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Effect of extrinsic grain-boundary dislocations on $M_{23}C_6$ precipitate nucleation in an austenitic stainless steel

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From a comparison of the isothermal precipitation curve for $M_{23}C_6$ grain-boundary precipitates in an austenitic stainless steel and of the spreading times of extrinsic grain-boundary dislocations (EGBDs), it has been shown that $M_{23}C_6$ precipitates cannot directly nucleate on EGBD lines lying on random high-angle grain boundaries. This process can occur only on coherent and incoherent twin and other special boundaries.

1. Introduction

The grain-boundary precipitation process is the determinant of a number of properties of aged alloys. It seems that one of the important factors connected with grain-boundary precipitation is the dependence of the precipitate nucleation process on grain-boundary dislocations.

Recently Jones *et al.* [1–3] investigated precipitation of NbC particles at grain boundaries in an austenitic stainless steel. They concluded that extrinsic grain-boundary dislocations (EGBDs) were the principal nucleation sites. Pumphrey and Gleiter [4], however, have found that EGBDs in austenitic steel are incorporated in a boundary by a spreading of their cores after 30 sec heating at 500° C. Alternatively, Pond and Smith [5] suggested that incorporation of EGBDs into the grain boundary occurs by dissociation of these dislocations followed by line rotation. However, other recent experimental [6] and theoretical [7, 8] work supports the idea that the spreading process occurs by the widening of the EGBD core.

As the precipitation temperature of NbC particles was 930° C, the question arises as to how NbC particles could nucleate at this temperature on the EGBD lines which disappeared at approximately 500° C.

To explain the role of EGBDs in precipitate nucleation, the times required for EGBDs spreading at constant temperature were compared with the isothermal precipitation curve for $M_{23}C_6$ carbides at grain boundaries determined with the aid of an electron microscope.

TABLE I Chemical composition of the steel investigated

C	Cr	Ni	Si	Mn
0.142	22.45	19.08	0.56	1.20

2. Experimental details

The material used in the investigation was an austenitic stainless steel of the composition shown in Table I. The initial phase which precipitates at grain boundaries in this particular type of steel during the heat-treatment procedure used is $M_{23}C_6$ carbide [9].

Rods, 3 mm diameter, were solution-treated at 1150° C for 1 h and subsequently quenched in water. Thin foils of the above material were observed in a Philips EM 300 electron microscope. At grain boundaries, no small precipitates were observed; large $M_{23}C_6$ carbides were occasionally seen both at grain boundaries and in the matrix. It can, therefore, be concluded that the cooling rate was sufficient for a solid solution to be obtained.

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Solution-treated rods were cut into slices, about 0.2 mm thick, to be aged in the temperature range 500 to 1000° C, for different periods of time and then again quenched in water. Grain boundaries in such foils prepared from the above material were subsequently examined to obtain an isothermal precipitation curve for $M_{23}C_6$ grain-boundary precipitates.

Several rods were slightly deformed in the supersaturated state and after being aged for 50 sec at 700° C. Thin foils were then examined in the heating holder of the electron microscope in order to observe the spreading of extrinsic grain-boundary dislocations. Observation of annealed boundaries was made with a change in the excitation of the first condenser lenses and with the excitation of the second condenser lenses adapted to the former. The illuminated area on the specimen is then considerably smaller. This observation technique developed from the fact that the heating sequence with an electron beam switched off, which was used by Pumphrey and Gleiter [4], did not show any positive results because of the very rapid oxidation of the thin foil.

