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The effect of creep deformation on the stability of intergranular carbide dispersions in an austenitic stainless steel

P. R. HOWELL
Department of Metallurgy and Materials Science, University of Cambridge, Cambridge, UK

J. O. NILSSON, G. L. DUNLOP
Department of Physics, Chalmers University of Technology, 402 20 Göteborg, Sweden

The stability of intergranular TiC in a 20% Cr–30% Ni, Ti stabilized stainless steel and the transformation of TiC to $M_{23}C_6$, has been investigated as a function of creep deformation over a wide range of stresses at 800° C. It was found that diffusion creep does not make a significant contribution to the general ageing process or to the transformation of TiC to $M_{23}C_6$. However, dislocation creep strongly accelerates this transformation and increases the general rate of coarsening of intergranular carbides. It is concluded that this acceleration occurs through the combined action of an increase in the number of available nucleation sites (extrinsic grain boundary dislocations) and dislocation enhanced diffusion.

1. Introduction

The relative stability of MC type carbides (for example TiC or NbC) with respect to chromium-rich carbides (e.g. $M_{23}C_6$) is of considerable significance for the service properties of stabilized austenitic stainless steels. For example, the precipitation of chromium-rich carbides at grain boundaries can result in the depletion of chromium, in a narrow zone in the matrix adjacent to grain boundaries, below the level which is necessary for passivation [1]. Thus, until this depleted zone is removed by the bulk diffusion of chromium, the steel can be susceptible to intergranular corrosion in aggressive environments (i.e. it is sensitized) [2]. Similarly, carbide stability is of major importance when high temperature mechanical properties are considered. Depending upon the thermomechanical treatment, TiC (or for example NbC) can be precipitated as a very fine dispersion in the matrix pinning the dislocation network, imparting a high creep strength [3]. Replacement of this fine precipitate dispersion by coarser chromium-rich carbides can result in a substantial loss in creep strength and since the chromium-rich carbides tend to precipitate at grain boundaries the creep ductility can also be substantially reduced by an increased susceptibility to intergranular creep cavitation and cracking. In other cases the TiC may be originally present as relatively coarse carbides which pin the grain boundaries and restrict grain boundary migration or grain growth [4]. Subsequent transformation to chromium-rich carbides results in a higher volume fraction of grain boundary carbides (since the metal/carbon atom ratio is higher) which may also lead to reduced creep ductilities.

This paper is concerned with the effect of creep deformation on the stability of intergranular TiC precipitates and the transformation to $M_{23}C_6$ carbides in a 20% Cr–30% Ni austenitic stainless steel (Alloy 800). In addition to its use in the steam generator tubes of nuclear power reactors [5] this alloy is also employed as furnace tubing in pyrolysis furnaces for the petrochemical industry. Here the operating temperatures lie in the range 800 to 1100° C with stresses usually in the range 1 to 10 MPa [6]. A parallel study to the present work [4] has shown that at 800° C, Coble diffusion creep is the dominating deformation mechanism at stresses less than 5 MPa while at higher stresses dislocation creep dominates.

It has previously been shown that extrinsic grain boundary dislocations or grain boundary ledges are often preferential sites for the nucleation of intergranular precipitates [7] including the precipitation of $M_{23}C_6$ in austenitic steels [8]. The rate of precipitation of $M_{23}C_6$ at grain boundaries increases with the degree of cold work prior to ageing since this increases the number of these line defects in grain boundaries [8]. It might be expected that creep deformation also has a strong effect on intergranular $M_{23}C_6$ precipitation, and therefore this paper examines the influence of creep processes on the stability of TiC.

