JOURNAL OF MATERIALS SCIENCE 18 (1983) 3213–3218

The effect of quenched-in vacancies on the martensitic transformation

T. Y. HSU (XU ZUYAO), YAN LINFAH
Department of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai, China

Experimental results show that in some decarburized Fe–Ni alloys, values of M_s decrease (and strength increases) with the increase in quenching temperature above 900° C with definite grain size of the parent phase. After short-time annealing of the quenched specimen, M_s values increase and strength decreases. According to the nucleation model suggested by Olson and Cohen and the observation of the fault nucleation by Smallman *et al.*, a model of the interaction of clustered point defect (vacancies) with partial dislocation is presented. It is suggested that the lowering of M_s is due to the pinning of clustered vacancies to partial dislocation, hindering the nucleation of martensite. Preliminary TEM observations of the substructure of austenite has confirmed this view. From this experiment the energy of formation of a vacancy is found to be 1.2 to 1.4 eV, which is in good agreement with the known values for Fe–Ni. The activation energy obtained in the annealing process is 0.18 eV, corresponding to the dissociation energy of the divacancies. The effect of quenching stress is also taken into consideration and it is concluded that the moderate cooling rate of 2500° C sec^{-1} seems just suitable for studying the effect of quenched-in vacancies on M_s.

1. Introduction

Our previous published work [1] revealed that M_s decreases and the yield strength of the parent phase increases with the increase in quenching temperature in Fe–Ni alloys with various carbon contents, and with definite equal grain size. After annealing of the quenched specimen, the yield strength of the parent phase decreases and M_s increases. The activation energies for the annealing process are 0.21 and 0.27 eV in Fe–29.87 wt % Ni alloy with 0.057 wt % C and 0.008 wt % C (after decarburizing) respectively, of the same order of magnitude as the calculated values for the dissociation of divacancies, and it is proposed that the quenched-in divacancies play an important role in hindering the nucleation of martensite. Based on the successive works on nucleation of martensitic transformation, Olson and Cohen [2] developed a fault nucleation model describing nucleation as propagation of partial dislocations. Brooks *et al.* [3] confirmed the effect of stacking fault directly on the nucleation process using high voltage transmission electron microscopy (TEM) observations. Some current theories concerning the interaction of vacancies with dislocations [4–6] or twin boundaries [7] have also been suggested. This work attempts to reproduce our previous results in greater detail and draw an explicit conclusion concerning the function of quenched-in clustered vacancies on M_s in decarburized Fe–Ni alloys.

2. Experimental details

Fe–29 wt % Ni, Fe–30 wt % Ni and Fe–31 wt % Ni alloys were vacuum-melted annealed, drawn to wire with 0.8 mm diameter and decarburized to various carbon contents (most of them in the range 0.01–0.02 wt % C). A wire 2 cm in length, was austenitized firstly above 1100° C in vacuum or in argon atmosphere to obtain a constant grain size of ASTM no. 4, and then quenched in alcohol from different temperatures with a cooling rate of 2500° C sec^{-1}. Such a rate is just suitable for the purposes of this study, since too high a rate will induce considerably quenching stresses which

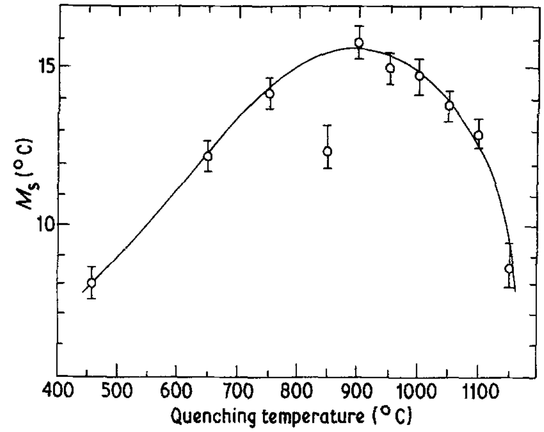

Figure 1 M_s against quenching temperature in Fe–29 wt % Ni–0.01 wt % C alloy which has first been austenitized at 1160° C.

might affect M_s and may increase the density of dislocation which in turn causes the loss of vacancies [8], while too low a rate will facilitate the annihilation of quenched-in vacancies.

