Effect of thermal cycling and Ti_2Ni precipitation on the stability of the Ni-Ti alloys

J. KWARCIAK, Z. LEKSTON, H. MORAWIEC
Institute of Physics and Chemistry of Metals, Silesian University, 12 Bankowa, Katowice, Poland

Two near-stoichiometric Ni-Ti alloys have been investigated. One of them contained Ti_2Ni phase in the matrix, the second did not. Using high-temperature X-ray measurements and differential thermal analysis it was found that the martensitic transformation occurs in several stages, via the R phase. The reverse transformation proceeds directly from the martensite to the parent phase. Thermal cycling causes a decrease in the characteristic temperatures and heats of transformation. This is associated with an increase in the number of defects in the matrix. In the alloy containing particles of Ti_2Ni phase further precipitation takes place during thermal cycling, causing destabilizing of the structure and properties of this alloy.

1. Introduction

Bearing in mind the importance of Ni-Ti alloys for practical applications (in military equipment, industry and medicine as connectors, aerials, reflectors, safety devices, valves etc.) the influence of cyclic reversible martensitic transformations on the stability of their properties, including shape recovery and characteristic temperatures of transformations, is of particular significance. Investigations of changes in properties and structure after successive transformation cycles and post-quench ageing at relatively low temperatures have been reported in several papers [1-6]. It is known that deviation from the stoichiometric composition (50 at % Ni-50 at % Ti) as well as ageing of the Ni-Ti alloys produces precipitation of the Ti_2Ni or Ni_3Ti phases which influence the transformation temperatures [5, 7, 8].

The aim of the present investigations was to study the influence of the small amount of Ti_2Ni phase occurring in the Ni-Ti alloy on the stability of the structure and properties during cyclic reversible martensitic transformation. For this reason two near-stoichiometric Ni-Ti alloys were chosen for these studies. In one alloy Ti_2Ni precipitates were observed in the matrix, while they were not present in the second. The effect of multiple thermal cycling on the thermoelastic martensitic transformation and its correlation with structural changes were studied in both Ni-Ti alloys.

2. Experimental procedure

The alloys studied here were prepared by vacuum induction melting in a graphite crucible. The ingots were hot-rolled, homogenized for 48 h at 850° C and quenched from 500° C in ice-water. The composition of the alloys was as follows:

(a) the alloy containing particles of Ti_2Ni phase after quenching contained 50.0 at % Ni and 50.0 at % Ti;

(b) the alloy without Ti_2Ni phase in the matrix contained 50.2 at % Ni and 49.8 at % Ti.

Phase analysis of specimens was performed using a Philips diffractometer with high-temperature X-ray camera enabling observations of phase transformations during cooling and heating. Filtered Cu$K\alpha$ radiation was used. Thermal measurements (DTA) were performed with a Mettler Ta 1 thermoanalyser. Temperatures of transformations were determined from DTA and X-ray measurements. The heats of transformations were calculated from the areas under the DTA curves when multiplying by the equivalent calories per unit area. The areas under the DTA curves were delimited by the straight line from the

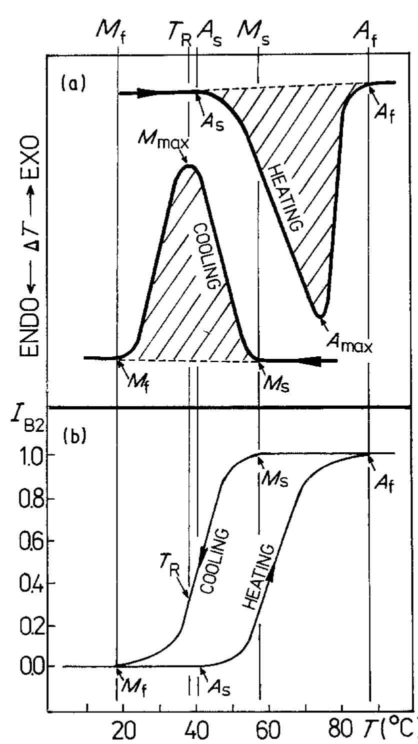

Figure 1 (a) DTA curves and (b) changes of X-ray line intensities of B2 phase for the alloy containing the Ti_2Ni phase. The rate of cooling and heating was 0.5 (° C) min^{-1}.