TABLE II The times elapsed before the first $M_{23}C_6$ carbides precipitated at grain boundaries were observed

Ageing temperature (° C)	Time (sec)	Ageing temperature (° C)	Time (sec)
500	7800	800	5–10
600	1800	900	2–5
700	30–40	1000	1–5

3. Correlation between the nucleation of $M_{23}C_6$ carbides at grain boundaries and the spreading of EGBDs

The times elapsed before the first carbides were observed on grain boundaries during ageing in the temperature range 500 to 1000° C are shown in Table II. After ageing, during periods of time shorter than those presented in Table II, no precipitates at any grain boundary were observed (about one hundred boundaries were examined for each particular temperature). Typical examples of images of precipitated carbides are shown in Fig. 1. On the basis of the data given in Table II, an approximate isothermal precipitation curve for $M_{23}C_6$ grain-boundary precipitates was drawn (Fig. 2). The disappearing times of EGBDs are also marked. Spreading experiments were made on grain boundaries with precipitated carbides (after ageing at 700° C for 50 sec deformation), and also on precipitate-free boundaries (after solution-treatment and deformation). Detailed

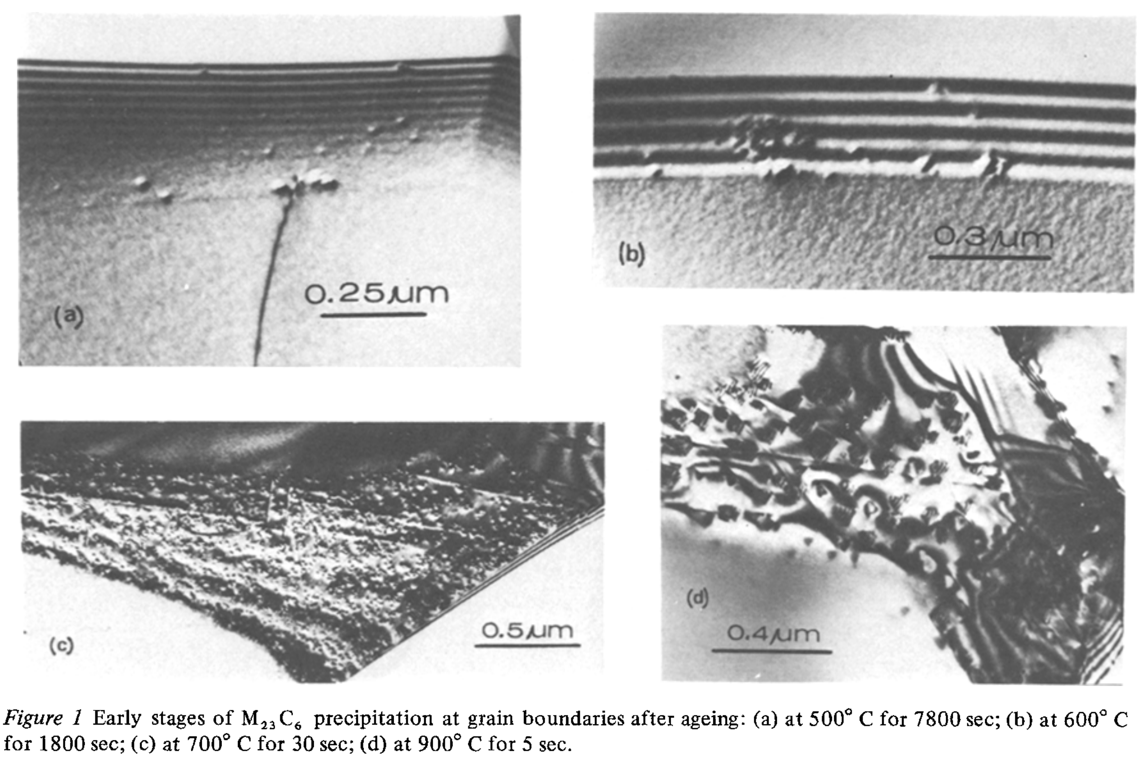

Figure 1 Early stages of $M_{23}C_6$ precipitation at grain boundaries after ageing: (a) at 500° C for 7800 sec; (b) at 600° C for 1800 sec; (c) at 700° C for 30 sec; (d) at 900° C for 5 sec.

