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Discontinuous Precipitation of $M_{23}C_6$ in Austenitic Steels

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Grain boundary precipitation of $M_{23}C_6$ has been studied in a 20% Cr – 35% Ni stainless steel with two grain sizes during creep deformation at 700°C as well as during an ordinary ageing treatment at 700°C. A special etching technique was applied which showed how the grain boundary precipitation gave rise to depletion of alloying elements in a zone of uniform thickness, independent of the carbide distribution, and with a gradual decrease of the depletion towards the grain interior. At some places the carbide precipitation and grain boundary migration co-operated and in these cases there was a sharp change in alloying content across the grain boundary. This process was more frequent in creep tested samples and the degree of co-operation was larger in the coarse-grained material where even a few cases of lamellar, eutectic-like precipitation was observed. Such a grain size dependence is expected theoretically and is caused by the large difference in diffusivity between carbon and the other alloying elements. It is proposed that the various degrees of co-operation between carbide precipitation and grain boundary migration are all examples of discontinuous precipitation. The various proposed mechanisms for grain boundary migration during discontinuous precipitation are discussed on the basis of the present results.

1. Introduction

Grain boundary precipitation of $M_{23}C_6$ carbide in austenitic steels has been shown earlier [1] to cause some movement of the grain boundary. This has been suggested [2] to represent the early stages of discontinuous precipitation. From observations on these materials it has been concluded [3] that the mechanism for migration of the grain boundary by discontinuous precipitation is similar to that proposed by Tu and Turnbull [4]. According to their proposal, the grain boundary starts to move under the driving force arising from the difference between the surface energies of the interfaces of a precipitated particle to the two matrix grains meeting at the grain boundary.

Although some precipitation-induced movement of grain boundaries has thus been observed in austenitic steels during precipitation of $M_{23}C_6$, the characteristic morphology of discontinuous precipitation, which resembles eutectic structures has not been reported. However, the latter has been observed in nickel-base alloys during $M_{23}C_6$ precipitation [5, 6] and there is no reason why it should not form in austenitic steels as well. The present authors have now observed this structure in austenitic steel samples used in a creep study. An etching technique was employed which made visible the difference in alloy composition and some observations could thus be made which may shed new light on the interplay between precipitation and grain boundary movements.

Some observations have been reported on aluminium alloys [7] that the simultaneous process of creep straining accelerates the grain boundary reactions during ageing. The observations made in the present study are further examples of this interplay.

2. Experimental Details

The material used in this work was a high-vacuum melted 20% Cr – 35% Ni stainless steel with the following chemical composition in wt %

C	Si	Mn	P	S	Cr	Ni	N	Bal
0.008	0.13	0.52	0.007	0.009	19.7	34.8	< 0.003	Fe

The material was examined metallographically after either a solution anneal, water quench and a creep test at 700° C or a solution anneal, water quench and an ageing treatment at 700° C. Prior to the solution anneal the material was cold swaged to a reduction of area of 55%. To produce two grain sizes, two alternative annealing operations were employed, 1200° C for 24 h and 1000° C for 10 min, the former giving an average grain diameter of about 200 μm and the latter one of 25 μm. The precise treatment of the four examined specimens is listed below:

Coarse-grain size ~ 200 μm	Fine-grain size ~ 25 μm
1200° C/24 h, w.q., aged at 700° C for 300 h. Specimen A	1000° C/10 min, w.q., aged at 700° C for 210 h. Specimen C
1200° C/24 h, w.q., creep tested at 700° C for 300 h and at 10 kg/mm². Specimen B	1000° C/10 min, w.q., creep tested at 700° C for 210 h and at 8.5 kg/mm² Specimen D

The metallographic specimens were polished mechanically, etched electrolytically in 10% oxalic acid at 7 V for about 7 sec and subsequently examined in an optical microscope.