2. Experimental

The alloy investigated had the composition (wt %): 0.014 C, 21.4 Cr, 33.2 Ni, 0.5 Ti, 0.5 Si, 0.6 Mn, 0.3 Al. The material was forged and hot-rolled into bar form and solution-treated at 1000° C for 30 min followed by ageing at 850° C for 100 h and slow furnace cooling to room temperature. Tensile creep testing was carried out in air at 800° C with applied stresses between 3 and 30 MPa. Table I gives the relevant data concerning the creep specimens which were examined by transmission electron microscopy in terms of the applied stress (σ), total strain (ϵ) and time (t). The effect of the applied stress on the steady state creep rate is shown in Fig. 1. It can be seen that the transition from diffusion-dominated to dislocation-dominated creep occurs at a stress of approximately 5 MPa. In all cases the undeformed grip sections of the creep specimens were also examined in order to determine the effect of static ageing at 800° C on the microstructure and to provide a basis for comparison with the effect of creep deformation.

TABLE I Stresses, strains and times of creep testing

σ(MPa)	ϵ(%)	t(h)
3	0.1	110
5	0.2	170
20	1	80
30	1	12
30	5	130
30	10	300

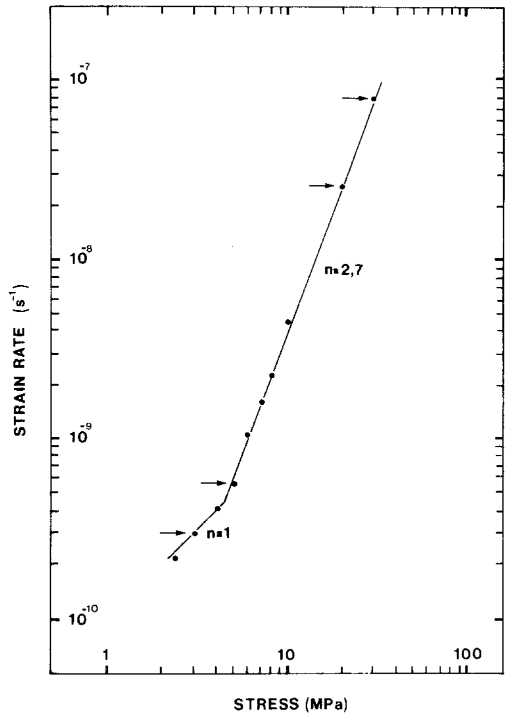


Figure 1 Steady state creep rates as a function of the applied stress. The arrows indicate the specimens which were examined by transmission electron microscopy.

3. Results

3.1. Starting material

The solution treatment of 30 min at 1000° C was insufficient to dissolve all of the TiC present so that some large intragranular precipitates of TiC were found in the starting material. These particles were found to bear no rational orientation relationship with the matrix. The original ageing treatment of 100 h at 850° C, plus furnace cooling, led to a fairly coarse dispersion of intergranular TiC precipitates, an example of which is given in

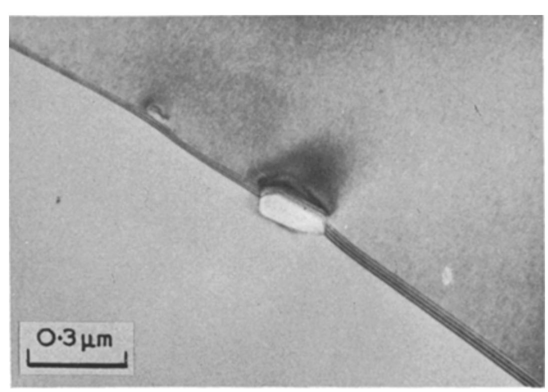


Figure 2 Typical intergranular precipitates of TiC in material prior to creep testing.

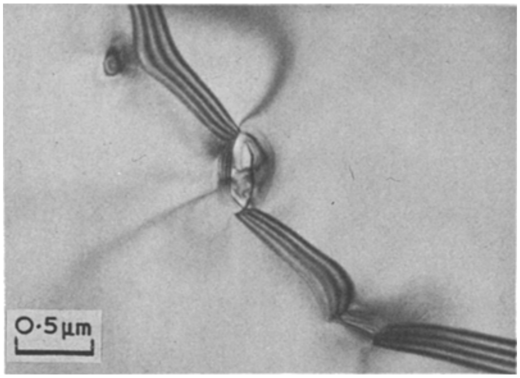


Figure 3 Intergranular TiC precipitates in material crept at a stress of 3 MPa. Note the extensive grain boundary bowing.