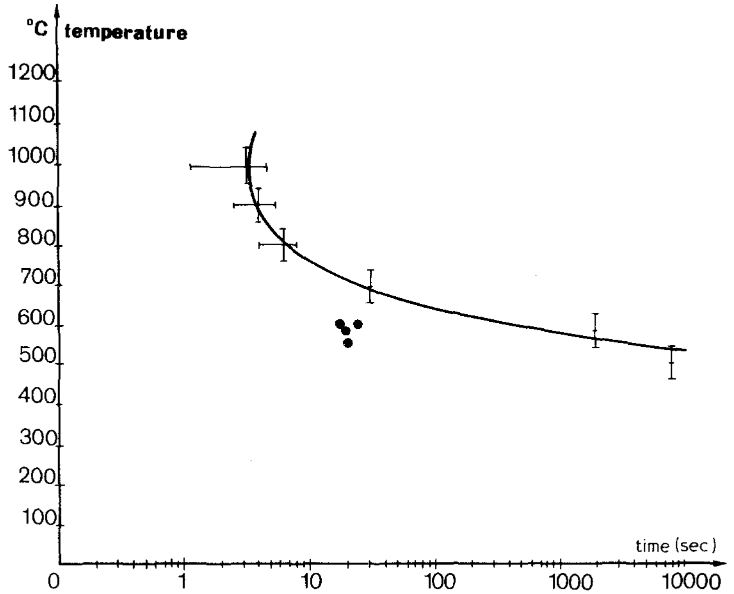

Figure 2 Approximate isothermal precipitation curve for $M_{23}C_6$ grain-boundary precipitates in the steel investigated. Black dots denote the disappearance times of EGBDs.

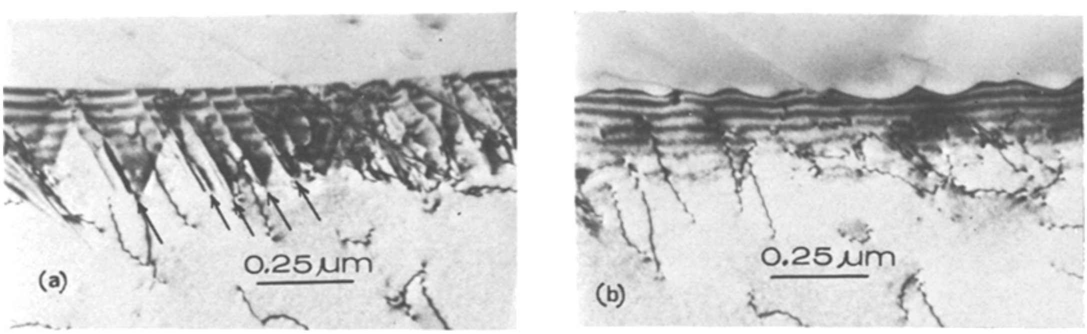

Figure 3 Bright-field micrograph of a grain boundary in austenitic stainless steel, (a) at room temperature, EGBDs arrowed, (b) after *in situ* heating at 600° C for 17 sec. EGBD images disappeared. Grain boundary with precipitated carbides.

