The precipitation of niobium carbide at grain boundaries in an austenitic stainless steel

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Electron microscopy has been used to show that the precipitation of niobium carbide at the grain boundaries of an austenitic stainless steel can occur in a spatially non-random fashion. Preferential nucleation and growth of carbides occurs on grain-boundary defect structures. Where present, these defect structures include extrinsic grain-boundary dislocations and topographical discontinuities. An example of the precipitation of niobium carbide on an intrinsic dislocation array is also shown.

1. Introduction

The precipitation of niobium carbide (NbC) in austenite commences with the heterogeneous nucleation of particles on lattice defects such as dislocations and grain boundaries (e.g. [1–3]). NbC particles form by a process of heterogeneous nucleation due to the large mismatch between this second phase and the parent austenite lattice; this mismatch being close to 25% [4]. Dislocation defects which act as intragranular sites for the nucleation of NbC particles also play an important role during particle growth, since climb of such defects between pinning particles can provide a source of vacancies; vacancies formed in this manner migrate by a mechanism of pipe diffusion to the particle matrix interface, providing strain relief [5].

While many important details of the intragranular nucleation and growth of NbC in austenite have been documented (e.g. [1–3]), very little experimental work has been published giving details of the grain-boundary precipitation of NbC in austenite [6, 7].

This paper will show that, in the presence of certain grain-boundary defect structures, the nucleation and growth of NbC particles at the grain boundaries of an austenitic stainless steel occurs in a spatially non-random fashion. It is felt that these observations will be found to be pertinent to other alloy systems where a fine dispersion of second phase particles, characterized by large mismatch with the matrix, nucleate and grow at grain boundaries.

2. Experimental details

The alloy used in the investigation was a 20 wt % chromium, 25 wt % nickel austenitic stainless steel, containing approximately 0.5 wt % niobium and 0.05 wt % carbon + nitrogen.

Strip specimens of the alloy were solution-treated at 1350° C in silica capsules containing an argon gas atmosphere. Following solution-treatment, specimens were given either a 5% or 10% cold-working treatment or no cold-working, prior to ageing (percentage deformation was defined as a reduction in specimen thickness). Specimens of the three cold-worked states were re-sealed in silica capsules and aged for ½ h at 930° C.

A further series of solution-treated and undeformed specimens were aged for a nominal period (~45 sec) at 930° C, to investigate the spatial distribution of precipitates in undeformed specimens at the earliest stages of ageing. It was felt that under these circumstances, the spatial distribution of boundary precipitates would be least affected by possible coarsening processes (processes which by their very nature must modify the distribution of precipitates).

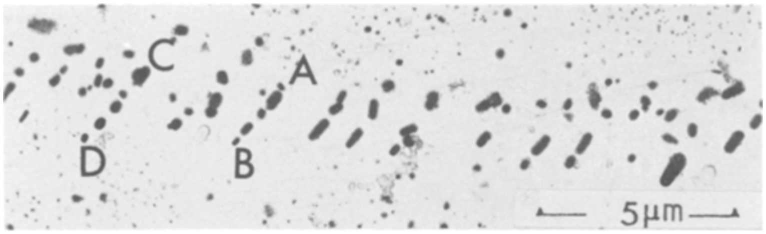

Figure 1 A carbon extraction replica from a specimen which had been deformed by 5% prior to ageing. Precipitates at the grain boundary are arranged in parallel lines (e.g. along AB and CD). Note the tendency for individual particles to be elongated along the direction of each line.

Thin foil specimens of the aged material were prepared from 3 mm diameter discs cut from the strips. Disc specimens were thinned to perforation using a twin-jet electropolishing unit. The electropolishing solution used consisted of perchloric acid (2% by volume) dissolved in 2-butoxyethanol. Carbon extraction replicas of the aged materials were also prepared, using standard techniques (e.g. [6]). All specimens were examined in a Philips EM 301 electron microscope, using a standard double tilt specimen holder.