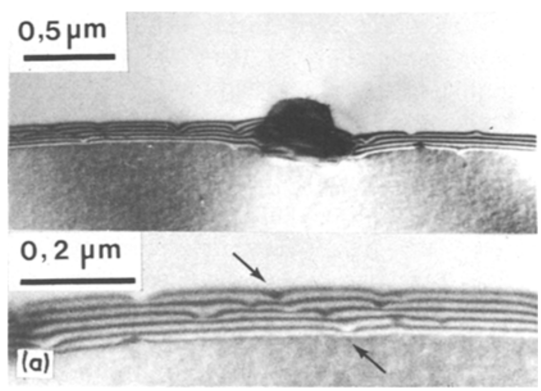
Fig. 2. Very little intragranular precipitation of TiC was observed. This could well be a consequence of the paucity of heterogeneous intragranular nucleation sites (the alloy being aged in the as-solution-treated condition). The TiC was mainly present on general high angle boundaries and, to a smaller degree, on the incoherent facets of primary twin boundaries. No precipitates were observed on the coherent planes of twin boundaries and there was no sign of $M_{23}C_6$ precipitation.

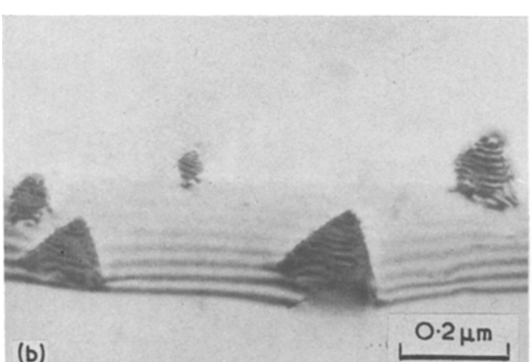
3.2. The effect of creep deformation

The changes in the precipitate distribution brought about during creep deformation will be described in this section. The effects noted will be presented in terms of the effect of increasing stress. However, it should be emphasized that these reflect microstructural changes due to a combination of deformation and high temperature ageing. A discussion of this is presented in Section 3.3 where the microstructure of creep deformed material is compared with that of statically aged material taken from the grip sections of creep specimens.

For the specimen which had been crept at 3 MPa for 110 h to a strain of 0.1% (predominantly diffusion creep), very little change was noted in the precipitate dispersion. The intergranular precipitates were still TiC and they tended to pin the grain boundaries which were bowing between the particles (Fig. 3).

Creep at 5 MPa for 170 h to a strain of 0.2% (approximately equal amounts of diffusion and dislocation creep) produced marked changes in the precipitate distribution with respect to both the starting material and the specimen deformed at 3 MPa. Figs. 4a to c show typical examples of the observed intergranular precipitation. Most of the grain boundaries were decorated with $M_{23}C_6$ particles (Fig. 4a) which in some cases had formed as triangular platelets (for example on the high angle boundary in Fig. 4b). Large precipitates of the same phase were seen at triple junctions. TiC precipitates were still observed on most grain boundaries although their number density was considerably reduced. In contrast, little change was observed in the twin boundary structure;





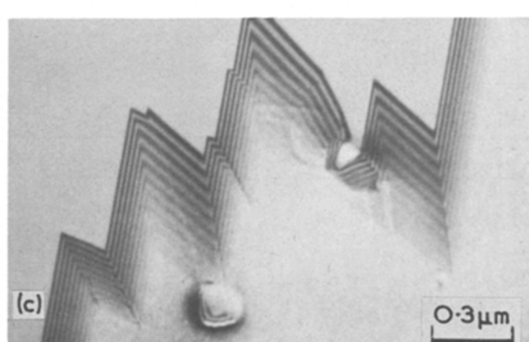


Figure 4 Intergranular precipitation in material crept at a stress of 5 MPa. (a) Large particles of $M_{23}C_6$ and apparent nucleation of $M_{23}C_6$ (arrowed, see text). (b) Triangular platelets of $M_{23}C_6$ on a high angle boundary. (c) TiC precipitates at incoherent twin boundary junctions.

