atom

Fig. 2. (a) and (b) Schematic diagram illustrating the basic ideas involved in analyzing a stacking fault by atom-probe field-ion microscopy. (c) and (d) Schematic diagram illustrating the basic ideas involved in analyzing a cylinder of alloy which is λ Å away from the stacking fault.

probe. It has been shown by Macrander *et al.* [23] that the number of ions detected during the atom-probe analysis is *inversely* proportional to δ^2 ; therefore, even though D_a is smaller at larger values of δ , the statistics of the atom-by-atom dissection are poorer. The different methods employed to determine a value of D_a are discussed in Appendix B.

4. EXPERIMENTAL RESULTS

4.1. Field-ion microscopy of Co-0.96 at.% Nb and Co-0.98 at. % Fe alloys

A typical FIM image obtained from the as-received wires, which were in a cold-worked state, is shown in Fig. 3. This micrograph was recorded at the specimen temperature (T_s) equal to 45 K, employing neon as an imaging gas (4×10^{-5} torr gauge pressure). Note that the density of stacking faults, which are identified from the stepped-ring or horseshoe contrast effect, is extremely high ($> 10^{11} \text{ cm}^{-2}$) in these specimens. It is impossible to determine either the crystal structure or the orientation of the specimen from the micrograph. Because of this high stacking-fault density, the FIM tips prepared from the as-received wires often failed catastrophically prior to their being fully developed. The same imaging conditions, as the ones used for the tips prepared from the as-received wires, were employed for both the Co-0.96 at.% Nb and Co-0.98 at.% Fe alloys.

While developing a thermal treatment to produce a reasonable stacking fault density—i.e. a few faults in the 10^{-10} cm^2 field-of-view—we observed FIM images of various orientations of both the f.c.c. and h.c.p. phases, as well as partially transformed specimens of Co-0.96 at.% Nb and Co-0.98 at.% Fe alloys. Typical FIM images from perfect h.c.p. and f.c.c. crystals are shown in Figs 4 and 5. No stacking faults are seen in these micrographs. Figure 4 is an [0002]-oriented crystal of the h.c.p. phase of a Co-0.96 at.% Nb alloy. This specimen had been annealed at 900°C for 18 days and then aged at 380°C for 7 days. Figure 5 is a [111]-oriented crystal of the f.c.c. phase of a Co-0.96 at.% Nb alloy. This specimen had been annealed at 900°C for 18 days.

Figure 6 exhibits a partially transformed f.c.c. crystal of a Co-0.96 at.% Nb alloy. The central portion of the micrograph contains a fully-ordered region having three-fold symmetry; while the outer region of the image appears somewhat disordered—indicating that the specimen had only partially transformed. This specimen had been annealed at 900°C for 7 days. The h.c.p.→f.c.c. transformation is very sluggish, even at 900°C; this is consistent with the idea that there is a thermal component to this allotropic transformation. In the case of the Co-0.96 at.% Nb alloy the reaction h.c.p.→f.c.c. occurs at 365°C, while the reverse transformation f.c.c.→h.c.p. takes place at 255°C [19]. Whereas for the Co-0.98 at.% Fe alloy the transition temperatures are equal to 390°C

Fig. 3. An FIM micrograph of an as-received Co-0.96 at. % Nb alloy. Note that the density of stacking faults, which are identified from the stepped ring contrast effect, is extremely high ($> 10^{11} \text{ cm}^{-2}$) in these specimens.

for the h.c.p.→f.c.c. transformation and 345°C for the f.c.c.→h.c.p. transformation [19].

Figure 7 exhibits an image of an [01 $\bar{1}$ 1]-oriented crystal of the h.c.p. phase of the Co-0.96 at.% Nb alloy. This specimen had been annealed at 450°C for 21 days. Note the presence of at least two stacking faults in the field-of-view, which are separated by a distance of about 20 Å. The characteristic horseshoe-like contrast effect is clearly visible in the (01 $\bar{1}$ 0) plane. The stacking faults are f.c.c. in an h.c.p. matrix and lie on (111) planes. The plane of the fault was verified by standard crystallographic procedures.

The FIM images show *no* evidence of precipitation on the faults. However, there is “bright spot” decoration of some of the faults. These “bright spots” may be interpreted as niobium atoms, but stacking faults in pure cobalt also exhibit this same “bright spot” decoration effect. Therefore, it is extremely dangerous to determine chemistry based solely on the presence of “bright spots” [24]. It is interesting to note that even though the composition measured, with the atom probe, for different faults is approximately the same, we found that some faults were decorated with a large number of “bright spots” along their traces, while others were not decorated at all. This observation indicates that the mechanism for imaging solute atoms on stacking faults is a function of the crystallographic plane(s) which the fault intersects.

A field evaporation sequence through the (01 $\bar{1}$ 1) plane is exhibited in Fig. 8. A series of 12 FIM micrographs out of the 104 recorded during the atom-by-atom dissection of the tip is shown. A schematic diagram of the plane and the traces of the two stacking faults are given below each FIM micrograph. To simplify the understanding of the contrast

Fig. 4. An FIM micrograph of an [0002]-oriented h.c.p. crystal of a Co-0.96 at.% Nb alloy. The specimen had been annealed at $T_a = 900^\circ\text{C}$ for 18 days and then aged at 380°C for 7 days. No stacking faults are present in the field-of-view.

effects produced by the two stacking faults intersecting the surface, a schematic diagram of an FIM specimen which contains the two faults is shown in Fig. 9. Figure 9(a) is a cross-section through a pole of an FIM tip, while Fig. 9(b) shows the contrast effects expected in the FIM image. The first frame in Fig. 8 shows an (011) plane with the diameter of the topmost ledge at its maximum size; i.e. right after the

preceding plane had been completely field evaporated. The planes on the bottom side of the first stacking fault trace are sheared up relative to those on the top side of the trace and sheared down relative to the planes which are on the bottom of the second stacking fault trace (Fig. 9). The process of field evaporation first removes the planes which are above the first stacking fault trace (frame 67), then it removes planes which are below the trace of the

Fig. 5. An FIM micrograph of a [111]-oriented f.c.c. crystal of a Co-0.96 at.% Nb alloy. The specimen had been annealed at $T_a = 900^\circ\text{C}$ for 18 days. No stacking faults are present in the field-of-view.