3. General aspects of the grain-boundary precipitation of NbC

It became obvious from examination of carbon extraction replicas prepared from the deformed and aged specimens, that in a large number of cases the spatial distribution of grain-boundary precipitate particles was non-random in nature. An example of such an observation is shown in Fig. 1. Here it can be seen that the extracted NbC particles at the grain boundary are arranged in parallel lines, e.g. along AB and CD. Further, the individual particles which make up these lines of precipitates tend to be elongated along the direction of the lines. To a very much smaller extent, such observations were also made on extraction replicas which had been obtained from specimens which were not deformed prior to ageing

The electron microscope investigation of thin foil specimens of the aged materials, which followed the examination of the carbon extraction replicas, revealed that the extraction replica observations outlined above were rather special instances of a more general association between grain-boundary particles of NbC and one or other of two main types of grain-boundary defect structure. The two types of grain-boundary defects in question were: (1) dislocations in grain boundaries; (2) grain-boundary topographical defects.

In the following sections, the close correlation between NbC particles nucleated at grain boundaries and the above two general classes of grain boundary defects are investigated in more detail.

4. Nucleation of NbC on grain-boundary dislocations

During the course of the investigation, the type of grain-boundary dislocation most commonly observed was the extrinsic grain-boundary dislocation [8]. In specimens which had been deformed by either 5% or 10% prior to ageing, every grain boundary contained extrinsic dislocations. This is not surprising, since extrinsic dislocations are the decomposition products formed when intra granular dislocations run in, or are forced into grain boundaries (e.g. at the head of dislocation pile-ups) [8, 9]. A typical example of the distribution of these dislocations in the deformed and aged specimens can be seen in Fig. 2, which shows

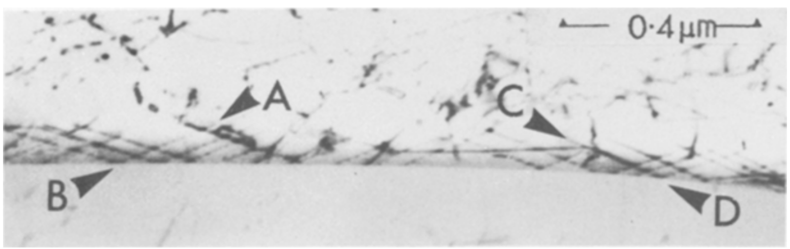

Figure 2 Extrinsic dislocations in a grain boundary in a specimen deformed by 10% prior to ageing. Two sets of these dislocations are present, with line vectors parallel to AB and CD.

extrinsic dislocations in a specimen which had been deformed by 10% prior to ageing. Two sets of extrinsic dislocations are apparent, each set having a different line vector, e.g. compare direction AB with direction CD. Extrinsic dislocations tend to occur in sets which have common line vectors because these line vectors often represent the intersection of an active slip plane in one or other of the two grains at the boundary with the boundary plane itself [8].

An example of the spatial correlation between NbC particles nucleated at grain boundaries with extrinsic dislocations is shown in the precipitate dark-field image (Fig. 3a). However, due to the proximity of the 0 0 2 precipitate reflection, used to form the image, and the 0 0 2 austenite reflection, some image overlap between the two dark-field images occurs (i.e. when a standard objective aperture is used, it is not generally possible to exclude all diffracted intensity characteristic of the austenite reflection). Thus, the image shows bright contrast from the precipitate particles, with an additional weak contribution of diffracted intensity from the austenite matrix. Although contrast from the austenite matrix is weak, it is sufficient to enable detection of most of the relevant structure at the grain boundary. It is apparent from this image that a large number of the grain-boundary NbC particles are localized at the positions of the lines of the extrinsic grain-boundary dislocations, e.g. along AB, CD and EF. It should also be noted that the precipitate particles at the extrinsic dislocation along EF are slightly elongated along the line of the dislocation. If, due to the geometry of deformation, only one set of extrinsic dislocations is present in a particular grain boundary, the information contained in Fig. 3a makes it easy to offer an explanation for the sort of carbon extraction replica observations noted in Fig. 1, i.e. nucleation at extrinsic dislocations followed by elongation of particles along the lines of the dislocations during growth will produce a "linear chain" morphology of grain-boundary precipitates.