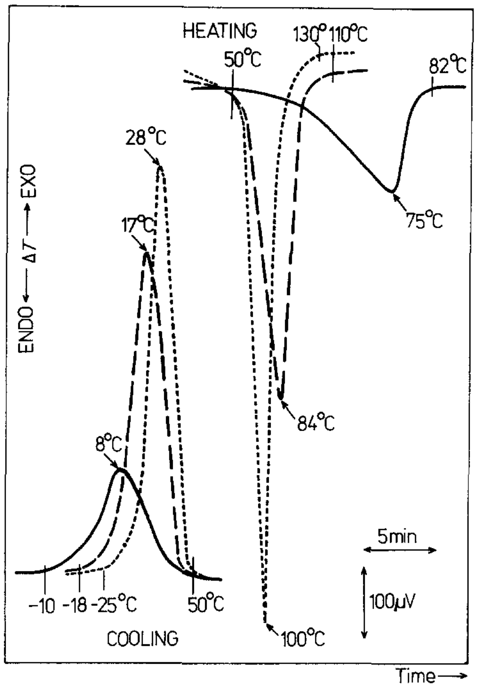

Figure 2 DTA curves for the alloy without Ti_2Ni phase obtained at different rates of heating and cooling: (—) 1, (– –) 10, (- - -) 25 (° C) min^{-1}.

beginning of the effects to the point where the DTA curves return to the baseline (see Fig. 1).

3. Results and discussion

3.1. Characteristic transformation temperatures

Characteristic temperatures of the martensitic and reverse transformations were determined by DTA

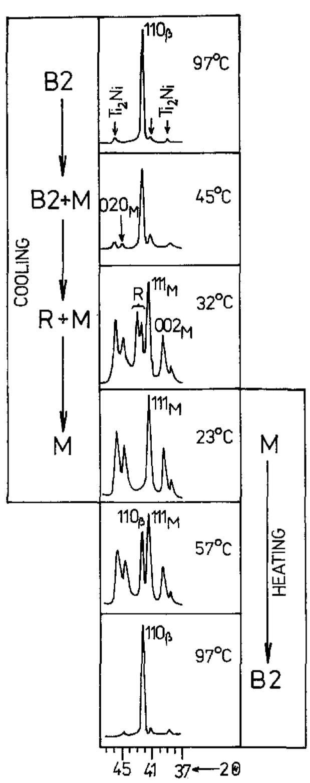

Figure 3 Scheme of the phase transformations on cooling and heating for the alloy with Ti_2Ni phase, showing how X-ray diffraction patterns change at different temperatures.

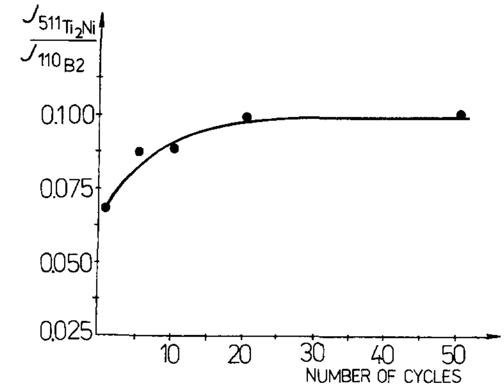

Figure 4 Increase of the Ti_2Ni phase amount with cycling for the alloy containing Ti_2Ni phase (arbitrary units).

(Fig. 1a) and X-ray measurements (Fig. 1b). As may be seen from Fig. 1, temperatures at the start of the martensite and parent phase are marked by the beginning of the DTA effects, while temperatures of finish of transformations are marked by the points of return of the DTA curves to the baseline. Characteristic temperatures, recorded during heating and cooling at a rate of 0.5 (° C) min^{-1}, for the alloy without Ti_2Ni phase are as follows: $A_s = 25°$ C, $A_f = 60°$ C, $M_s = 30°$ C, $M_f = -10°$ C and for the alloy containing Ti_2Ni phase $A_s = 45°$ C, $A_f = 90°$ C, $M_s = 57°$ C, $M_f = 15°$ C. Temperatures recorded on the DTA curves, however, depend on the rate of temperature change. Increase in the rate of cooling or heating causes a shift of temperatures of the transformations towards higher values (Fig. 2). Hence it is important to take into consideration the rate of temperature change used during measurements.

3.2. Mechanism of transformations

Analysis of X-ray measurements of phase transformations during cooling and heating showed that the martensitic transformations in both the investigated alloys takes place in stages, via the R phase, B2 → (B2 + M) → (R + M) → M (Fig. 3). The appearance of the R phase is due to splitting of the 1 1 0 line of the B2 phase [9]. The reverse transformation, however, proceeds directly from the martensite to the parent phase (M → B2). The R phase was not observed in this transformation. Analysis of DTA measurements did not indicate a martensitic transformation taking place in several stages. This is probably due to the fact that the temperature of the maximum DTA effect and the T_R temperatures (at which the R phase appears) overlap.