Fig. 6. An FIM micrograph of a partially-transformed f.c.c. crystal of a Co-0.96 at.% Nb crystal. The specimen had been annealed at $T_a = 900^\circ\text{C}$ for 7 days.

Fig. 7. An FIM micrograph of a $[01\bar{1}1]$ -oriented crystal of the h.c.p. phase of a Co-0.96 at.% Nb alloy. The specimen had been annealed at $T_a = 450^\circ\text{C}$ for 21 days. Arrows point to two stacking faults in the field-of view. A characteristic horseshoe-like contrast effect is clearly visible.

second stacking fault (frame 81), and finally it removes the planes above the trace of the first stacking fault (frame 104).

Cobalt is a non-refractory metal and, therefore, the rate at which the FIM tips failed during imaging was quite high. Very frequently, however, a phenomenon illustrated in Fig. 10 was observed in our study of cobalt-based alloys. When the FIM specimen shown in Fig. 5—a perfect f.c.c. crystal—was field-evaporated, an abrupt change in the FIM pattern occurred; in this particular case the change occurred at $V_{d.c.}$ equal to 12.5 kV. Figure 10 shows the same tip after $V_{d.c.}$ was raised to 14.4 kV—no field-evaporation occurred during this voltage increase. Note the presence of an extremely high stacking fault density, in the field-of-view, after the abrupt change had occurred in the FIM pattern. We want to emphasize that the effect just described was very common during our study of both Co-0.96 at.% Nb and Co-0.98 at.% Fe alloys. One possible mechanism for the observed phenomenon is based on the fact that the specimens had a mixture of the f.c.c. and h.c.p. phases, and the tip may have yielded along the interphase interface under the influence of the mechanical shear stresses associated with the electric evaporation-field. The difficulty of obtaining a single-phase specimen of cobalt or cobalt-based alloys has been demonstrated by a number of experimental techniques; e.g. transmission electron microscopy

Fig. 8. A pulse field-evaporation sequence through a $(01\bar{1}1)$ plane. Twelve micrographs out of a sequence of 104 frames of ciné film are shown. The traces due to two stacking faults are indicated by arrows. A schematic diagram of the situation is indicated below each diagram.

Fig. 9.(a) A cross-sectional view of a single pole on the surface of an FIM tip which is intersected by two stacking faults. (b) Contrast effect produced in the FIM image by two stacking faults when they intersect the surface of the tip.

[14], X-rays [12] and nuclear magnetic resonance [13]. The specimens almost always contained a mixture of f.c.c. and h.c.p. phases; the relative amounts were a function of T_a and annealing time.

4.2. Atom-probe field-ion microscopy of Co-0.96 at.% Nb and Co-0.98 at.% Fe alloys

Typical mass spectra—number of events vs the mass-to-charge ratio—for Co-0.96 at.% Nb and Co-0.98 at.% Fe alloys have been published elsewhere [10, 20]. We discovered during a series of detailed control experiments that the measured solute concentration is a function of both f and T_s for a fixed pulse frequency (60 Hz)—with the average number of ions per pulse in the range 0.01–0.05. Under certain experimental conditions quite opposite behavior was observed in these alloys—*preferential field-evaporation* of solute atoms in the Co-0.98 at.% Fe alloy and *preferential retention* of solute atoms in the Co-0.96 at.% Nb alloy occurred. The correct solute concentrations were obtained by using the following experimental parameters: (1) T_s of less than or equal to 60 K; and (2) f of greater than, or equal to 0.10 [20].

4.3. Atom-probe FIM results on solute segregation to stacking faults in Co-0.96 at.% Nb and Co-0.98 at.% Fe alloys

4.3.1. Co-0.96 at.% Nb alloy. The Nb concentration in the stacking faults was measured for specimens which had been equilibrated at 450, 525 and

575 C. Also the Nb composition in a region adjacent to stacking faults ($\lambda = 3$ and 4 Å)—see Figs 2(c) and (d) as well as in a region far away (~ 150 Å) from the faults was determined. A summary of all the results for the Co-0.96 at.% Nb alloy is given in Tables 2 and 3.

The composition of the analyzed cylinder of alloy was determined from the slope of the integral profile. The Nb integral profiles are presented in Figs 11–18. The approximate depth scale is indicated on the top of horizontal axis of each integral profile. The *smallest* vertical step corresponds to the detection of *one* Nb event. For a cylinder of alloy which contained a stacking fault the *average* slope of the integral profile yields the value of $\langle c_{\text{Nb}}^f \rangle_u$, whereas for a cylinder of alloy which did *not* contain a stacking fault the average slope gives the value of the bulk Nb composition $\langle c_{\text{Nb}} \rangle$. For specimens which had been equilibrated at $T_u = 450$ C the values of $\langle c_{\text{Nb}}^f \rangle_u$ for three different stacking faults (SF1, SF2 and SF3) are equal to 2.85 ± 0.17 , 3.09 ± 0.55 and 3.34 ± 0.35 at.% Nb—see Figs 11, 13 and 14. The integral profile from SF3 consists of two distinct regimes of composition 3.34 ± 0.35 and 1.55 ± 0.14 at.% (Fig. 14). The composition in the first regime corresponds to $\langle c_{\text{Nb}}^f \rangle_u$. The Nb concentration in the second regime is greater than $\langle c_{\text{Nb}} \rangle$ and less than $\langle c_{\text{Nb}}^f \rangle_u$. This can be explained as follows. At the completion of the experiment it was observed that this stacking fault, although aligned over the probe hole, was not positioned over the *center* of the probe hole. Apparently the fault was slightly inclined to the tip axis and had shifted during the field-evaporation process. This implied that some of the atoms located in the stacking fault plane didn't have trajectories that passed through the probe hole. The values of the corrected Nb concentration $\langle c_{\text{Nb}}^f \rangle^*$ for SF1, SF2 and SF3 are equal to 28.8 ± 1.9 , 30.5 ± 0.5 and 30.6 ± 2.1 at.%

Fig. 10. An FIM image of a Co-0.96 at.% Nb alloy after the tip, shown in Fig. 5, had yielded under the influence of the mechanical shear stresses produced by the electric evaporation-field.