Values of M_s or M_b were determined by means of resistance measurement and the error in M_s (or M_b) was measured to within ± 0.5° C. The whole procedure for M_s measurement was accomplished within less than 8 min. M_s values of quenched specimens after annealing for up to 2 h were also determined. Vickers hardness values were measured on plate specimens after simulating the quenching and annealing performed on the wire specimen.

A comparison of dislocation configurations in austenite between the specimens quenched from 1160 and 900° C (after austenitizing at 1160° C) was conducted using TEM.

The stress distribution of quenched specimens was taken into consideration and determined by Vickers hardness, H_V, measurements. In this work alcohol was used as the quenching medium. The cooling curves of various quenching mediums have been determined carefully and the result is analogous with that of Jackson's work [9]. The measured maximum cooling rate was about 2500° C sec^{-1} when alcohol was used as quenching medium, and it became 20 000° C sec^{-1} when water was the quenching medium; this result is consistent with the calculated results of Wu and Wang [10, 11]. There would be rather low stresses formed in the quenched specimen with a cooling rate of 2500° C sec^{-1}. Use of such a rate would guarantee a negligible effect of stress on M_s and also no considerable dislocations induced by quenching.

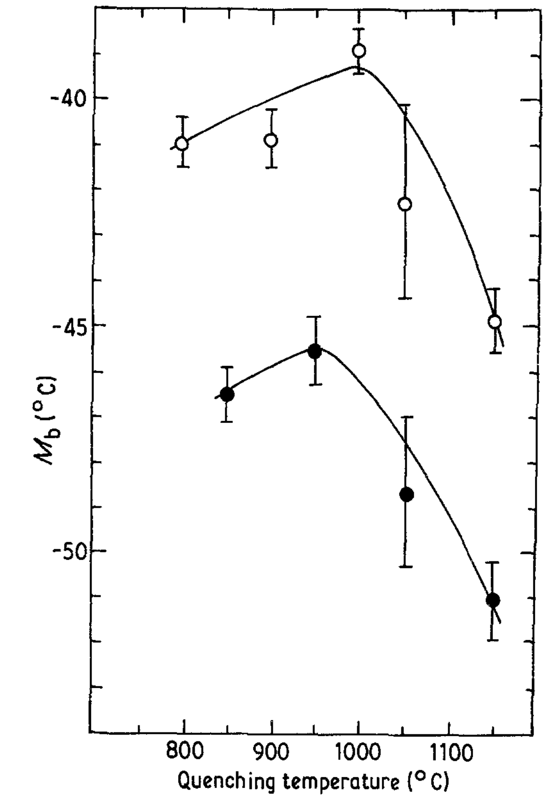

Figure 2 M_b against quenching temperature in Fe–31 wt % Ni–0.02 wt % C (open circles) and Fe–31 wt % Ni–0.023 wt % C (closed circles) alloys after first austenitizing at 1150° C.

3. Results

The experimental results of M_s against quenching temperature in various alloys, as shown in Figs. 1 to 4, reveal identical characteristics: M_s decreases with increasing quenching temperature when the quenching was above 900° C (Figs. 1 to 3) or 800° C (Fig. 4), and M_s decreases with decreasing

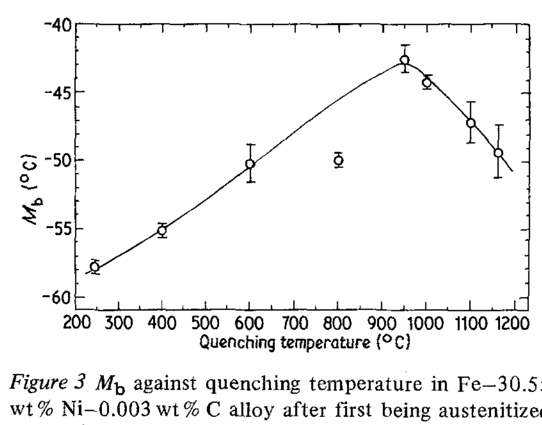

Figure 3 M_b against quenching temperature in Fe–30.55 wt % Ni–0.003 wt % C alloy after first being austenitized at 1160° C.