3.3. Heats of transformation

Heats of transformation were calculated from the area under the DTA curves in the temperature range M_s–M_f and A_s–A_f. The heat of martensitic transformation ($Q_{P\rightarrow M}$) for the alloy containing Ti_2Ni phase was 33.8 ± 2 J g^{-1} and for the alloy without Ti_2Ni phase it was 35.2 ± 2 J g^{-1}. The heat of the reverse transformation ($Q_{M\rightarrow P}$) was 25.5 ± 2 J g^{-1} for the alloy containing Ti_2Ni phase and 27.1 ± 2 J g^{-1} for the second alloy, which is equal to 0.8 times the heat of the martensitic transformation. During thermal

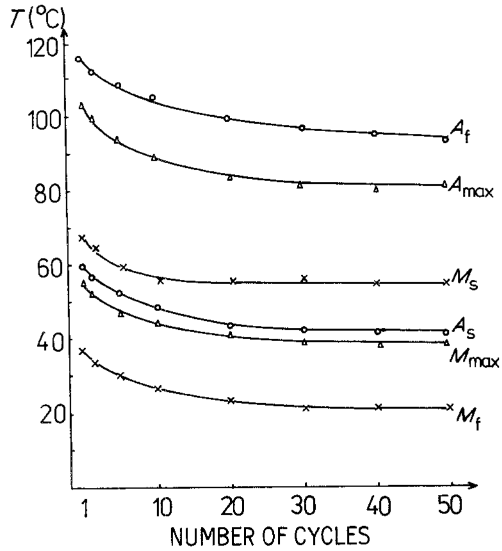

Figure 5 Variation of the transformation temperatures with cycling for the alloy containing Ti_2Ni phase, obtained from DTA measurements.

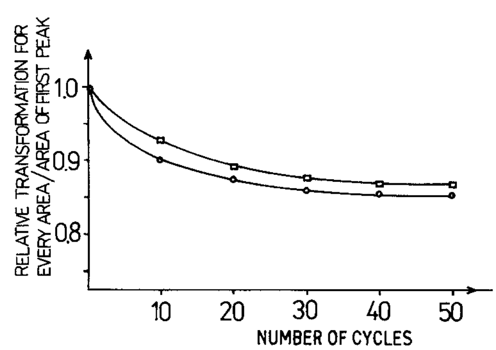

Figure 7 Variation in total heat of transformations with cycling for the alloy containing Ti_2Ni phase. (○) P → M (cooling), (□) M → P (heating).

cycling of these alloys the heats of transformation decrease but the relationship $Q_{M \rightarrow P}/Q_{P \rightarrow M}$ maintains a value of about 0.8. For the thermoelastic martensite the heats of martensitic and reverse transformations should be the same. However, in our case, the mechanism of these transformations differ. The martensitic transformation proceeds via the R phase while the reverse does not, which may be the reason for the different values of heats of transformations ascertained.

3.4. Martensitic transformation cycling effects

Samples of both alloys were heated and cooled in the temperature range from -20 to $+130°$ C. The DTA curves and X-ray results indicate that thermal cycling caused changes of the temperatures, heats of transformations and shape of X-ray lines. On the basis of X-ray measurements it was ascertained that in the alloy containing particles of Ti_2Ni phase the precipitation process proceeds further during thermal cycling, while in the second alloy this process was not observed.

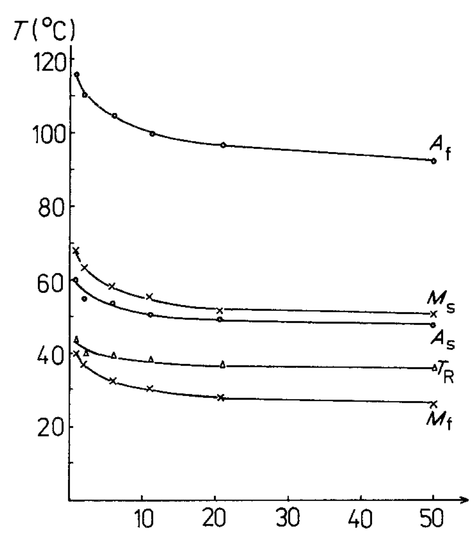

Figure 6 Variation of the transformation temperatures with cycling for the alloy containing Ti_2Ni phase, obtained from X-ray measurements.

