Letters

The Distinction between Ion Damage and the Early Stages of Carbide Precipitation in Nickel Alloys

Ion-damage during examination of samples in the electron microscope was originally observed by Pashley and Presland [1] in thin foils of gold and copper. Subsequent work, predominantly on intentionally irradiated materials, has been the subject of a number of publications by, for example, Wilkens and Rühle [2], Rühle [3] and Wilkens [4]. Damage appears as small strain-field images (< 100Å diameter) with black/white lobes of contrast. It is the purpose of this note to report the occurrence and characteristics of electron-microscope-induced ion-damage in a Ni/2 wt. % Ti/0.4 wt. % C alloy and to discuss how small precipitates can be recognised in its presence.

The alloy mentioned above was melted by rf. induction heating and cast in a horizontal water-cooled copper boat under one atmosphere of argon. The alloy was then homogenised at 1250°C for 48 h in argon-filled silica capsules and cold-rolled to strip, 0.02 mm thick. For intermediate anneals, samples were again sealed in argon-filled silica capsules and heated to 1250°C for 2 h. After the final annealing treatment, the strip was quenched into water at room-temperature, aged at 600°C for periods up to 200 h and again water-quenched. Thin foils suitable for examination in a Philips EM-300 electron microscope operated at 100 kV were prepared by electropolishing in a solution of ethanol – 10% perchloric acid maintained at – 50°C and using a potential of 30 volts.

It was observed that the density of defects can build up very rapidly during normal examination of specimens in the electron microscope. The appearance of a sample after 1.5 h examination is shown in fig. 1. The defects can be clearly seen and have the following characteristics which suggest that they are formed as a result of ion-damage:

(i) Stereo-microscopy has shown that the defects lie within 100Å of the surface of the specimen facing the electron gun.

(ii) The defects form in the alloy independently of its thermal history and are also observed in pure nickel.

(iii) The defects are not confined to the area irradiated by the electron beam. This is a consequence of the fact that the ion-path is little affected by the magnetic lenses in the microscope.

(iv) The loop diameter (~ 80Å) is consistent with the formation of each loop from an individual ion-impact. An 100 kV oxygen ion produces 10^3 Frenkel pairs [5] and the maximum loop diameter produced by clustering of the vacancies, if all the interstitials escape to the foil surface, is ~ 80Å.

(v) The loop density after 3 h is ~ 10^3 μm^{-2}, which gives a rate of defect production similar to that reported by Pashley and Presland [1] for gold specimens. Assuming that each loop corresponds to an individual ion-impact, the above loop production rate corresponds to an ion-irradiation rate of ~ 10^7 cm^{-2} sec^{-1}, in good agreement with the measurements reported by Howe, McGurn and Gilbert [6].

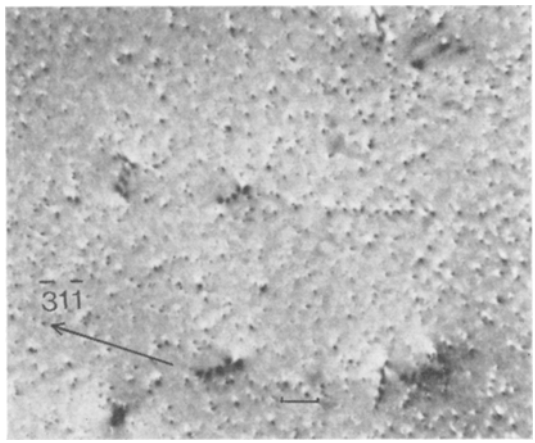

Figure 1 Dark field micrograph of defects, formed in the nickel alloy during normal operation of the electron microscope. A detailed study of their images indicated that these defects are vacancy Frank loops formed in the surface of the foil facing the electron gun. Beam direction [011]. Marker–1000Å.

Following the convention adopted by Wilkens and Rühle [2], a vector **l** is defined joining the centres of the black to the white contrast lobes. It was found that **l** was always parallel to the projection of ⟨111⟩ into the diffraction pattern, i.e. the defects are Frank loops lying on {111} planes. The value of **g.l** was positive for almost all of these small Frank loops, as shown in fig. 1, Since the defects lie within 100Å of the foil

surface, they can be identified as vacancy in character as they lie within the first layer of depth contrast oscillations [2, 7] for (200) and (113) reflections. The formation of Frank vacancy loops as a result of ion-damage during electron-microscope observations is in agreement with the results of Rühle [8] in copper. Both quenching [9] and neutron-irradiation [8] also produce Frank vacancy loops in nickel.

In considering the influence of ion-damage in electron microscope studies of the early stages of precipitation, two types of precipitate image must be considered [10]:

(*a*) Large black/black images of diameter $\sim \xi_g$ for which the parameter

$$\epsilon \mathbf{g} r_0^3 / \xi_g^2 \gtrsim 0.2$$

where ϵ is the constrained mismatch of a misfitting precipitate of radius r_0, $\mathbf{g}$ is the reciprocal of the reflecting plane spacing, and ξ_g is the extinction distance of the diffracted beam.