Table 2. Summary of the results on a Co-0.96 at.% Nb alloy

Run number	Region analyzed	Annealing temperature T_a (°C)	Number of atoms detected		Uncorrected measured Nb concentration† $\langle c'_{Nb} \rangle_u$ (at.%)	Corrected Nb concentration $\langle c'_{Nb} \rangle$ (at.%)	Diameter of the analyzed cylinder† D_a (Å)
			Co	Nb			
1	SF1	450	9346	274	2.85 ± 0.17	28.8 ± 7.9	52
2	$\lambda = 150 \text{ Å}$ from SF1	450	1678	16	0.94 ± 0.24	—	47
3	SF2	450	1003	32	3.09 ± 0.55	30.5 ± 0.5	49
4	SF3	450	2578	89	3.34 ± 0.35	30.6 ± 2.1	44
5	SF4	525	1161	20	1.69 ± 0.38	12.8 ± 0.5	53
6	SF5	525	3224	57	1.74 ± 0.23	9.9 ± 0.1	38
7	$\lambda = 4 \text{ Å}$ from SF5	525	4196	38	0.90 ± 0.15	—	36
8	SF6	525	2744	46	1.65 ± 0.24	11.0 ± 0.8	51
9	SF7	575	3453	47	1.34 ± 0.20	7.3 ± 0.2	52
10	$\lambda = 3 \text{ Å}$ from SF7	575	3282	30	0.91 ± 0.17	—	51

†The uncertainty is equal to the ratio of the square root of the number of Nb atoms to the total number of Co plus Nb atoms.

‡This value of D_a is the average value calculated by the first two methods described in Appendix B.

Table 3. A summary of the results on the composition of solute-rich fluctuations in a Co-0.96 at.% Nb alloy

Stacking fault	Annealing temperature T_a (°C)	Uncorrected Nb concentration of the fluctuation $\langle c'_{Nb} \rangle_{u,fl}$ (at.%)	The size of the fluctuation l (Å)	Corrected Nb concentration of the fluctuation $\langle c'_{Nb} \rangle^*_{fl}$ (at.%)	
				Lower limit†	Upper limit‡
SF4	525	3.43 ± 1.40	7	37.5 ± 1.4	—§
		3.55 ± 1.45	7	39.3 ± 1.5	—§
		3.21 ± 1.43	6	34.1 ± 1.3	—§
SF5	525	3.55 ± 0.95	13	29.1 ± 0.3	72.6 ± 0.4
SF6	525	3.20 ± 0.72	17	31.1 ± 2.2	78.0 ± 2.5
SF7	575	2.19 ± 0.61	16	19.6 ± 0.8	46.5 ± 1.7
		2.64 ± 0.61	22	26.0 ± 1.0	50.9 ± 2.0

†This value is calculated by taking the shape of the fluctuation to be a rectangle whose dimensions are $l \times D_a$.

‡This value is calculated by taking the shape of the fluctuation to be a square with dimensions $l \times l$.

§In this case the values of $\langle c'_{Nb} \rangle^*_{fl}$ are greater than 100%. This implies that the actual dimensions of these fluctuations are greater than $l \times l$.

Nb, respectively. Thus at 450°C the stacking faults have a stoichiometry which is approximately Co_2Nb .

Three different stacking faults (SF4, SF5 and SF6) were also chemically analyzed in specimens which had been annealed at $T_a = 525^\circ\text{C}$; their corresponding Nb integral profiles are given in Figs 15–17. The

values of $\langle c'_{Nb} \rangle_u$ in this case are equal to 1.69 ± 0.38 , 1.74 ± 0.23 and 1.65 ± 0.24 at.% Nb. The corresponding values of $\langle c'_{Nb} \rangle^*$ are equal to 12.8 ± 0.5 , 9.9 ± 0.1 and 11.0 ± 0.8 at.% Nb.

Note the presence of local solute fluctuations in some of the Nb integral profiles. Three such

Fig. 11. The Nb integral profile for a cylinder of alloy which contained a stacking fault (SF1): $\langle c'_{Nb} \rangle_u = 2.85 \pm 0.17$ at.% Nb—this value is a lower limit to the actual Nb composition at a stacking fault (see text). This specimen had been annealed at $T_a = 450^\circ\text{C}$ for 21 days.

Fig. 12. The Nb integral profile for a region 150 Å away from a stacking fault (SF1): $\langle c'_{Nb} \rangle = 0.94 \pm 0.24$ at.% Nb. This value is in good agreement with the atom-probe determinations of the same quantity for specimens which did not contain any stacking faults in the field-of-view.

Fig. 13. The Nb integral profile for a cylinder of alloy which contained a stacking fault (SF2): $\langle c_{\text{Nb}}^f \rangle_u = 3.09 \pm 0.55$ at. % Nb. The specimen had been annealed at $T_a = 450^\circ\text{C}$ for 21 days.

Fig. 14. The Nb integral profile for a cylinder of alloy which contained a stacking fault (SF3): $\langle c_{\text{Nb}}^f \rangle_u = 3.34 \pm 0.35$ at. % Nb. The specimen had been annealed at $T_a = 450^\circ\text{C}$ for 21 days. See text for an explanation of the two regimes.

Fig. 15. The Nb integral profile for a cylinder of alloy which contained a stacking fault (SF4): $\langle c_{\text{Nb}}^f \rangle_u = 1.69 \pm 0.38$ at. % Nb. Note the presence of local solute fluctuations; $\langle c_{\text{Nb}}^f \rangle_{u,ls} = 3.43 \pm 1.40, 3.55 \pm 1.45$ and 3.21 ± 1.43 at. % Nb. This specimen had been annealed at $T_a = 525^\circ\text{C}$ for 14 days.