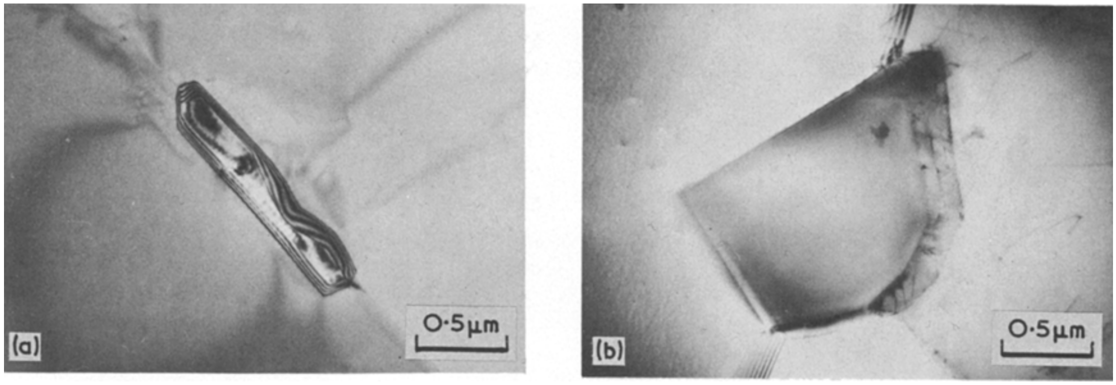


Figure 5 Intergranular precipitation in material crept at a stress of 20 MPa. (a) A large TiC particle. (b) $M_{23}C_6$ at a triple junction.

incoherent facets and the intersections between coherent and incoherent facets being decorated with TiC precipitates (Fig. 4c), with no precipitation on the coherent facets. It is interesting to note that many high angle grain boundaries contained a relatively high density of features causing perturbations in the depth fringes (arrowed in Fig. 4a). The size of these point features was too small to allow identification by electron diffraction but it is believed that they are due to freshly nucleated $M_{23}C_6$.

Creep testing at 20 MPa for the shorter time of 80 h but to the considerably higher strain of 1% resulted in microstructural changes, which were dissimilar to those described for creep at 3 and 5 MPa. Fig. 5 shows typical examples of the intergranular precipitate distribution. The majority of the precipitates were TiC and coarsening of these particles had occurred (Fig. 5a). Some precipitation of $M_{23}C_6$ was evident: mainly at triple junctions (Fig. 5b) but also as isolated precipitates on high angle grain boundaries.

The most marked changes in intergranular precipitate distribution occurred during creep at 30 MPa. Three different specimens were investigated, which had been strained to 1%, 5% and 10% during times of 12, 130 and 300 h respectively. At this stress level large intergranular particles of $M_{23}C_6$ formed rapidly and were present at all three strains. After 1% strain, large particles of $M_{23}C_6$ were observed at triple junctions (their appearance being similar to triple junction carbides found in the 20 MPa material). At 5% strain large $M_{23}C_6$ particles were observed on grain facets (Fig. 6a) and at triple junctions (Fig. 6b). Some intergranular TiC precipitates were still observed and considerable coarsening and coalescence of these particles was evident.