(*b*) Small black/white images of diameter ~ 0.25 ξ_g for which the parameter

$$\epsilon \mathbf{g} r_0^3 / \xi_g^2 \lesssim 0.2 .$$

Unless the mismatch or shape of the precipitate changes with increasing size, then the radius alone will determine the image type.

Case (*a*) is illustrated in fig. 2 which is a bright-field image of the nickel alloy aged for 200 h at 600°C. The small black/white defects, A, are ion-damage but the large defects, B, are carbide precipitates similar to "matrix-dot" carbides that have been observed in austenitic stainless steels [11–18] and in nickel alloys [19]. These precipitates can eaily be distinguished from ion-damage. If they lie well within the foil, their images consist of two dark lobes such as those shown at B in fig. 2. When they are within ξ_g of the foil surfaces, larger black/white images such as discussed by Ashby and Brown [20, 21] are observed.

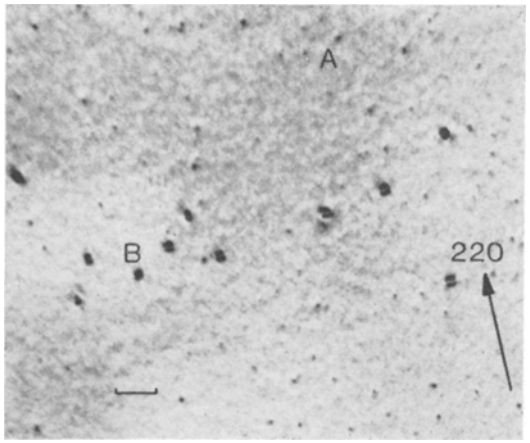

Figure 2 Bright field micrograph of large "matrix-dot" titanium carbide precipitates, B, in the nickel alloy. Vacancy Frank loops as a result of ion-damage are observed at many points, for example, at A. Marker–1000 Å.

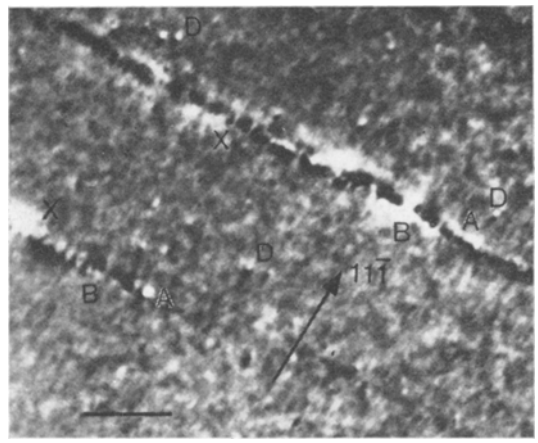

Figure 3 Rows of small TiC particles precipitated in the wake of a climbing dislocation. The particles, A, are close to the bottom surface of the foil and each particle along the line AX lies at successively higher levels, e.g. the particles B lie within the second layer of depth oscillations in contrast. The TiC particles appear interstitial in nature. A significant amount of ion-damage, exhibiting the contrast of vacancy loops, is present in this area e.g. at D. Marker–1000 Å.

Case (*b*) for very small precipitates is illustrated in fig. 3. This shows a row of small titanium carbide particles precipitated in the wake of a climbing dislocation in the manner suggested by Silcock and Denham [16]. The particles A are within 0.3 ξ_g of the bottom surface of the foil and each particle along the lines AX lies at successively higher levels in the foil. For example, particles B lie within the second layer of the depth oscillations of contrast [2, 7], i.e. in the range 0.3 to 0.7 ξ_g. The sign of $\mathbf{g} \cdot \mathbf{l}$ reverses with depth and the images behave like those of small interstitial loops.

It is important to realise that in studies of the very early stages of precipitation, ion-damage effects could have a major influence on precipitate density measurements, since the general

black/white form of the image is the same. In normal operation, defect densities up to $10^3 \mu m^{-2}$ have been measured after examining samples for up to 3 h. In a foil of thickness 1000Å, this is equivalent to a defect density of $\sim 10^{16}$ cm^{-3}, i.e. of the same order of magnitude as measured densities of small precipitates [16, 22]. If it is necessary to determine the onset of a precipitation process, e.g. the point at which small "matrix dot" precipitates begin to form in austenitic stainless steel [14], the precipitate can be recognised by the appearance of a significant number of black/white images with different signs of **I**. Such a criterion is independent of the sign of the strain-field of the precipitate. However, if either precipitate density or the sign of the strain field of the precipitate is to be measured, the most effective method is to ignore images within the characteristic ion-damage depth for the material concerned.

Acknowledgements

The authors would like to thank Drs M. Hill and C. Schüler for constructive comments throughout the course of this work. We are also grateful to Mr F. Häussermann and Dr M. Wilkens of the Max-Planck-Institut für Metallforschung for making quantitative stereo measurements.

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Received 8 June
and accepted 25 June 1971

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