Increase in the quantity of Ti_2Ni phase as a result of the precipitation process is shown on Fig. 4. The decrease in temperatures of transformation (Figs 5 and 6) confirms the precipitation of Ti_2Ni phase. The precipitation of Ti_2Ni phase causes an increase in the nickel content in the matrix, leading to a drop in the M_s temperature [7, 8]. The increase in quantity of Ti_2Ni phase during thermal cycling causes a decrease of the Ni–Ti matrix which is transformed during cooling and heating. As a consequence a decrease in the heats of transformation was observed since this heat is proportional to the mass of the reacting substances. A decrease of about 12% was observed in heats of transformations after 50 P ↔ M cycles, in comparison with values after the first transformation (Fig. 7). This means that about 12% of the matrix mass should precipitate as Ti_2Ni phase. The increase of nickel content should then be about 1.3% and the M_s temperature should be about $-40°$ C [7, 8]. After 50 cycles the M_s temperature in the alloy containing Ti_2Ni phase was about 50° C, which suggests that there are some other reasons for the decrease in heats of transformations. One of these reasons is the presence of structural defects produced as a result of thermal cycling. This is evidenced by the changes in shape of X-ray lines of martensite and parent phase (Fig. 8). Moreover, as a result of cycling the DTA peaks become more spread, i.e. become slightly lower and wider, as shown in Fig. 9. These effects are summarized schematically in Fig. 10. The changes of transformation heats as well as in shape of the DTA peaks are associated with increases in lattice defects.

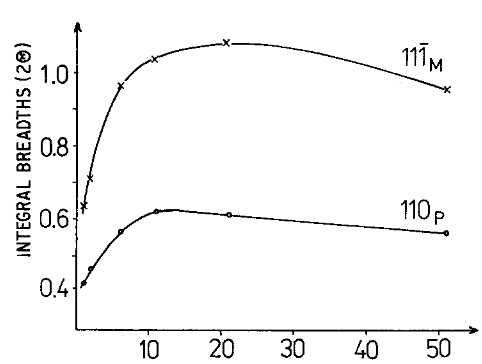

Figure 8 Variation of the integral breadths of X-ray lines of the martensite and parent phase with cycling for the alloy containing Ti_2Ni phase.

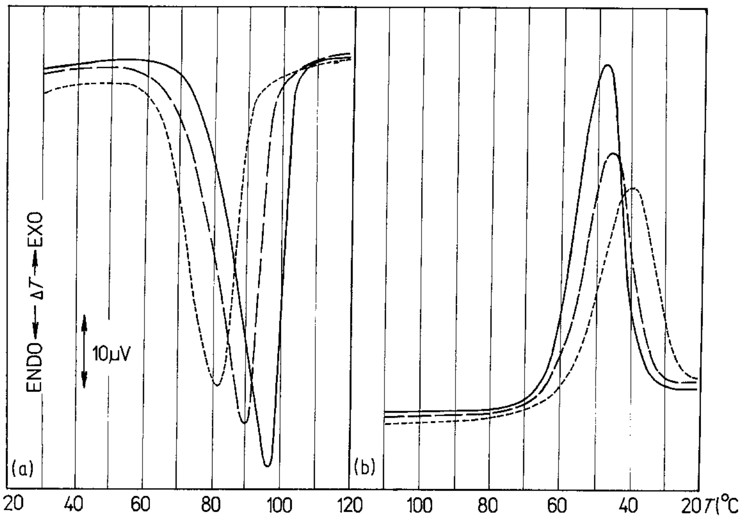

Figure 9 Variation of the DTA peak shape with cycling for the alloy containing Ti_2Ni phase: (a) heating and (b) cooling at 4(°C) min^{-1}. (—) First cycle, (– –) after 10 cycles, (- - -) after 50 cycles.

After about 20 complete thermal cycles saturation of these effects is reached, and the mentioned parameters remain virtually constant during further cycling. Saturation of defects resulting from thermal cycling is then reached. The first workers to note that thermal cycling generate dislocation in the Ni–Ti alloys were Perkins [6] and Sandrock *et al.* [10].