Fig. 16. The Nb integral profiles for: (1) a cylinder of alloy which contained a stacking fault (SF5); and (2) a region 4 Å away from a stacking fault (SF5)— $\langle c_{\text{Nb}}^f \rangle_u = 1.74 \pm 0.23$ at. % Nb and $\langle c_{\text{Nb}}^f \rangle_u = 0.90 \pm 0.15$ at. % Nb. Note the presence of a local solute fluctuation in (1); $\langle c_{\text{Nb}}^f \rangle_{u,ls} = 3.55 \pm 0.95$ at. % Fe. This specimen had been annealed at $T_a = 525$ for 14 days.

fluctuations are indicated in Fig. 15 (SF4); the values of the *uncorrected* Nb concentration in these fluctuations ($\langle c_{\text{Nb}}^f \rangle_{u,ls}$)—where the subscript is on the bracket stands for a solute rich island—are equal to $3.43 \pm 1.40, 3.55 \pm 1.45$ and 3.21 ± 1.43 at. % Nb. Table 3 lists all the information concerning these localized solute fluctuations. That is, their size in one dimension (l) and their corrected Nb compositions ($\langle c_{\text{Nb}}^f \rangle_u$). We have listed upper and lower limits to $\langle c_{\text{Nb}}^f \rangle_{u,ls}$. The lower limit is calculated by taking the shape of the fluctuation to be a rectangle whose dimensions are $l \times D_a$. The upper limit is calculated by taking the shape of the fluctuation to be a square with dimensions $l \times l$.

Fig. 17. The Nb integral profile for a cylinder of alloy which contained a stacking fault (SF6): $\langle c_{\text{Nb}}^f \rangle_u = 1.65 \pm 0.24$ at. % Nb. Note the presence of a local solute fluctuation; $\langle c_{\text{Nb}}^f \rangle_{u,ls} = 3.20 \pm 0.72$ at. % Nb. The specimen had been annealed at $T_a = 525^\circ$ for 14 days.

Fig. 18. The Nb integral profiles for: (1) a cylinder of alloy which contained a stacking fault (SF7); and (2) a region 3 Å away from a stacking fault (SF7)— $\langle c'_{\text{Nb}} \rangle_u = 1.34 \pm 0.20$ at. % Nb and $\langle c_{\text{Nb}} \rangle = 0.91 \pm 0.17$ at. % Nb. Note the presence of local solute fluctuations in (1); $\langle c'_{\text{Nb}} \rangle_{u,is} = 2.19 \pm 0.61$ and 2.64 ± 0.61 at. % Nb. This specimen had been annealed at $T_a = 575^\circ\text{C}$ for 14 days.

Finally, $\langle c'_{\text{Nb}} \rangle_u$ for a fault (SF7) was obtained in a specimen equilibrated at $T_a = 575^\circ\text{C}$ —it was deduced from Fig. 19 and is equal to 1.34 ± 0.20 at. % Nb. The corresponding value of $\langle c'_{\text{Nb}} \rangle^*$ is equal to 7.3 ± 0.2 at. % Nb. This profile also contains local solute fluctuations whose values of $\langle c'_{\text{Nb}} \rangle_{u,is}$ are equal to 2.19 ± 0.61 and 2.64 ± 0.61 at. % Nb. The upper and lower limits to $\langle c'_{\text{Nb}} \rangle_u^*$ are listed in Table 4 for SF7.

The fact that at $T_a = 450, 525$ and 575°C the values $\langle c'_{\text{Nb}} \rangle_u$ are greater than $\langle c_{\text{Nb}} \rangle$ by factors of 3.0, 1.7 and 1.3, respectively, and the value of $\langle c'_{\text{Nb}} \rangle^*$ are greater than $\langle c_{\text{Nb}} \rangle$ by factors of 30, 12 and 7 clearly indicates that Nb atoms segregate to stacking faults in a Co-0.96 at. % Nb alloy.

For specimens annealed at $T_a = 450^\circ\text{C}$ the Nb composition in a cylinder 150 Å away from the fault is equal to 0.94 ± 0.24 at. % Nb (Fig. 13). The Nb concentration in a cylinder immediately adjacent to stacking faults— $\lambda = 3$ or 4 Å—is equal to 0.91 ± 0.17 and 0.90 ± 0.15 at. % Nb, for specimens equilibrated at $T_a = 575$ and 525°C , respectively (Figs 22, 24).

Fig. 19. The Fe integral profile for a cylinder of alloy which contained a stacking fault (SF8): $\langle c'_{\text{Fe}} \rangle_u = 1.72 \pm 0.18$ at. % Fe. The specimen had been annealed at $T_a = 450^\circ\text{C}$ for 21 days.

These values of the Nb composition are in good agreement with $\langle c_{\text{Nb}} \rangle$.

Recent theoretical calculations by Simon *et al.* [25] of the interaction energies between a single transition element solute atom and a stacking fault, in compact transition metals, indicate that this interaction is very short ranged—it is typically zero at two to three (111) interplanar spacings. Also, Williams and Nason [26] have shown that the surface composition of an alloy approaches the bulk composition within a few atomic planes. The experimental Nb concentration values for $\lambda = 3$ or 4 Å indicate that the Nb concentration profile is falling off very quickly with distance—certainly within less than 4 Å from the plane of the fault the concentration is $\langle c_s \rangle$. These results in combination with the above theoretical calculations suggest that Nb segregation is most likely confined to the plane of the fault (see Part II).

The presence of local Nb fluctuations in the integral profiles for $T_a = 525$ and 575°C (SF5, SF6, SF7) indicates the existence of small Nb-rich regions (~ 5 – 20 Å diameter)† in the plane of the stacking fault whose composition differs strongly from $\langle c'_{\text{Nb}} \rangle^*$. These large Nb fluctuations do not exist at

Table 4. Summary of the results on a Co-0.98 at. % Fe alloy

Run number	Region analyzed	Annealing temperature $T_a(^{\circ}\text{C})$	Number of atoms detected		Uncorrected measured Nb concentration† $\langle c'_{\text{Fe}} \rangle_u$ (at.%)	Corrected Nb concentration $\langle c'_{\text{Fe}} \rangle^*$ (at.%)	Diameter of the analyzed cylinder‡ $D_a(\text{\AA})$
			Co	Fe			
1	SF8	450	5328	93	1.72 ± 0.18	9.6 ± 0.5	40
2	$\lambda = 2 \text{ \AA}$ from SF8	450	1145	12	1.04 ± 0.30	---	41
3	SF9	500	2955	43	1.43 ± 0.22	5.8 ± 0.2	33
4	$\lambda = 3 \text{ \AA}$ from SF9	500	4414	40	0.90 ± 0.14	---	38
5	SF10	500	3204	45	1.38 ± 0.21	6.9 ± 0.2	51
6	SF11	575	5155	64	1.22 ± 0.15	4.2 ± 0.2	46
7	SF12	575	1987	25	1.24 ± 0.25	4.0 ± 0.3	39

†The uncertainty is equal to the ratio of the square root of the number of Fe atoms to the total number of Co plus Fe atoms.
‡This value of D_a is the average value calculated by the first two methods described in Appendix B.