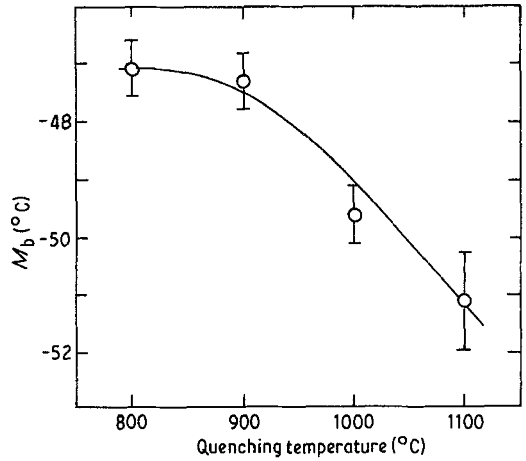

Figure 4 M_b against quenching temperature in Fe–31 wt % Ni–0.012 wt % C after first being austenitized at 1100° C.

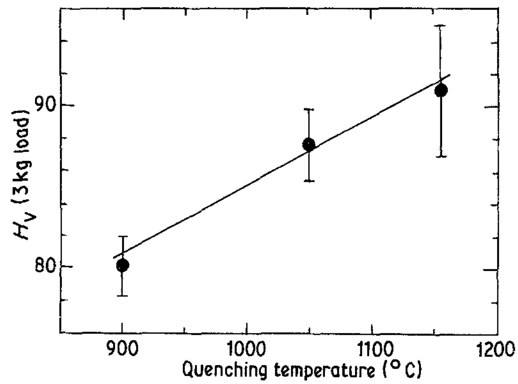

Figure 6 H_V against quenching temperature in Fe–30 wt % Ni–0.03 wt % C alloy.

quenching temperature when quenching was below about 900° C (Figs. 1 to 3).

Equal grain sizes of austenite were obtained by first austenitizing certain temperatures indicated in the figures.

M_s decreases after annealing of the quenched specimen following quenching from 900° C, like the phenomenon shown in the work on thermal stabilization in Fe–Ni–C [12]. As annealing following quenching at 1160° C, M_s increases after annealing for less than 1 h, and prolonged annealing again leads to thermal stabilization as shown in Fig. 5. H_V values (3 kg load) of the parent phase after quenching, and those from quenching followed by annealing are shown respectively in Figs. 6 and 7, in comparison with Fig. 5, showing that M_s is inversely proportional to the strength of the parent phase.

Quenching stress is expressed through measurement of H_V (100 g load) at room temperature across the specimen (0.8 mm diameter) from various heat treatments of Fe–31 wt % Ni–0.012 wt % C alloy in the austenite state, shown in Fig. 8a, indicating slight stress existing in the surface, and Fe–29 wt % Ni–0.01 wt % C alloy in the form of a partly transformed state, shown in Fig. 8b, indicating lower hardness on the surface of specimen. It is known that tensile stresses may promote and compression stress may hinder the martensitic transformation. Metallography has confirmed, in the partly transformed specimen, that there is a considerable amount of martensite formed at the centre but no martensite around the very thin rim, about 50 μm in width. During quenching, the higher the quenching temperature the higher will

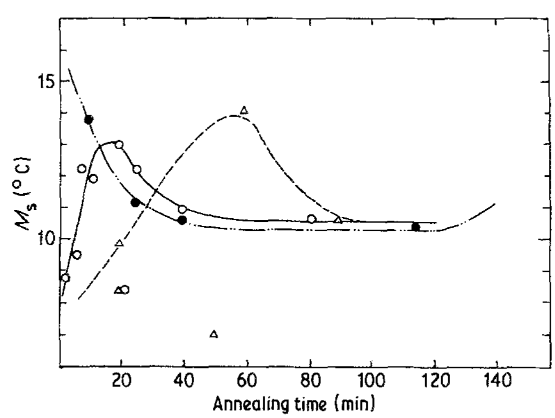

Figure 5 M_s against annealing time in Fe–29 wt % Ni–0.01 wt % C alloy: –○– 1160° C quenching, 100° C annealing; –●– 900° C quenching, after first austenitizing at 1160° C, 100° C annealing; – – △ – – 1160° C quenching, 25° C annealing.