Fig. 3b, which is a bright-field micrograph from a specimen which had been deformed by 5% prior to ageing, shows a very regular array of linear chains of precipitate particles at a grain boundary. An analysis of the crystallography of this particular grain boundary revealed that the two grains on either side of the boundary were close to a primary twin orientation. However, the grain-boundary plane was dissimilar in each grain, being (0 2 0) for grain A and ($\bar{2}$ 4 4) for grain B. The line of the precipitate chains was consistent with [$\bar{1}$ 0 1] in grain A and [4 1 1] in grain B. The geometry of

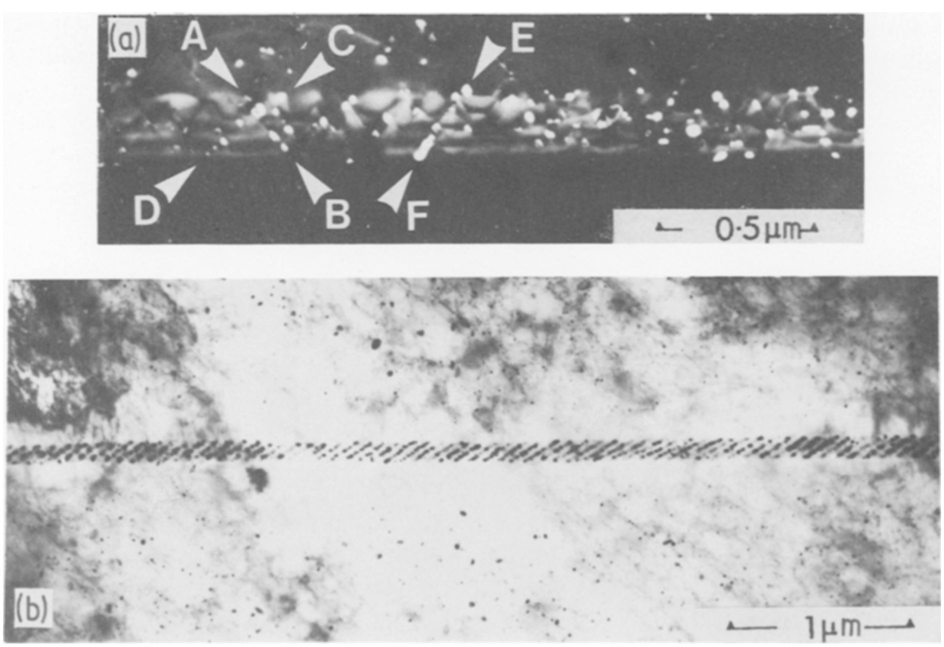

Figure 3(a) An NbC centred dark-field image, showing particles in association with the faint traces of extrinsic dislications (e.g. along AB, CD and EF. (b) A bright-field image showing linear chain precipitation of NbC at a grain boundary in a 5% deformed specimen.

the grain boundary shown in Fig. 3b requires the presence of a set of intrinsic dislocations of spacing and orientation which is consistent with the spacing and orientation of the precipitate chains observed in the micrograph.

It should be noted that intrinsic dislocations differ from extrinsic dislocations in that they are required to be present by the geometry of the grain boundary itself, whereas, extrinsic dislocations are produced as a consequence of the specimen thermomechanical history. The majority of the observations of association of NbC precipitates with extrinsic grain-boundary dislocations were restricted to the specimen material which had been deformed prior to ageing. It is possible that "linear chain" structures of grain-boundary precipitates could be formed in specimens which are not deformed prior to ageing by processes similar to those illustrated in Fig. 3b, where nucleation and growth occurs on widely spaced sets of intrinsic grain boundary dislocations. However, no further observations of such phenomena were obtained from high-angle boundaries during the course of the present investigation.

5. Precipitation on grain-boundary topographical defects

Grain-boundary topographical defects such as steps, ledges and discontinuities in the grain-boundary plane were found to be decorated with NbC precipitates in specimens of all thermomechanical states. An example of precipitation at grain-boundary topographical defects in a specimen deformed by 10% prior to ageing is shown in Fig. 4a. Two large steps can be seen at A and B in a grain boundary which has an otherwise planar morphology; both steps being decorated with large precipitate particles. A similar example of precipitation at topographical defects can be seen in Fig. 4b, where two discontinuities in the grain-boundary plane can be distinguished along the lines AB and CD. These discontinuities in the boundary plane are emphasized by the visible changes in spacing and orientation of the intrinsic dislocations (arrowed) on each distinct facet of the grain-boundary plane. For this grain boundary, as was the case for the grain boundary shown in Fig. 4a, NbC precipitate particles can be seen to decorate the topographical discontinuities.