3. Observations

Samples A, B and C all showed ordinary grain boundary precipitates of $M_{23}C_6$ and the etching revealed that the grain boundaries were surrounded by depleted zones of fairly uniform thickness, independent of the distribution of carbide particles (fig. 1a). The depth of etching decreased gradually towards the interior of the grain, revealing a gradual approach to the initial alloy content. In a few places a very sharp line can be observed between the grain boundary groove and the flat surface of the interior of the grain, (fig. 1a), revealing a steep change in alloy content. This phenomenon was observed in the fine-grained, unstressed specimen C; it was more pronounced in the coarse-grained unstressed specimen B. Figs. 1a-g show a series of structures which are presumed to represent various degrees of co-operation between grain boundary movement and precipitation. It is quite evident from the geometry of many of the structures that the sharp lines represent a grain boundary moving into the interior of a grain, e.g. fig. 1d. Grain boundary precipitation can thus occur far away from the initial position of a grain boundary, e.g. fig. 1e. In a few cases a high degree of co-oper-

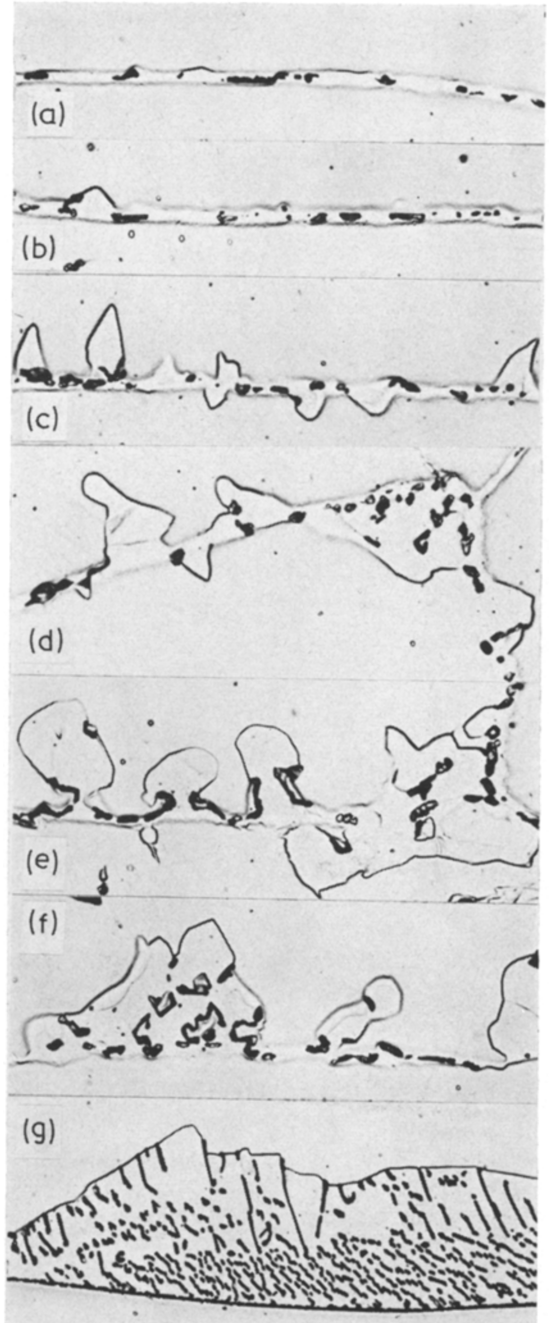

Figure 1 Specimen B. a and b demonstrate the existence of a zone depleted of alloying elements at the grain boundaries caused by grain boundary precipitation. Note the abrupt change in depth of etching at some places. These sharp lines represent grain boundaries moving into the grain interior. The entire sequence of micrographs, a-g, shows increasing grain boundary migration and various degrees of co-operation between grain boundary migration and $M_{23}C_6$-precipitation (× 1100).

ation was established and a very eutectic-like geometry was formed (fig. 1g).

The stressed sample of the fine-grained material, sample D, showed almost as much grain boundary movement as the coarse-grained material but no precipitation outside the initial position of the grain boundaries (fig. 2a). In spite of this, the areas, over which the grain boundaries have passed, show alloy depletion. It is also interesting to note that when a grain boundary has moved in such a way that it crosses its initial position, it causes some filling in of the depleted zone. Some examples of this effect are shown in figs. 2b and c.