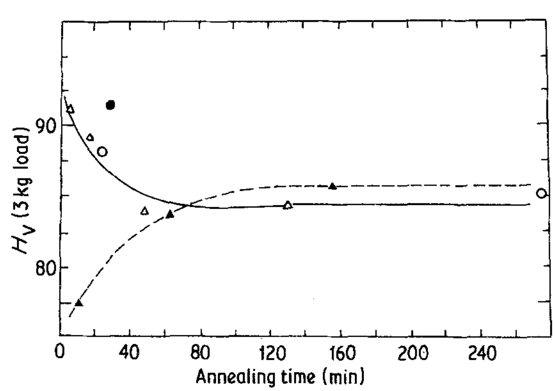

Figure 7 H_V against annealing time in Fe–30 wt % Ni–0.03 wt % C alloy: –△– 1160° C quenching; ○ 1050° C quenching, after first austenitizing at 1160° C; – – ▲ – – 1160 to 900° C quenching, after first austenitizing at 1160° C; ● 1160° C air cooling.

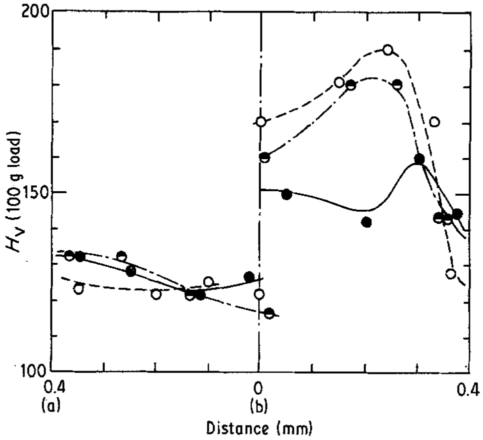

Figure 8 H_V (100 g load) values across section of specimens: (a) Fe–31 wt % Ni–0.012 wt % C alloy, (b) Fe–29 wt % Ni–0.01 wt % C alloy. —·–•–·— water quenching at 1160° C; –•– alcohol quenching at 1160° C; – –o– – alcohol quenching at 900° C, after first austenitizing at 1160° C.

be the stress induced and M_s may increase by inner tensile stress, but this is not the case in this investigation, as shown in Figs. 1 to 3, when the specimen has been quenched from temperatures above 900° C. Therefore, the effect of stress on M_s in this work is very small owing to the moderate cooling rate used in all the quenching processes as mentioned above.

TEM observations of Fe–31 wt % Ni–0.04 wt % C alloy revealed that there are straight and nearly parallel dislocation lines in austenite quenched from 900° C (Fig. 9a) but bowed dislocation lines and moderate amounts of dislocation loops in austenite quenched from 1160° C (Fig. 9b), both with austenite grain sizes equal to that of ASTM no. 4.

4. Discussion

From experimental results (Figs. 1 to 3), as quenching from temperatures below 900° C, M_s increases with the increase in quenching temperature. That might be due to the formation of Cottrell atmosphere by carbon, and may also be the result of the Suzuki effect. While quenching from temperatures above 900° C, M_s decreases with the increase in quenching temperature (Figs. 1 to 4). This phenomenon, repeating the result of our previous work, may be the result of the interaction of quenched-in vacancies with partial dislocations. Since single vacancies annihilate more easily, this work focuses on the pinning effect of clustered vacancies on partial dislocations. According to the nucleation model suggested by Olson and Cohen [2], the shearing stress required to drive the partial dislocation, τ, is proportional to the stacking fault energy which increases with increasing ΔG^{chem}. As the partial dislocation was pinned by vacancies, $\Delta\tau$ may be proportional to

$$\Delta\tau \propto \frac{\partial \Delta G^{\text{chem}}}{\partial T} \Delta T \qquad (1)$$

where ΔT is ΔM_s in the case of this work. It is known that within a range of temperatures, $\partial \Delta G^{\text{chem}}/\partial T$ is nearly constant in Fe–Ni [13]. $\Delta\tau$