In the alloy with composition 50.2% Ni and 49.8% Ti no Ti_2Ni phase was determined after thermal cycling, but decreases in the temperatures (Figs 11 and 12) and in heats of transformations (Fig. 13) were observed. These effects are smaller than those found in the alloy containing Ti_2Ni phase. Moreover, in the alloy with Ti_2Ni phase the heats of transformation decrease continuously, while in the alloy without Ti_2Ni phase the heats of transformation decrease during 10 cycles and subsequently show stable values. These differences are associated with the decomposition process. Hence we may conclude that the presence of the intermetallic phase particles decreases the stability of the alloy characteristic parameters. For the alloy without Ti_2Ni phase it was also ascertained that a second peak appears on the DTA curves during cooling (M_2 in Fig. 14) as a result of thermal cycling. For the reverse transformation one endothermic peak was observed. This supports the postulate that the martensitic transformation proceeds in two stages, unlike the reverse transformation. However, it is necessary to explain why two stages of martensitic transformation were not recorded on the DTA curve for the alloy containing Ti_2Ni phase and why, for the alloy without these precipitates, these effects were recorded as a result of thermal cycling. This could be explained by shifts of transformation temperatures. For the alloy containing Ti_2Ni phase, the temperature of the DTA peak of martensitic transformation (M_{max} in Fig. 5) approximately corresponds to the temperature in which the R phase appears (T_R in Fig. 6). These temperatures decrease simultaneously during thermal cycling and at the same time the M_s temperature also decreases. Thus, during thermal cycling the hystereses M_s-M_{max} and M_s-T_R continue to remain unaffected, and the temperature T_R continues to correspond to the DTA effect maximum. In the alloy without Ti_2Ni phase the temperature of the DTA effect maximum (M_1 in Figs 11 and 14) and T_R temperature (Fig. 12) are similar and also shift during thermal cycling. The M_s temperature, however, changes very little. Hence the hystereses M_s-M_1 and M_s-T_R increase sufficiently for the second DTA maximum M_2 to appear. Thus the DTA measurements indicate that transformations of B2 phase to martensite

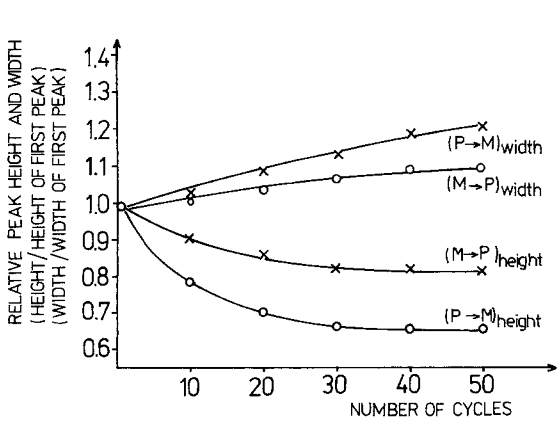

Figure 10 Variation of the DTA peak height and width against number of cycles for the alloy containing Ti_2Ni phase.

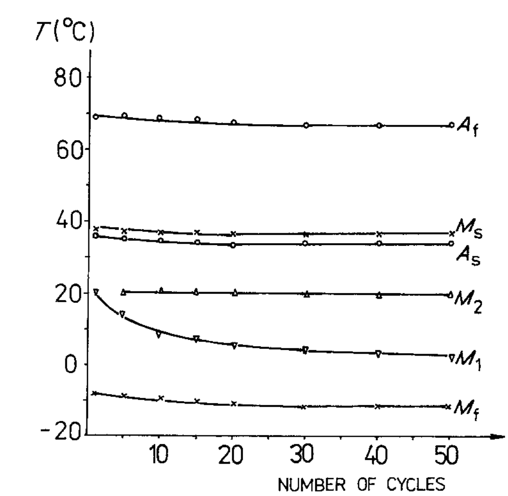

Figure 11 Variation of the transformation temperatures with cycling for the alloy without Ti_2Ni phase, obtained from DTA measurements.

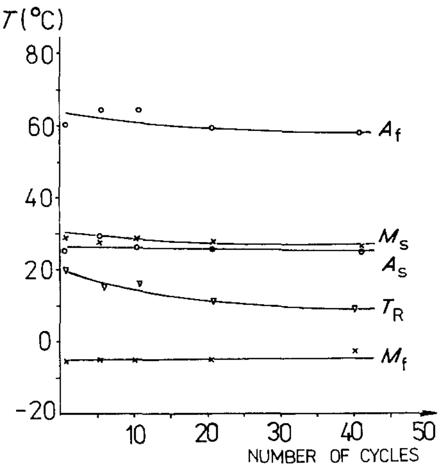

Figure 12 Variation of the transformation temperatures with cycling for the alloy without Ti_2Ni phase, obtained from X-ray measurements.