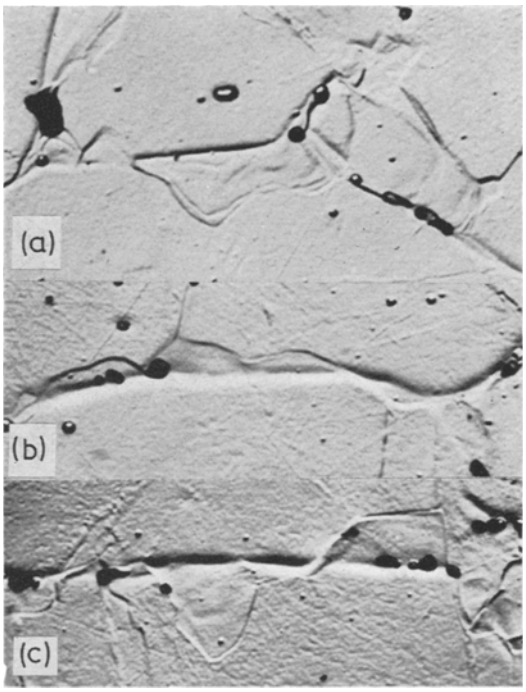

Figure 2 Specimen D. These micrographs show grain boundary migration and its relation to carbide precipitation and alloy depletion in the fine-grained, stressed specimen. b and c show how filling-in of alloying elements has occurred where the line representing the present position of the grain boundary crosses the groove, representing the site of the original grain boundary. Oblique illumination (× 1800).

4. Discussion

4.1. Ternary Effects

Most studies of discontinuous precipitation have been made on binary alloys. Some of the observations made in the present study can be explained as ternary effects, using the general description of the process of grain boundary precipitation in an 18-8 stainless steel given by Stawström and Hillert [8]. They based their description on the assumption that the process is controlled by volume diffusion of chromium to the grain boundaries, the grain boundary diffusion being sufficiently rapid to transport chromium sideways to the carbide particles distributed over the grain boundary area. This model is essentially confirmed by the observation of depleted zones of uniform thickness (fig. 1a). The fact that the diffusivity of carbon is several orders of magnitude higher than that of chromium, results in a gradual decrease of the carbon content in the interior of the austenite grains as well as in the austenite in contact with the growing carbide. This, in turn, results in a gradual increase of the equilibrium chromium content in austenite in contact with carbide. These gradual changes will occur faster the finer the grain size.

Accepting that the grain boundaries act as short circuits for chromium diffusion to the carbide particles, the filling in of the depleted zone formed at an early stage at the initial position of a grain boundary, which occurs later at the point of intersection between the new and old position of the boundary (figs. 2b and c), can be taken as an indication of the gradual increase in chromium content of austenite in contact with the carbide.

The gradual decrease of the carbon content will decrease the driving force for the precipitation of carbide. The observation that the carbide does not grow together with the migrating grain boundaries in the fine-grained material, as it does in the coarse-grained material (figs. 1e and f), may be taken as an indication that the driving force for its formation has decreased much faster in the fine-grained material, as expected from the effect of grain size on the rate of decrease of the carbon content. Furthermore, in view of this effect, one should expect to find more and more of the eutectic-like discontinuous precipitation with the coarser grain sizes.

In a binary alloy, the driving force for discontinuous precipitation does not change with time, unless there is a competing reaction, and the precipitation does not stop until the whole volume has been transformed. The fact that only a minor part of the volume was reacted in the present alloy is easily explained by the gradual decrease of the carbon content. This is a true ternary effect and depends upon the fact that the reaction makes use of volume diffusion of one alloying element, carbon, and boundary diffusion of another alloying element, chromium.