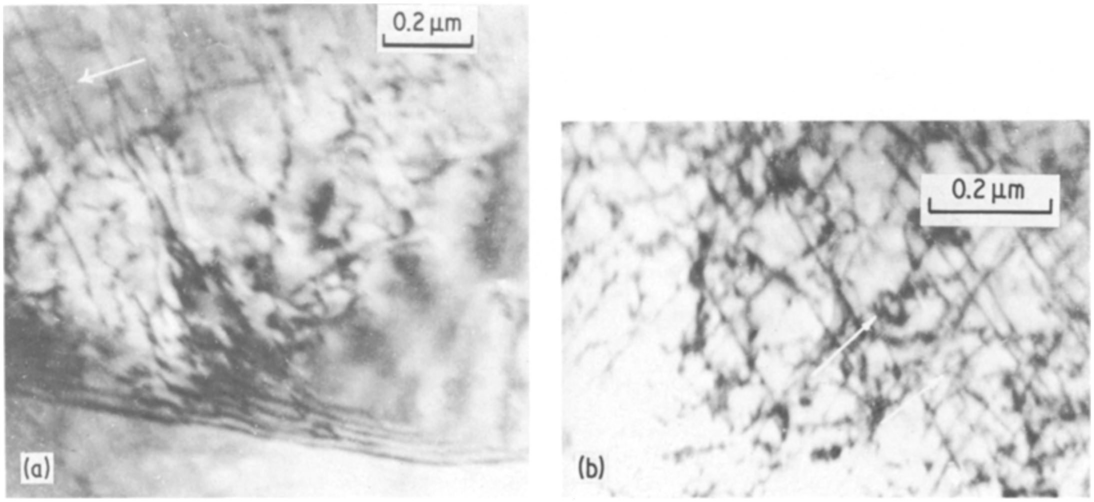

Figure 9 Substructure in austenite of Fe–31 wt % Ni–0.04 wt % C alloy quenched from 900° C (a) and 1160° C (b) with grain size the same as that in ASTM no. 4.

is also proportional to the concentration of vacancies pinning the partial dislocation, so we have:

$$\Delta M_s = A \exp\left(\frac{-Q+W}{KT_q}\right) \qquad (2)$$

where A is a constant including the entropy factor, W is the interaction energy of point defects with dislocations and supposed to vary little within the quenching temperatures, T_q, studied, and Q is formation energy of vacancies and is given by

$$Q = nE_v^f - E_{nv}^B \qquad (3)$$

in which $n = 1$ for single vacancies, $n = 2$ for divacancies, and $n \geqslant 3$ for clustered vacancies. E_v^f is the formation energy of single vacancies, E_{nv}^B is the binding energy of clustered defects containing n vacancies and

$$E_{nv}^B = nE_v^f - E_{nv}^f \qquad (4)$$

Taking 900° C as the reference quenching temperature for Fe–29 wt% Ni–0.01 wt% C alloy (see Fig. 1) and 800° C for Fe–31 wt% Ni–0.012 wt% C alloy (see Fig. 4), we obtain $(-Q+W) = -1.59$ and -2.1 eV respectively. Clustered vacancies of $n > 3$ are more stable but there are no available data on $E_{>3v}^B$ yet. We have to take $E_{2v}^B =$ 0.25 eV as in nickel [14]. If there exists interaction of screw dislocations with vacancies, referencing $W = 0.27$ eV in bcc isotropic metal [6] we may take $W = 0.50$ eV for divacancies. By applying the experimental data and using Equations 2, 3 and 4, we obtain $E_v^f = 1.2$ and 1.4 eV for 29 and 31 wt% Ni alloys respectively. These values are close to 1.80 eV [15] and 0.73 eV [10, 11] for Fe–Ni alloy. If we suppose $W = 0$, we get $E_v^f =$ 0.92 and 1.17 eV that are also consistent with the known data 0.73 to 1.80. Since the SFE in Fe–Ni with nickel content below 40 at% is rather high [16] and SFE will increase with the increase in quenching temperature, the screw dislocations almost would not propagate above the reference temperature, and the carbon concentration around the screw dislocation would nearly equal the average value. So, during quenching from temperatures above the reference temperature, M_s may depend only on the pinning effect of clustered vacancies and in turn of its concentration around partial dislocations.

From Fig. 5, we can obtain the activation energy of the initial annealing process in Fe–29 wt% Ni–0.01 wt% C alloy is 0.18 eV. During the initial annealing, the clustered vacancies may dissociate. As divacancies are taken into consideration, the dissociation energy will be $E_{2v}^B + \frac{1}{2}E_v^m$, where E_v^m is the migration energy of a single vacancy, being 0.9 to 1.1 eV [15] 1.81 eV [10, 11] in Fe–Ni. Taking $E_{2v}^B = 0.2$ eV, $E_v^m =$ 1.0 eV, yields the dissociation energy of 0.7 eV, which is of the same order of magnitude as the experimental values of this work (0.18 eV) and previous work (0.27 eV [1]).