After 10% strain at 30 MPa the distribution of the $M_{23}C_6$ carbides was similar to that observed after 5% strain. Extremely few intergranular TiC particles were observed and TiC was also seen to be replaced by $M_{23}C_6$ on incoherent twin facets (Fig. 7). In this micrograph the triangular shaped

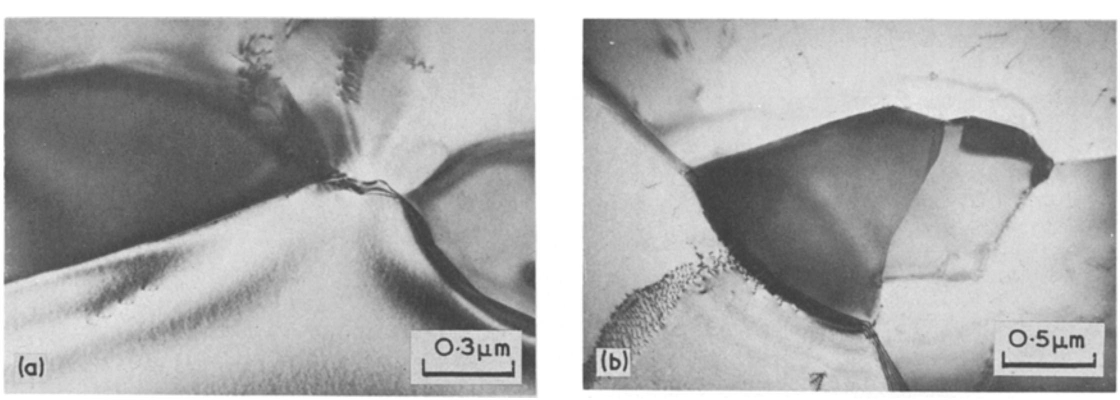


Figure 6 Intergranular precipitation in material crept at a stress of 30 MPa. (a) $M_{23}C_6$ particles after 130 h (5% strain). (b) $M_{23}C_6$ at a triple junction (130 h, 5% strain).

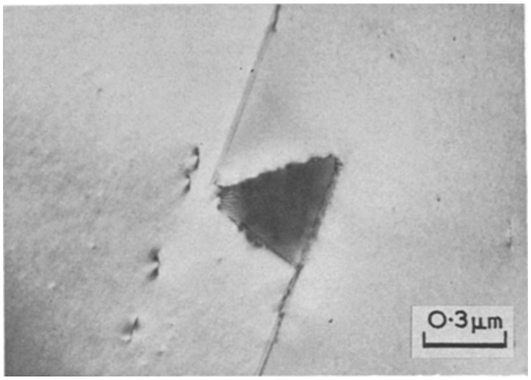


Figure 7 An example of an $M_{23}C_6$ precipitation which has nucleated on an incoherent step in a twin boundary (300 h, 10% strain).

particle has grown to a size similar to the incoherent step. Many incoherent twin boundaries were, however, free of both TiC and $M_{23}C_6$ precipitates. No precipitation had occurred on the coherent twin facets.

3.3. The effect of static ageing

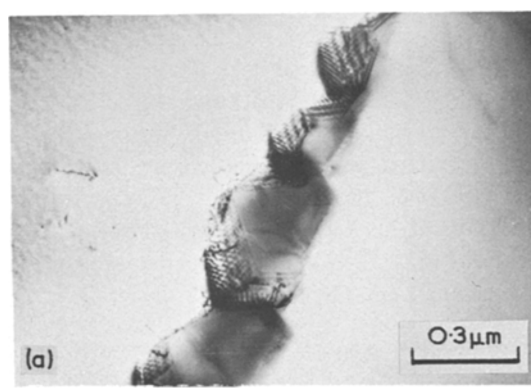
This section describes microstructural changes occurring during static ageing (i.e. in the specimen grip sections) at the temperature of creep testing (800° C). Three ageing times are considered: 110, 170 and 300 hours (see Table I).

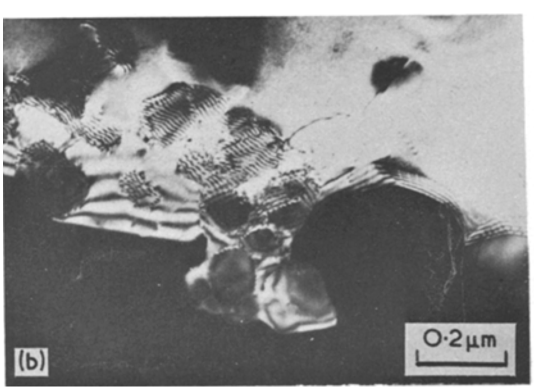
Ageing for 110 h and 170 h produced precipitate distributions which were very similar to those observed in the corresponding strained specimen gauge lengths (i.e. at 3 and 5 MPa). Thus, after ageing for 110 h no $M_{23}C_6$ was observed, while after 170 h partial replacement of TiC by $M_{23}C_6$ had occurred.