It is not surprising that particles of NbC should be found to decorate topographical defects in a similar manner to the way in which they decorate grain boundary extrinsic dislocations, since topographical defects can have strain fields associated with them which are of similar magnitude to those associated with intrinsic/extrinsic dislocations.

Finally, it should be noted that precipitation of NbC at topographical defects was of less importance in terms of nucleation at specific sites in the cold-worked and aged specimens than in the specimens which were undeformed prior to ageing. This is a result of the very high density of alterna-

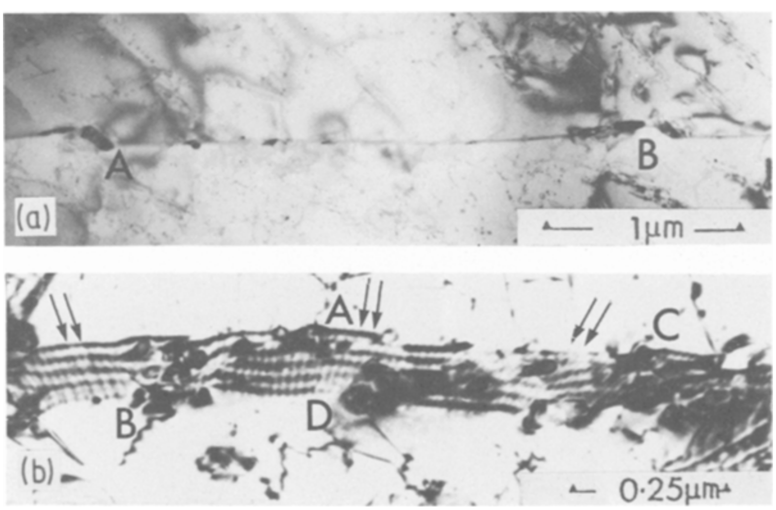

Figure 4(a) A grain boundary containing two large steps (at A and B) in a specimen deformed by 10% prior to ageing. Large NbC particles can be seen to decorate the steps. (b) Precipitation of NbC at two topographical defects (arrowed) in a 5% deformed and aged specimen. Note the change in orientation of the intrinsic grain-boundary dislocations on either side of each defect.

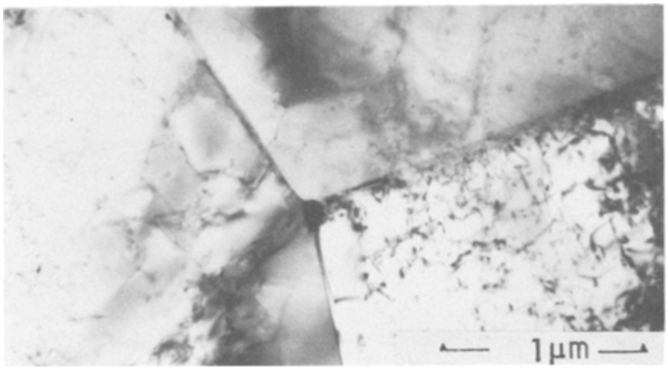

Figure 5 NbC precipitation at a triple point in a specimen deformed by 5% prior to ageing.

tive (extrinsic dislocation) specific nucleation sites which existed in the specimens which were cold-worked prior to ageing.

6. The spatial distribution of precipitation in undeformed and lightly aged specimens

The examination of undeformed specimens aged for $\frac{1}{2}$ h at 930° C showed that topographical defects such as steps, ledges, and triple junctions (e.g. see Fig. 5) were important as specific sites for the nucleation of NbC. However, the boundary facets in such specimens were also observed to be decorated with NbC particles.

Thus, undeformed specimens aged for very short periods (~45 sec) at 930° C were examined in an attempt to see whether intrinsic dislocations were specific sites for the nucleation of NbC particles on planar boundary facets in the absence of extrinsic dislocation arrays.