Another mechanism which may also be suggested is the interaction of carbon atoms with vacancies during annealing, and the interaction energy Q_{Cv} will be:

$$Q_{Cv} = E_C^m - E_{Cv} \qquad (5)$$

where E_C^m is the migration energy of carbon in Fe–Ni and E_{Cv} the dissipation energy induced from the trapping of a carbon atom by a vacancy. Taking $E_C^m = 1.2$ eV from [10, 11] and $E_{Cv} =$ 0.8 eV from α-iron [17], we get $Q_{Cv} = 0.4$ eV using Equation 5, which is in good agreement with the experimental value activation energy (0.18 eV). After annealing for longer time, the decrease in M_s may be due to the thermal stabilization of austenite.

Bowing of dislocations and the occurrence of dislocation loops in austenite quenched from higher temperature (e.g. 1160° C) as shown in Fig. 9b, indicates the consequence of condensation of quenched-in vacancies around dislocations [18], which results in the strengthening of austenite (Fig. 7). Straight and nearly parallel dislocation lines in the parent phase existing from low-temperature quenching (e.g. 900° C), in Fig. 9a, may be the ideal configuration of dislocations to nucleate martensite, which leads to higher M_s values (Figs. 1 to 3).

5. Conclusions

This work reproduces our previous experiment results on Fe–Ni alloy, showing that M_s decreases with the increase in quenching temperature after austenitization at constant temperature, and studies this phenomenon in more detail. The effect of quenched-in vacancies on the martensitic transformation occurs after quenching from higher temperatures, i.e. forming a higher concentration of vacancies through the interaction of clustered vacancies with partial dislocations, hindering the nucleation of martensite. Preliminary TEM observations of the substructure of austenite seems to confirm this view. After annealing of the quenched specimens for a short time, M_s increases owing to the dissociation of clustered vacancies or the trapping of carbon atoms by vacancies. Prolonged annealing leads to the lowering of M_s because of the thermal stabilization of the parent phase. From the activation energies of the lowering of M_s, the energy of formation of vacancies is found to be 1.2 to 1.4 eV, being in good agreement with the known values for Fe–Ni. The activation energy of the annealing process (ageing), 0.18 eV, corresponds to the dissociation energy of divacancies in Fe–Ni, or the interaction energy of a carbon atom and a vacancy.

Acknowledgement

The authors would like to express their sincere gratitude to Professor Morris Cohen of MIT for valuable discussions.

References

1. XU ZUYAO (T. Y. HSU), "Martensitic Transformation and Martensite" (Science Press, Beijing, 1980, 1981) pp. 370–71.
2. G. B. OLSON and M. COHEN, *Met. Trans.* 7A (1976) 1897, 1905, 1915.
3. J. W. BROOKS, M. H. LOROTTE and R. E. SMALLMAN, *Acta Metall.* 27 (1979) 1829, 1839.
4. J. O. SCHIFFGENS and D. H. ASHTON, *J. Appl. Phys.* 45 (1974) 1023.
5. K. W. INGLE and A. G. CROCKER, *Acta Metall.* 26 (1978) 1461.
6. L. L. BOYER and J. R. HARDY, *Phil. Mag.* 26 (1972) 225.
7. K. W. INGLE, P. D. BRISTOWE and A. G. CROCKER, *Phil. Mag.* 33 (1976) 663.
8. R. M. EMRICK, *J. Phys. F: Met. Phys.* 8 (1978) 1353.
9. J. J. JACKSON, *Acta Metall.* 11 (1963) 1245.
10. T. L. WU and C. M. WANG, *Acta Phys. Sinica* 14 (1958) 356.
11. *Idem, Sci. Sinica* 7 (1958) 1029.
12. K. R. KINSMAN and J. C. SHYNE, *Acta Metall.* 15 (1967) 1527.
13. XU ZUYAO (T. Y. HSU), *Acta Metall. Sinica* 16 (1980) 420.
14. R. A. JOHNSON, *Phys. Rev.* 152 (1966) 629.
15. A. CAPLAIN and W. CHAMBRON, *Acta Metall.* 25 (1977) 1001.
16. R. S. SCHRAMM and R. P. REED, *Met. Trans.* 7A (1976) 359.
17. M. MONDINO and A. SEEGER, *Scripta Metall.* 11 (1977) 817.
18. R. E. SMALLMAN, "Modern Physical Metallurgy", 3rd edn (Butterworths, London, 1970) pp. 375–6.

Received 9 February
and accepted 24 February 1983