4.2. Mechanism of Grain Boundary Migration

Discontinuous precipitation may be defined as the simultaneous precipitation of a new phase and the migration of a matrix grain boundary taking place under some co-operation between the two processes. There is a chemical driving force for the precipitation, but the nature of the driving force for the grain boundary migration is not clear. At least four mechanisms have been suggested:

(i) Plastic deformation causes grain boundary migration if the temperature is sufficiently high and results in recrystallisation. Two decades ago it was generally believed that essentially the same mechanism operated in discontinuous precipitation [9].

(ii) A particle that nucleates at a grain boundary may often have a close orientation relationship to one of the two matrix grains and the surface energies may then favour the growth of this grain in contact with the particle [10].

(iii) The concentration gradient in a depleted zone gives rise to coherency stresses if the lattice parameter varies with the alloy content. This may provide a driving force for the migration of a boundary into the stressed region [11].

(iv) A driving force may be supplied thermodynamically if the grain boundary migration is sufficiently rapid to make the concentration profile so steep that there is a deviation from local equilibrium between the grain boundary material and the retracting grain [12].

All four mechanisms seem to have a sound physical basis and may each be of importance. Extensive studies are needed in order to clarify their roles in various cases. Some conclusions may be drawn from the present study.

In order to operate, mechanisms (iii) and (iv) need a high concentration gradient. The observation of a sharp concentration step at the migrating boundaries, made by means of the present etching technique, thus indicates that they could operate in the present case. However, the fact that the effect of chromium on the lattice parameter of austenite is very small [13] seems to rule out mechanism (iii).

The bulging out of the grain boundary without being accompanied by the precipitate phase, as shown most typically in figs. 1c-e, indicates that mechanism (ii) is not operative. On the other hand, a favourable orientation relationship between the precipitate and the growing grain may be important for the establishment of the high degree of co-operation which yields a eutectic-like geometry (fig. 1g). It seems probable that the orientation relationship was not particularly favourable in figs. 1d-f, where the resulting structure is very irregular. It is interesting to note that a similar geometry was observed by Sulonen [14] in a case where the precipitate phase was a liquid and no orientation relationship could exist.

A comparison between the fine-grained material in unstressed and stressed conditions indicates that mechanism (i) operates very efficiently in the stressed condition. It should be observed that this is not simply a case of recrystallisation, because the grain boundary migration caused changes in composition which were revealed by the etching technique. It seems unlikely that mechanism (i) could operate in the unstressed condition.

An important question which remains to be answered is how the steep concentration gradient which is necessary to make mechanism (iv) operate, is initially formed. The following sequence of events may be suggested. Initially, precipitate particles form at the grain boundaries. After some precipitation, a readjustment of the positions of the grain boundaries occurs, possibly by means of mechanism (ii) or by purely geometric reasons. Mechanism (i) may dominate in a creep specimen. Once an element of the grain boundary has started to move, a steep concentration gradient will automatically develop and mechanism (iv) can operate and make the boundary bulge out.

5. Conclusions

(*a*) Discontinuous precipitation of $M_{23}C_6$ carbide has been observed in an austenitic stainless steel.

(*b*) The discontinuous fashion of the precipitation reaction is more evident in creep specimens than in unloaded ones and more evident in coarse-grained specimens than in fine-grained ones.

(*c*) The grain boundaries are often observed to bulge out far ahead of the precipitate. This indicates that discontinuous precipitation cannot be explained solely by the effect of a favourable orientation relationship.

(*d*) An etching technique was applied which revealed that there is a steep concentration gradient in the matrix ahead of a migrating grain boundary. This indicates that the driving force for the boundary migration may come from a deviation from chemical equilibrium.

(*e*) A large variety of geometries was observed and might depend upon different orientation relationships.

(*f*) A number of observations can be explained as ternary effects:

(i) The depleted zone at the initial position of a grain boundary can be filled in at a later stage by an intersecting grain boundary.

(ii) The fine-grained material showed very little precipitation outside the initial position of the grain boundaries.

(iii) The discontinuous precipitation stops already after a minor part of the volume has been transformed.

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