Fig. 6 shows an example of a grain boundary containing a series of widely spaced dislocations

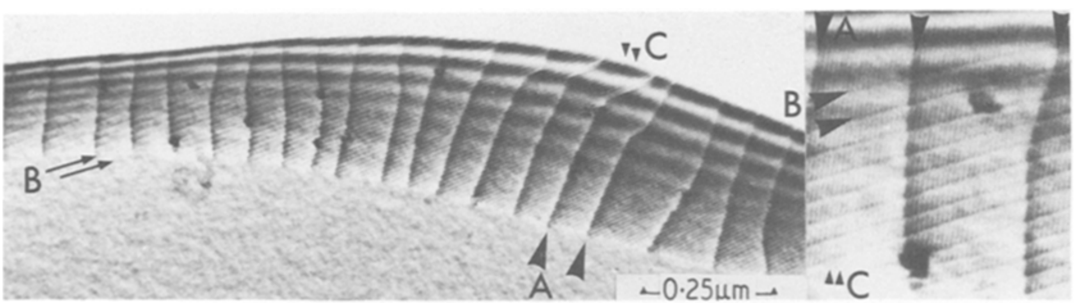

Figure 6 A grain boundary in an undeformed specimen aged for a minimum period at 930° C. Nearly all the NbC precipitates are associated with the widely spaced set of grain-boundary dislocations (arrowed A). A set of intrinsic dislocations are also apparent (arrowed B), Moiré fringes run from the "top" to the "bottom" of the grain boundary (arrowed C, and see inset). Note the distortion of the intrinsic dislocations (arrowed B) in the vicinity of the precipitate particles.

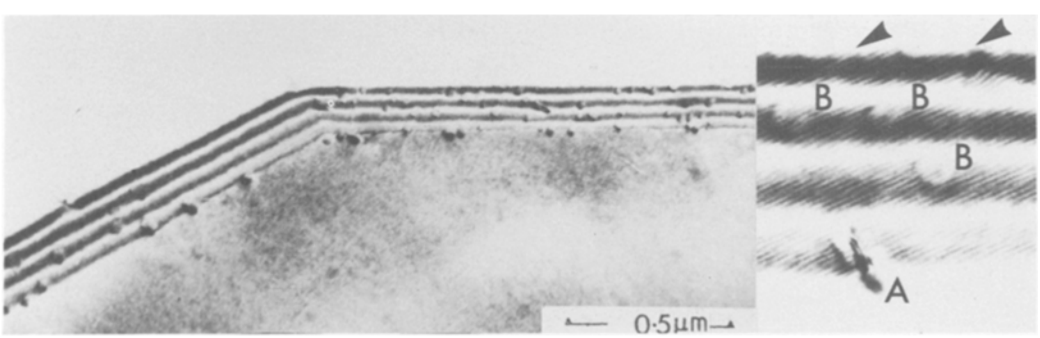

Figure 7 A grain boundary in an undeformed and lightly aged specimen, showing a difference in number density and size distribution of NbC precipitate particles on each of two different facets of the grain-boundary plane. Two different morphologies of precipitate particle are present, e.g. at A and B. A set of intrinsic dislocations are present in the grain boundary (arrowed on inset).

(arrowed, A) with which there are associated a number of small NbC particles. The dislocations shown in this figure appear to be similar to the extrinsic dislocations which were universally present in the grain boundaries of the deformed specimens. However, in this particular example it was impossible to verify whether the dislocations were extrinsic or whether they belonged to a set of widely spaced intrinsic dislocations. It should be appreciated that although in this example the end result (that is the spatial distribution of NbC particles in the boundary) is the same whether the dislocations are considered as intrinsic or extrinsic in character, the physical reason for the presence of each type of dislocation is distinct and separate. Examples of the nucleation of NbC particles in similar instances to those shown in Fig. 6 were rarely seen in the specimens examined during this part of the investigation.

An interesting example of the effect of grain-boundary plane on nucleation behaviour is shown in Fig. 7. The number density and size range of NbC particles on this grain boundary can be seen to be different on each facet of the boundary. This example would seem to indicate that the orientation of the grain-boundary plane itself can affect the overall characteristics of the nucleation of NbC particles; in this instance, as was the case generally when examining boundary facets in undeformed specimens, it was impossible to determine whether individual intrinsic dislocations acted as the nucleation sites for individual NbC particles. The reasons for the apparent lack of correlation between the intrinsic dislocations and the sites of grain-boundary precipitates would appear to be a function of a variety of factors.