Ageing for 300 h at 800° C resulted in the virtually complete replacement of TiC by $M_{23}C_6$ (Figs. 8a to c) although the distribution of $M_{23}C_6$ differed markedly from the corresponding material deformed in creep (30 MPa, 10% strain). For general high angle grain facets, a high number density of particles were observed. These precipitates were smaller than in the creep deformed material, and often impinged (Figs. 8a and b). The occurrence of such a high number density of particles often resulted in the development of a discontinuous-type precipitation reaction [9] and led to highly convoluted boundary morphologies (Fig. 8b). The incoherent twin boundaries were copiously decorated with triangular platelets of $M_{23}C_6$ (Fig. 8c) while the coherent twin facets were again devoid of precipitation.

4. Discussion

It has been shown in Section 3 that intergranular TiC, which had been originally precipitated during ageing for 100 h at 850° C, transforms to $M_{23}C_6$ on subsequent ageing at 800° C. Similar effects have also been shown previously in other Ti-





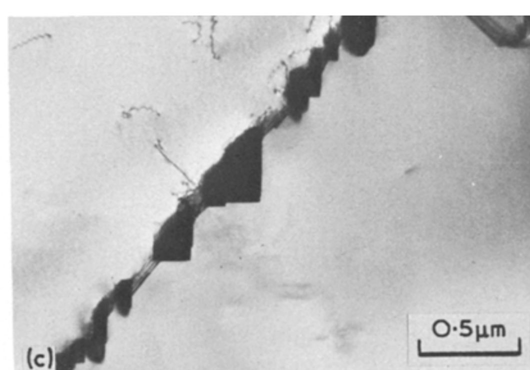


Figure 8 Examples of intergranular $M_{23}C_6$ precipitation in material which had been aged for 300 h. (a) Impinging boundary precipitates. (b) A convoluted boundary at the early stages of a discontinuous reaction. (c) Triangular platelets on an incoherent twin boundary facet.

stabilized stainless steels [10]. The present observations are also consistent with the work of other authors who have shown that in 20% Cr–25% Ni–Nb stabilized steels an initial dispersion of NbC precipitates can transform to M_6C [11–13]. It is thus apparent that, at least within certain temperature ranges, TiC is unstable with respect to $M_{23}C_6$. A likely explanation for this is that in the presence of an excess of Ti*, the free energy of formation of $M_{23}C_6$ becomes more negative through solution of Ti in the chromium-rich carbide. This may result in $M_{23}C_6$ being more stable than TiC at certain temperatures.

The results concerning the effect of creep deformation on the ageing process can be simply summarized as:

(1) Diffusion creep does not appear to make a significant contribution to the rate of transformation and neither does it seem to significantly influence the process of growth and coarsening of TiC and/or $M_{23}C_6$;

(2) Dislocation creep strongly accelerates the transformation of intergranular carbides and increases the rate of coarsening of both TiC and $M_{23}C_6$.

For static ageing and ageing during deformation by predominantly diffusion creep, the transformation commences at some time between 110 and 170 h. However, when deformation is predominantly by dislocation creep the onset of the transformation occurs at considerably shorter times. For material crept at a stress of 20 MPa the transformation was initiated during 80 h of testing while at 30 MPa evidence of transformation was found after only 12 h of testing.