Table 5. A summary of the results on the composition of solute-rich fluctuations in a Co-0.98 at.% Fe alloy

Stacking fault	Annealing temperature T_a (°C)	Uncorrected Nb concentration of the fluctuation $\langle c'_{Nb} \rangle_{u,rs}$ (at.%)	The size of the fluctuation l (Å)	Corrected Nb concentration of the fluctuation $\langle c'_{Nb} \rangle_u$ (at.%)	
				Lower limit†	Upper limit‡
SF9	500	3.30 ± 0.80	14	22.0 ± 1.2	69.2 ± 1.9
SF10	500	2.77 ± 0.77	14	23.1 ± 1.1	68.5 ± 1.9
SF11	575	2.25 ± 0.52	23	13.7 ± 0.9	30.8 ± 1.4
		2.05 ± 0.68	15	11.9 ± 0.8	36.1 ± 1.0
		2.23 ± 0.56	22	13.9 ± 0.9	31.5 ± 1.2

†This value is calculated by taking the shape of the fluctuation to be a rectangle whose dimensions are l and D_u .

‡This value is calculated by taking the shape of the fluctuation to be a square with dimensions $l \times l$.

450°C, but only become significant at the two elevated temperatures. At 450°C the entire stacking fault has a composition which approaches that of Co₂Nb. In [22] we also show quantitatively, using a statistical theory of fluctuations, that the probability of the occurrence of such large Nb fluctuations, in a random solid solution is *nil*. The physical origin of the Nb-rich fluctuations is most likely the result of a disorder-order transformation—within the stacking fault—as the annealing temperature decreases.

4.3.2. Co-0.98 at.% Fe alloy. The Fe concentration in the stacking faults was measured for specimens equilibrated at 450, 500 and 575°C. Also the Fe composition in a region adjacent to stacking faults ($\lambda = 2$ and 3 Å) was determined. A summary of all the results for the Co-0.98 at.% Fe alloy are given in Tables 4 and 5.

The composition of the analyzed cylinder for this alloy was determined in the same way as for the Co-0.96 at.% Nb alloy; i.e. from the slope of each Fe integral profile. The results are shown in Figs 19–25. For a specimen which had been annealed at $T_a = 450^\circ\text{C}$ the value of $\langle c'_{Fe} \rangle_u$ from SF8 is equal to 1.72 ± 0.18 at.% Fe (Fig. 19). The corresponding value of $\langle c'_{Fe} \rangle^*$ is equal to 9.6 ± 0.5 at.% Fe. Figure 20 shows an integral profile for a cylinder immediately adjacent to SF8 ($\lambda = 2$ Å); the value of 1.04 ± 0.30 at.% Fe is in good agreement with $\langle c_{Fe} \rangle$.

Two stacking faults (SF9 and SF10) were analyzed in specimens which had been equilibrated at $T_a = 500^\circ\text{C}$; the values of $\langle c'_{Fe} \rangle_u$ in this case were deduced from the integral profiles shown in Figs 21 and 22 and are equal to 1.43 ± 0.22 and 1.38 ± 0.21 at.% Fe. The corresponding values of $\langle c'_{Fe} \rangle^*$ are equal to 5.8 ± 0.2 and 6.9 ± 0.2 at.% Fe. The Fe composition for a cylinder immediately adjacent to SF9 is equal to 0.90 ± 0.14 at.% Fe; this value is in good agreement with $\langle c_{Fe} \rangle$. The integral profiles from SF9 and SF10 show the presence of local solute fluctuations; see Table 5 for details.

Finally, for specimens which had been annealed at $T_a = 575^\circ\text{C}$ the values of $\langle c'_{Fe} \rangle_u$ for two different stacking faults (SF11 and SF12) are equal to 1.22 ± 0.15 and 1.24 ± 0.25 at.% Fe (Figs 23 and 26).

The corresponding values of $\langle c'_{Fe} \rangle^*$ are equal to 4.2 ± 0.2 and 4.0 ± 0.3 at.% Fe. The integral profile from SF11 (Fig. 23) has three local solute fluctuations whose values of $\langle c'_{Fe} \rangle_{u,rs}$ are equal to 2.23 ± 0.56 , 2.05 ± 0.68 and 2.25 ± 0.52 at.% Fe; see Table 5 for further details.

The fact that at $T_a = 450, 500$ and 575°C the value of $\langle c'_{Fe} \rangle_u$ is greater than $\langle c_{Nb} \rangle$ by factors of 1.7, 1.4

Fig. 20. The Fe integral profile for a region 2 Å away from a stacking fault (SF8): $\langle c_{Fe} \rangle = 1.04 \pm 0.30$ at.% Fe.

Fig. 21. The Fe integral profiles for: (1) a cylinder of alloy which contained a stacking fault (SF9) and (2) a region 3 Å away from a stacking fault (SF9)— $\langle c'_{Fe} \rangle_u = 1.43 \pm 0.22$ at.% Fe and $\langle c_{Fe} \rangle = 0.90 \pm 0.14$ at.% Fe. Note the presence of a local solute fluctuation in (1); $\langle c'_{Fe} \rangle_{u,rs} = 3.30 \pm 0.80$ at.% Fe. This specimen had been annealed at $T_a = 500^\circ\text{C}$ for 14 days.

†Note that the depth scale is given on the top axis in Figs 11–14.

Fig. 22. The Fe integral profile for a cylinder of alloy which contained a stacking fault (SF10)— $\langle c_{Fe}^I \rangle_u = 1.38 \pm 0.21$ at. % Fe. Note the presence of a local solute fluctuation; $\langle c_{Fe}^I \rangle_{u,ls} = 2.77 \pm 0.77$ at. % Fe. The specimen had been annealed at $T_a = 500^\circ\text{C}$ for 14 days.

and 1.2, respectively, and $\langle c_{Fe}^I \rangle^*$ is greater than $\langle c_{Fe} \rangle$ by factors of 10, 6 and 4 clearly indicates that Fe atoms segregate to stacking faults in the Co-0.98 at. % Fe alloy.