Firstly, the image width of each precipitate (even after very short ageing times) is large compared with the normal intrinsic dislocation spacing (< 10 nm) and it is thus unlikely that any one precipitate will be associated, in the image, with any one single intrinsic dislocation (a notable exception being the image shown in Fig. 6).

Secondly, the very large density of possible nucleation sites (i.e. all the individual intrinsic dislocations) will encourage competitive growth/coarsening to occur from virtually the onset of nucleation. Thus, individual nuclei will not be expected to be observed on every dislocation and similarly, "linear chain" precipitation is not necessarily expected.

Even though it was impossible to determine which, if any, specific nucleation sites generally operate on boundary facets, it was absolutely clear that the number density and size distribution of NbC particles on boundary facets in the specimens examined varied greatly from boundary to boundary (compare Fig. 8a and b) and also along the boundary itself (Fig. 7).

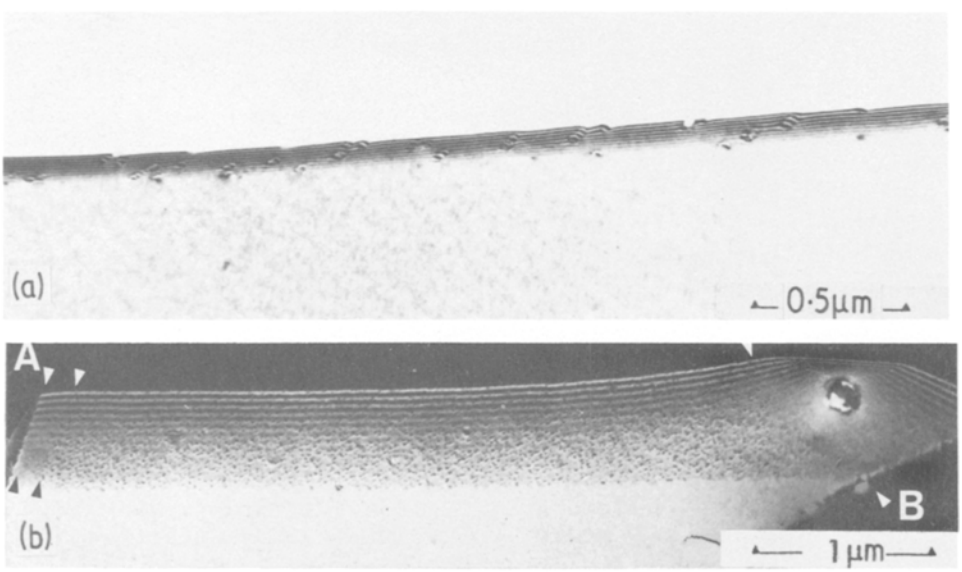

Figure 8(a) A number of large, widely spaced precipitate particles present in a grain boundary in an undeformed and lightly aged specimen. (b) A large number density of small precipitate particles in a grain boundary from an undeformed and lightly aged specimen. Note the depletion of small precipitates in the grain boundary close to the triple point (A) and the large boundary pinning precipitate (B).

7. Discussion

The results outlined in this paper have shown that the nucleation and growth of second phase particles of NbC on grain boundaries in austenite can be considered to occur in a spatially non-random fashion in the presence of certain grain-boundary structural defects. Specifically, nucleation and growth of NbC particles at grain boundaries is favoured at: (1) extrinsic grain-boundary dislocations; (2) grain-boundary topographical defects.

There is also evidence to suggest that, under certain conditions, grain-boundary particles of NbC can nucleate and grow in association with widely spaced intrinsic grain-boundary dislocations. Nucleation of NbC occurs on grain facets in the absence of extrinsic dislocations, although in these circumstances it was not possible to identify specific nucleation sites.

The size and number density of NbC particles nucleated on grain boundaries appears to be affected by the orientation of the grain-boundary plane; sizes and number densities of particles also vary widely from boundary to boundary and from specimen state to specimen state. These latter points, concerning the quantitative aspects of grain-boundary precipitation are considered, in more detail, in the companion paper [10].

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