It is well known that high temperature plastic deformation by dislocation movements can accelerate ageing processes and phase transformations (see for example [14]). Adamson and Martin [8] have shown that certain types of line defects in grain boundaries provide suitable heterogeneous nucleation sites for the precipitation of $M_{23}C_6$ in austenitic steels. These line defects are almost certainly extrinsic dislocations within the grain boundary [15]. Similarly the nucleation on intergranular precipitates in aluminium alloys [7] and of NbC in stainless steels [16–18] also takes place preferentially on extrinsic dislocations. Dislocation creep results in the continual production of extrinsic dislocations in the grain boundaries [5], although these defects dissociate rapidly at the creep temperature into intrinsic dislocations [19] unless pinned by precipitation. Thus dislocation creep provides a high density of nucleation sites for precipitation which are continually replenished during deformation. Some evidence of the early stage of $M_{23}C_6$ precipitation was presented in association with Fig. 4a. It is believed that the perturbations in the depth fringes of this boundary arise from very small $M_{23}C_6$ particles. The lack of visibility of the actual features causing the perturbations may depend jointly upon their very small size and the very low lattice mismatch between austenite and $M_{23}C_6$.

It is clear that dislocation creep accelerates the coarsening of both $M_{23}C_6$ and TiC. An effect of this can be seen by comparing deformed material (Fig. 6) with statically aged material (Fig. 8). In the statically aged material the $M_{23}C_6$ particles were generally thinner and exhibited Moiré fringe contrast, while after dislocation creep the $M_{23}C_6$ particles were considerably larger. It has been shown previously that the rate of coarsening of fine coherent matrix particles is greatly enhanced by pipe diffusion along matrix dislocations [20], and it would appear that similar interactions also occur between coarsening particles and grain boundary dislocations [7]. As is evident in many of the micrographs shown in the present paper, dislocation creep increases the density of matrix dislocations around grain boundary carbides. We would suggest, therefore, that the increased coarsening rate of intergranular carbide particles is a direct result of enhanced diffusion via matrix and/or grain boundary dislocations. This effect may also be influenced by the increased vacancy fluxes due to climbing dislocations, both in the matrix and in the grain boundaries.

A further comparison between material statically aged for 300 h and material which had undergone creep for the same period at 30 MPa shows that in the former case a high number density of $M_{23}C_6$ precipitates were observed on incoherent twin boundaries (Fig. 8c) whereas after creep deformation the same types of boundary were often devoid of precipitates. This disparity would seem to indicate that deformation-enhanced

*The Ti:C atomic ratio is approximately 10, which implies that excess Ti will be retained in solid solution after precipitation of TiC.

coarsening increased the rate of dissolution at these boundaries in favour of particles growing at triple junctions and general high angle boundaries.

The $M_{23}C_6$ precipitation on incoherent twin boundaries was similar in morphology to that described by other authors for the early stages of such precipitation in austenitic steels with higher carbon contents [9, 21, 22]. However, the later stages observed by these authors where lamellae of $M_{23}C_6$ emanate from the incoherent twin boundaries did not occur in the present case. Presumably this is largely because of the considerably lower carbon content. However, since formation of the lamellae requires the emission of either a Shockley partial dislocation [21] or a thin twin band [22] from a growing particle, the effect of the high nickel content providing a high stacking fault energy [23] may also be a contributing factor.

Irrespective of the thermomechanical history of the specimen material, no carbides were found on the coherent facets of annealing twin boundaries. Again, this might be a reflection of the low C content and the consequent competition for C between the various possible nucleation/growth sites.

Finally, it is worth noting that no sigma phase was observed in any of the material conditions examined.

5. Conclusions

(1) Intergranular dispersions of TiC in Alloy 800 were found to be unstable with respect to $M_{23}C_6$ at 800° C.

(2) Diffusion creep does not seem to make a significant contribution to the general ageing process or the transformation of TiC to $M_{23}C_6$.

(3) Dislocation creep strongly accelerates the transformation of TiC to $M_{23}C_6$ and increases the general rate of coarsening of intergranular carbides.

(4) This acceleration occurs through the combined action of an increase in the number of available nucleation sites and dislocation enhanced diffusion.

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