The experimental Fe concentration values for $\lambda = 2$ or $3 \text{ \AA}$ indicate that the Fe concentration profile falls off very rapidly with distance from the plane of the fault. This result in combination with theoretical calculations [25, 26] suggests that Fe segregation is also most likely confined to the plane of the fault (see Part II).

The presence of large local Fe fluctuations in the integral profiles for $T_a = 500$ and 575°C (SF9, SF10, SF11) in the Co-0.98 at. % Fe alloy also indicates the presence of Fe-rich regions ($\sim 20 \text{ \AA}$ dia) in the plane of the stacking fault whose composition differs

Fig. 23. The Fe integral profile for a cylinder of alloy which contained a stacking fault (SF11): $\langle c_{Fe}^I \rangle_u = 1.22 \pm 0.15$ at. % Fe. Note the presence of local solute fluctuations; $\langle c_{Fe}^I \rangle_{u,ls} = 2.23 \pm 0.56$, 2.05 ± 0.68 and 2.25 ± 0.52 at. % Fe. This specimen had been annealed at $T_a = 575^\circ\text{C}$ for 2 days.

strongly from $\langle c_{Fe}^I \rangle^*$. At 500°C $\langle c_{Fe}^I \rangle_u$ approaches the composition of an ordered two-dimensional phase (see Table 5). These large Fe fluctuations do not exist at 450°C , but only become significant at the two elevated temperatures. The fact that $\langle c_{Fe}^I \rangle_u$ at these temperatures is greater than $\langle c_{Fe}^I \rangle^*$ at 450°C indicates that local equilibrium conditions may not have been achieved at 450°C .

5. SUMMARY

(1) The atom-probe FIM has been used to measure solute atom segregation effects to individual stacking faults in Co-0.96 at. % Nb and Co-0.98 at. % Fe alloys. These bulk compositions correspond to values within the primary solid solution phase field for the annealing temperatures employed. No evidence of either precipitation on the stacking faults or in the matrix was observed in the FIM images.

(2) The temperature dependence of the stacking fault composition has been determined in the range 450 – 575°C . The faults were f.c.c in a h.c.p. matrix. Thus, the specimens were not in global thermodynamic equilibrium. However, simple diffusion calculations indicated that the stacking faults were most likely in local thermodynamic equilibrium with the volume surrounding them; i.e. with their solute reservoirs.

(3) The diameter of the analyzed cylinder of alloy was ~ 30 – $50 \text{ \AA}$. It was shown experimentally that solute concentration profile falls off very quickly with distance—within less than $4 \text{ \AA}$ —from the plane of the fault in both alloys. These results in combination with theoretical calculations [25, 26] suggest that Nb or Fe segregation is most likely confined to the plane of the fault (see Part II).

(4) Very strong solute atom segregation effects to individual stacking faults have been observed in both alloys. After due correction for the matrix contribution to the measured composition, the Nb concentrations in the stacking faults in a Co-0.96 at. %

Fig. 24. The Fe integral profile for a cylinder of alloy which contained a stacking fault (SF12): $\langle c_{Fe}^I \rangle_u = 1.24 \pm 0.25$ at. % Fe. The specimen had been annealed at $T_a = 575^\circ\text{C}$ for 2 days.

Nb alloy are greater than the bulk composition by factors of 30, 12 and 7 at the annealing temperatures of 450, 525 and 575 °C.

(5) The corrected Fe concentrations in the stacking faults in the Co-0.98 at.% Fe alloy are greater than the bulk composition by factors of 10, 6 and 4 at the annealing temperatures of 450, 550 and 575 °C.

(6) Local solute composition fluctuations have been observed in the integral profiles in the Co-0.96 at.% Nb alloy at $T_a = 525$ and 575 °C. These fluctuations are due to solute-rich regions (~ 5 –20 Å dia) in the plane of the stacking fault, whose concentration differs significantly from the average fault composition. For the Co-0.96 at.% Nb alloy the corrected composition of these fluctuations approaches that of a two-dimensional ordered phase. The corrected composition of the stacking faults at 450 °C is close to that of Co_2Nb . This suggests that in addition to solute-atom segregation, we also have evidence for a disorder-order transformation within the plane of the fault with decreasing temperature.

(7) Local solute composition fluctuations have also been observed in the integral profiles in the Co-0.98 at.% Fe alloy at $T_a = 550$ and 575 °C. The fluctuations are due to solute-rich regions (~ 20 Å dia) in the plane of the stacking fault, whose concentration differs significantly from the average fault composition. For the Co-0.98 at.% Fe alloy the corrected Fe composition of these fluctuations approaches that of a two-dimensional ordered phase (Co_3Fe).

(8) It is shown that even though the composition measured with the atom probe for different stacking 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. This indicates that the mechanism for imaging solute atoms on stacking faults is a function of the crystallographic plane(s) which the fault intersects. It also indicates the danger of using "bright spot" decoration effects to deduce compositional effects [24].

(9) The metallurgy of both Co-0.96 at.% Nb and Co-0.98 at.% Fe alloys was studied. We have obtained FIM micrographs of these alloys in various states; i.e. pure f.c.c., pure h.c.p. and partially transformed crystals.

(10) The contrast effects produced by stacking faults in the FIM images were enumerated, and a field-evaporation sequence through one pole of an FIM specimen containing two closely-spaced stacking faults— ~ 20 Å apart—was presented.

(11) It was not found possible to distinguish among the different topologically possible types of stacking faults in the experimental FIM images.

Acknowledgements—This work has been supported by the National Science Foundation through the Materials Science Center at Cornell University. The support of the U.S. Department of Energy is acknowledged for certain technical facilities. We wish to thank Mr Robert Whitmarsh for enthusiastic technical assistance in all phases of the experimental program. Professor J. M. Blakely for many illu-

minating discussions on the analogous subject of surface segregation. Professor M. E. Fisher and Dr D. Huse for a discussion on the subject of solid-state fluctuations and Professor H. H. Johnson for enthusiastic encouragement.