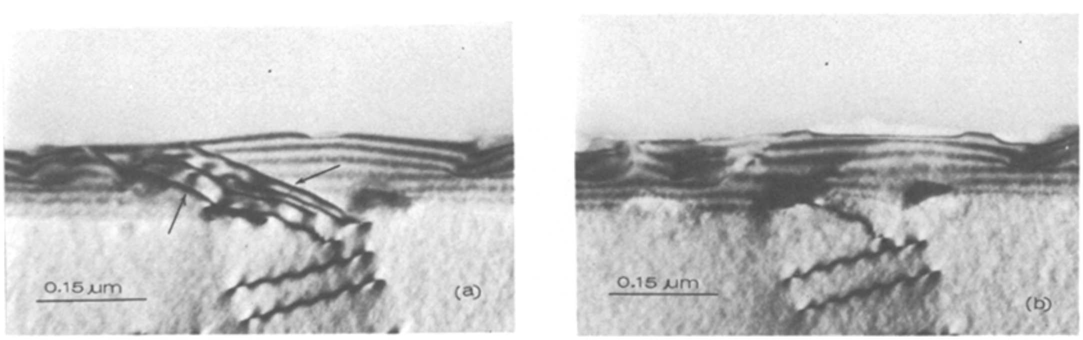

Figure 4 Bright-field micrograph of a grain boundary, (a) at room temperature, EGBDs arrowed, (b) after *in situ* heating at 545° C for 20 sec. EGBD images disappeared. Boundary with precipitated carbides.

procedure of *in situ* heating experiments will be published separately. It must be noted, however, that on the majority of the boundaries, the EGBDs disappeared at 600° C after an average time of about 20 sec (Fig. 3), irrespective of whether precipitate particles were present or not on the grain boundaries. Only sporadically, on some of the boundaries with precipitated carbides, did the EGBDs disappear at 550° C after the same time as at 600° C (Fig. 4). In particular, the EGBDs were

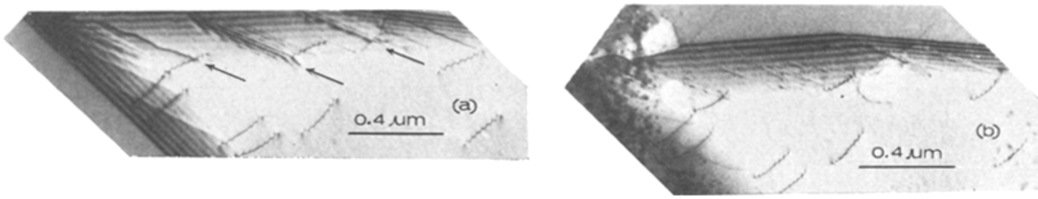

Figure 5 Bright-field micrograph of an incoherent twin boundary, (a) at room temperature, EGBDs arrowed, (b) after *in situ* heating at 700° C for 45 sec. EGBD images disappeared.

extremely stable up to high temperatures on coherent and incoherent twins (Fig. 5) and other special (coincidence) boundaries [10]. From a comparison of the spreading times of EGBDs at 600° C with the time after the lapse of which carbides were observed at some grain boundaries after ageing at 600° C (cf. Fig. 1b and Fig. 3), it is evident that the spreading time is 100 times shorter than the time required in order that grain-boundary precipitates may be observed in an electron microscope. It may, therefore, be presumed that $M_{23}C_6$ carbides are in no way likely to nucleate directly to EGBD lines as was suggested by Adamson and Martin [11]. The work of Jones *et al.* [1–3] is related to the precipitation of NbC in austenitic steel and, at the ageing temperature (~ 930° C), the incubation time for the precipitation of NbC is extremely short such that precipitation on EGBDs may well be possible. On the other hand, however, one can estimate using the data from Pumphrey and Gleiter's [4] work, that the spreading time of EGBDs in austenitic steel at 930° C, is about 5×10^{-3} sec. Therefore, it seems unlikely that the incubation time for NbC precipitates at this temperature is of a comparable order.

The isothermal precipitation curve represents the period which is required for the particles to grow to a size observable in an electron microscope. It cannot, therefore, be ruled out that precipitates nucleated on EGBD lines much earlier than they were observed in the electron microscope, and that they stabilized EGBD lines during further high-temperature annealing. This idea was recently developed by Howell *et al.* [12]. To check the above possibility, the initial stages of precipitate growth were examined.