REFERENCES

1. W. C. Johnson and J. M. Blakely (editors), *Interfacial Segregation*. Am. Soc. Metals, Metals Park, OH (1979).
2. H. Suzuki, *Sci. Rep. Res. Inst. Tohoku Univ. A* **4**, 452 (1952).
3. H. Suzuki, *J. Phys. Soc. Japan* **17**, 322 (1962).
4. T. Ericson, *Acta metall.* **14**, 853 (1966); A. Korner and H. P. Karnthaler, *Phil. Mag. A* **48**, 469 (1983).
5. T. C. Tisone, *Acta metall.* **21**, 229 (1973).
6. A. Wagner, T. M. Hall and D. N. Seidman, *Rev. scient. Instrum.* **46**, 1032 (1975).
7. T. M. Hall, A. Wagner, A. S. Berger and D. N. Seidman, *Scripta metall.* **10**, 485 (1976).
8. T. M. Hall, A. Wagner and D. N. Seidman, *J. Phys. E Sci. Instrum.* **10**, 884 (1977).
9. A. Wagner, T. M. Hall and D. N. Seidman, *J. nucl. Mater.* **69**, & **70**, 413 (1978).
10. R. Herschitz and D. N. Seidman, *Scripta metall.* **16**, 849 (1982).
11. O. S. Edwards and H. Lipson, *Proc. R. Soc. A* **180**, 268 (1942).
12. C. R. Houska, B. L. Averbach and M. Cohen, *Acta metall.* **8**, 81 (1960).
13. D. Creagh, S. G. Bailey and G. Y. H. Wilson, *Phil. Mag.* **32**, 405 (1975).
14. S. Mahajan, D. Brasen and T. Wakiyama, *Metall. Trans. A* **9A**, 1817 (1978).
15. F. C. Frank, *Phil. Mag.* **42**, 1014 (1951).
16. W. T. Read, *Dislocations in Crystals*, p. 94. McGraw-Hill, New York (1953).
17. L. Kaufman, in *Phase Stability in Metals and Alloys* (edited by P. S. Rudman, J. Stringer and R. I. Jaffe), p. 128. McGraw-Hill, New York (1967).
18. J. P. Hirth and J. Lothe, *Theory of Dislocations*, pp. 334–336. McGraw-Hill, New York (1968).
19. M. Hansen and K. Anderko, *Constitution of Binary Alloys*, pp. 472–484. McGraw-Hill, New York (1958).
20. R. Herschitz and D. N. Seidman, *Surf. Sci.* **130**, 63 (1983).
21. H. M. Otte and A. G. Crocker, *Physica status solidi* **9**, 441 (1965).
22. R. Herschitz and D. N. Seidman, *Acta metall.* **33**, 1565 (1985).
23. A. T. Macrander, M. Yamamoto, D. N. Seidman and S. S. Brenner, *Rev. scient. Instrum.* **54**, 1077 (1983).
24. P. R. Howell, D. E. Fleet, A. Hildon and B. Ralph, *J. Microsc.* **107**, 155 (1976).
25. J. P. Simon, A. M. Papon and P. Guyot, *Phil. Mag. B* **44**, 69 (1981).
26. F. L. Williams and D. Nason, *Surf. Sci.* **45**, 377 (1974).
27. M. Badia and A. Vignes, *Acta metall.* **17**, 177 (1969).
28. P. M. Morse and H. Feshbach, *Methods of Theoretical Physics*, pp. 434–435. McGraw-Hill, New York, (1953).
29. D. G. Brandon, *J. Sci. Instrum.* **43**, 708 (1966).
30. J. Amano, A. Wagner and D. N. Seidman, *Phil. Mag. A* **44**, 199 (1981).

APPENDIX A

On the subject of solute atom equilibrium and redistribution during a quench

The root-mean-square diffusion distance $(x^2)^{1/2}$ was estimated from the equation

$$(\overline{x^2})^{1/2} = (6Dt)^{1/2}, \quad (\text{A1})$$

where D is the tracer diffusion coefficient of Fe in Co and t is the annealing time.

The expression for D is given by

$$D = D_0 \exp\left(-\frac{Q}{k_B T}\right) \quad (\text{A2})$$

where D_0 is the pre-exponential factor, Q is the activation energy for tracer diffusion, k_B is Boltzmann's constant and T is the temperature. The values of D_0 and Q for Fe in Co are equal to $0.11 \text{ cm}^2 \text{ s}^{-1}$ and $2.63 \text{ eV atom}^{-1}$ [27]. In the absence of diffusion data on the Co(Nb) system we used the tracer diffusivity of Fe in Co to estimate $(x^2)^{1/2}$ of Nb in Co.

We now present a simple qualitative argument that justifies the use of diffusion data for a Co(Fe) alloy for the Co(Nb) system. When diffusion occurs by a vacancy mechanism—it is accepted that this mechanism operates in a number of f.c.c. and h.c.p. metals—the diffusion coefficient is determined by the product of the probability that a given neighboring site is vacant times the frequency with which an atom jumps into the vacant neighboring site. The atomic volumes of Co and Fe are approximately the same, whereas the atomic volume of Nb is $\sim 62\%$ greater than of Co—as a result large strains are produced in the matrix of Co(Nb) alloy—and hence vacancies will tend to be attracted to Nb atoms. This, in turn, may lead to faster diffusion of Nb in a Co matrix, compared to Fe diffusion in Co, due to an enhanced vacancy concentration in the Co(Nb) alloy. And therefore the values given for $(x^2)^{1/2}$ are lower bounds for the Co(Nb) system. This is consistent with our suggestion that the Fe segregation effect at 450°C may not have achieved local equilibrium.

The integrated number of jumps (n_j) during a quench was estimated by first evaluating the effective value of Dt during that period, i.e.

$$\overline{Dt} = \int_0^t D(t) dt; \quad (\text{A3})$$

where the limits on the integral cover the quench period. The diffusion coefficient $D(t)$ is equal to

$$D(t) = D_0 \exp\left[-\frac{Q}{k_B T(t)}\right] \quad (\text{A4})$$

where $T(t)$ is the quench rate.