3.1. Precipitate growth

Growth kinetics were studies in detail for $M_{23}C_6$ at 700° C. Average precipitate radii R as a function of the ageing time are give in Table III. It is generally accepted that the relationship which exists between an average precipitate size and the time, has the form $r = k \cdot t^n$ [13–17]. However, for the purpose of the present work, it was assumed that the incubation time cannot be disregarded and the law of growth, therefore, takes the form $R = k \cdot (t - \tau)^n$, where τ is the incubation time. Using values from Table III, parameters k and n, and also the incubation time, were calculated by the regression method. Approximate results are shown in Table IV. Thus, it follows that the growth of $M_{23}C_6$ carbides on grain boundaries at 700° C obeys the relationship

$$R = 23.71\,(t - 26)^{0.413}. \quad (1)$$

It is evident that the incubation time is considerable. The rate of growth from $R \simeq 0$ (at first approximation it can be assumed that the critical nucleus size is close to zero) to $R = 44$ Å (after 30 sec ageing) therefore equals 10 Å sec^{-1}, and the

TABLE III Experimentally observed changes of average precipitate radius versus ageing time at 700° C

Ageing temperature (° C)	Ageing time (sec)	Number of measurements of particle diameter	Average precipitate radius R (Å)	Confidence intervals for confidence limit 0.95 (Å)
700	30	48	44	± 6
	40	28	54	± 4.2
	60	114	135	± 19.5
	300	262	225	± 9.7

TABLE IV Calculated values of k and n in growth relationship $R = k(t - \tau)^n$

$k\left(\dfrac{\text{Å}}{\sec^{0.413}}\right)$	n	Incubation time, τ (sec)	Correlation coefficient r^2
23.71	0.413	26	0.911

carbides grow very rapidly in the earliest stages of their development.

Analysis of the growth kinetics for $M_{23}C_6$ carbides at 600° C was not as detailed as that made at 700° C, because of the considerably longer period of time required for the particles to grow to a definite size for each ageing time. However, it may reasonably be assumed that the rate of growth changes with temperature in the same manner as the grain-boundary diffusion coefficient. Using the value of the average activation energy for grain-boundary diffusion in austenitic steel [18], it is found that $D_{(700)} = 13.3D_{(600)}$. Thus, it follows that the rate of growth at 600° C in the earliest stage of carbide development is 13 times slower than at 700° C, being approximately equal to 0.75 Å $\sec^{-1}$. The average precipitate radius following annealing at 600° C for 1800 sec (see Table III) was $R = 155$ Å. The time required for the particles to grow from $R \simeq 0$ to $R = 155$ Å with a growth rate of 0.75 Å $\sec^{-1}$, is approximately 200 sec, and the incubation time approximately 1800–200 = 1600 sec, i.e. 80 times more than the spreading time at the same temperature. In consequence, the probability of correctness of the hypothesis that precipitates nucleate at EGBD lines and then stabilize them, seems to be extremely unlikely.

Direct nucleation of precipitates on EGBD lines is, however, possible on coherent and incoherent twins and other special boundaries, because EBGDs in such boundaries are extremely stable up to high temperatures, compared with random high-angle grain boundaries (see Fig. 5 and compare with Fig. 4). On random boundaries the effect of EGBDs on the precipitation process is indirect. Jones *et al.* [1–3] have found that the average size of grain boundary NbC carbide increases as the amount of previous cold-work is increased (this is probably the result of the increased density of EGBDs). Pumphrey [19] and Gleiter [20], on the other hand, have shown that after the spreading of EGBDs, boundaries are in a non-equilibrium state. Therefore, it may be supposed that the more "open" structure of such non-equilibrium boundaries accelerates both the growth and coarsening of grain-boundary precipitates by an increased diffusion of solute in a grain boundary plane.

5. Conclusions

Precipitates of $M_{23}C_6$ carbide cannot directly nucleate onto EGBD lines and stabilize such lines lying on random grain boundaries, because the EGBDs spread considerably more rapidly than stable nuclei may be formed. Direct nucleation of precipitates onto EGBD lines is only possible on coherent or incoherent twin boundaries (or other special boundaries) because the spreading time on this type of boundary and the time required for the formation of stable nuclei, may be of the same order of magnitude.

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