We assumed a linear quench rate, so that

$$T(t) = T_a - \alpha t \quad (\text{A5})$$

where T_a is the annealing temperature and α is the quench rate constant. By combining equations (A3), (A4) and (A5)

we obtain the following expression

$$\overline{Dt} = -\frac{D_0}{\alpha} \int_{T_a}^{T_f} \exp\left[-\frac{Q}{k_B T(t)}\right] dT \quad (\text{A6})$$

where T_f is the final temperature. Since quenching was done into iced water, $T_f = 273 \text{ K}$. To evaluate the above integral we let $y = Q/k_B T(t)$, hence it becomes

$$\overline{Dt} = \frac{D_0 Q}{\alpha k_B} \int_y^\infty \frac{\exp(-y)}{y^2} dy. \quad (\text{A7})$$

Integrating equation (A7) by parts we obtain

$$\overline{Dt} = \left(\frac{D_0 Q}{\alpha k_B} - \frac{e^{-y}}{y} + \int_y^\infty \frac{e^{-y}}{y} dy\right) \quad (\text{A8})$$

where the integral on the right-hand side is known as $-Ei(-y)$ and is given by [28]

$$-Ei(-y) = \int_y^\infty \frac{e^{-y}}{y} dy \approx \frac{e^{-y}}{y} \times \left[1 - \frac{1}{y} + \frac{2!}{y^2} - \dots + \frac{(-1)^n n!}{y^n}\right]. \quad (\text{A9})$$

By using the first two terms of the solution, we obtained

$$\overline{Dt} = \frac{D_0 T_a^2 k_B}{\alpha Q} \exp\left(-\frac{Q}{k_B T_a}\right) \quad (\text{A10})$$

The numerical answer is essentially the same if one uses 36 terms instead of just two terms. We have estimated an upper limit to the effective value of $(x^2)^{1/2}$ by setting $\alpha = 10 \text{ K}^{-1}$. This value is less than 1 Å , indicating that there was no significant redistribution of solute atoms during a quench. Thus the solute distributions we measured correspond to the distributions characteristic of T_a .

APPENDIX B

Quantitative determination of A_p and D_a

Three different methods were employed to determine the values of the probed area A_p and D_a . In the first method the FIM image is assumed to be a stereographic projection—see Fig. A1; for small values of the angle ϕ about the center of the image this is an excellent approximation [29]. The FIM tip is taken to be hemispherical in shape.

The value of A_p corresponds to the surface area of a spherical cap (shown cross-hatched in Fig. A1) and is equal to

$$A_p = A_{\text{cap}} = 2\pi R_i (AA') \quad (\text{B1})$$

where $AA' = R_i (1 - \cos\phi)$; therefore

$$A_p = 2\pi R_i^2 (1 - \cos\phi). \quad (\text{B2})$$

Thus, in order to estimate A_p it is necessary to determine the value of ϕ . From the similar triangles ΔPAC and $\Delta PA'C'$ we have,

$$\frac{AC}{A'C'} = \frac{PA}{PA'} \quad (\text{B3})$$

where $PA = R_i (1 + \cos\phi)$, $PA' = 2R_i$, and $AC = R_i \sin\phi$, and hence

$$A'C' = \frac{2R_i \sin\phi}{1 + \cos\phi}. \quad (\text{B4})$$

From similar triangles $\Delta PA''C''$ and $\Delta PA'C'$ we have

$$\frac{A''C''}{A'C'} = \frac{PA''}{PA'} \quad (\text{B5})$$

where $PA'' = 2R_i + \delta$, and $A''C'' = \rho/2$, thus

$$A'C' = \frac{R_i \rho}{2R_i + \delta} \quad (\text{B6})$$

Fig. A1. A schematic illustration of the FIM specimen and its relationship to the image intensification system. See Appendix B for the derivation of the expression used in evaluating D_a .

Finally, from equations (B4) and (B6) we obtained the following relation for ϕ

$$\tan \frac{\phi}{2} = \frac{\rho/2}{2R_i + \delta} \quad (\text{B7})$$

or

$$\phi = 2 \arctan \left(\frac{\rho/2}{2R_i + \delta} \right). \quad (\text{B8})$$

By substituting equation (B8) into equation (B2) we obtained the final expression for A_p

$$A_p = 2\pi R_i^2 \left\{ 1 - \cos \left[\arctan \left(\frac{\rho/2}{2R_i + \delta} \right) \right] \right\}. \quad (\text{B9})$$

The value of D_a at small ϕ simply corresponds to $2R_i$, ϕ and is equal to

$$D_a = 4R_i \arctan \left(\frac{\rho/2}{2R_i + \delta} \right). \quad (\text{B10})$$

Since R_i is always much less than δ equations (B9) and (B10) are given to a high degree of accuracy by

$$A_p = 2\pi R_i^2 \left\{ 1 - \cos \left[2 \arctan \left(\frac{\rho}{2\delta} \right) \right] \right\} \quad (\text{B11})$$

and

$$D_a = 4R_i \arctan \left(\frac{\rho}{2\delta} \right). \quad (\text{B12})$$

The second method is also based on geometrical considerations; it does *not*, however, require a knowledge of δ . Figure A2 is a schematic diagram showing cross-sectional and top views of the FIM specimen. The diameter of the probed area is given by

$$D_a = r_n + r_x, \quad (\text{B13})$$

where r_n is the radius of the last ledge which is covered by the probe-hole and r_x is the distance from the central axis of the tip to the closest edge of the probe hole. It can be shown that

$$r_n \cong 2R_i d_{hk1} n. \quad (\text{B14})$$

The quantity r_x is deduced from the proportionality relationship

$$r_x = r_1 \frac{R_x}{R_i} \quad (\text{B15})$$

where r_1 is the radius of the topmost ledge, R_i is the radius of the topmost ledge as measured on the FIM micrograph and R_x is the distance from the central axis of the tip to the closest edge of the probe-hole, also as measured on the FIM micrograph.

By substituting equations (B14) and (B15) into equation (B13) we obtain

$$D_a = \left(2R_i d_{hk1} n + r_1 \frac{R_x}{R_i} \right). \quad (\text{B16})$$

Fig. A2. A schematic diagram showing the cross-sectional and top views of the FIM specimen. It illustrates the relationship between the physical dimensions of the FIM tip to D_a .

This expression was derived under the assumption that the probe hole is centered about the central axis of the tip.

In case the probe-hole is positioned to one side of the central axis, then

$$D_a = r_n - r_x. \quad (\text{B17})$$

Thus, a completely general expression for D_a is given by

$$D_a = \left(2R_i d_{hk1} n \pm r_1 \frac{R_x}{R_i} \right). \quad (\text{B18})$$

The third method involves counting the number of atoms in each plane field evaporated and is described in great detail in [30]. This 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 found that the calculated diameters of the cylinder analyzed are the same to within less than $\sim 15\%$.

The values of D_a reported in this paper are the average values calculated by the first two methods.