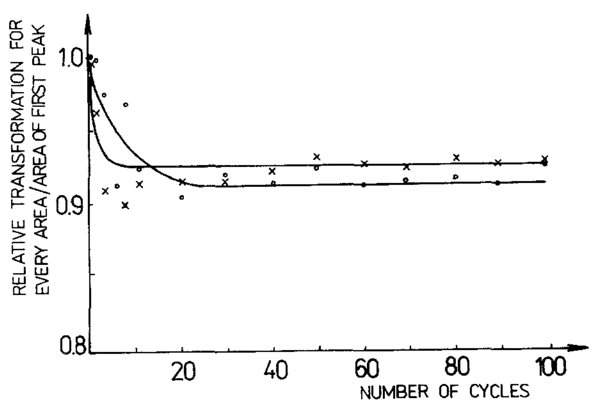

Figure 13 Variation of the total heat of transformation with cycling for the alloy without Ti_2Ni phase. (O) P → M (cooling), (x) M → P (heating).

and B2 to R phase can be regarded as separate thermal effects.

4. Conclusions

1. The observed broadening of the X-ray and DTA peaks during thermal cycling of Ni–Ti alloys are the result of dislocation generation. The cycling caused a decrease in the characteristic martensitic temperatures and in the corresponding heats of transformation.

2. Thermal cycling of the alloy containing Ti_2Ni phase causes a precipitation process to take place, while in the alloy without Ti_2Ni phase this process was not observed. It may be concluded that the presence of the intermetallic phase causes increased destabilization of the properties and structure of the Ni–Ti alloy during thermal cycling, and hence the alloy is less useful for practical applications.

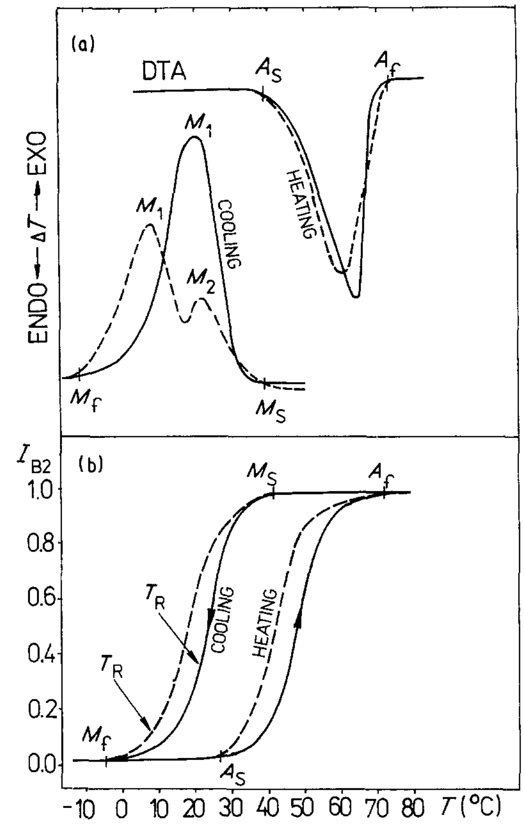

Figure 14 Schematic diagram of the changes in (a) DTA and (b) X-ray results with cycling for the alloy without Ti_2Ni phase. (—) First cycle, (- - -) after 40 cycles.

References

1. W. A. JOHNSON, J. A. DOMINIQUE and S. H. REICHMAN, *J. Phys. Collog. C4* **43** (1982) 285.
2. W. BUHRER, R. GOTTARDT, A. KULIK and O. MERCIER, *ibid.* **43** (1982) 219.
3. S. MIYAZAKI, Y. OHMI, K. OTSUKA and Y. SUZUKI, *ibid.* **43** (1982) 255.
4. T. SABURI, T. TATSUMI and S. NENNO, *ibid.* **43** (1982) 261.
5. Z. LEKSTON, PhD thesis, Silesian University, Poland (1985).
6. J. PERKINS, *Metall. Trans.* **4** (1973) 2709.
7. W. N. CHACZIN, J. I. PASKAL, W. E. GIUNTER, A. A. MONASEWICZ and W. P. SIWOCHA, *Fiz. Met. Metall.* **46** (1978) 511 (in Russian).
8. G. BENSMANN, F. BAUMGART and J. HARTWIG, *Tech. Mitt. Krupp* **37** (1979) 21.
9. H. C. LING and R. KAPLOW, *Metall. Trans.* **11A** (1980) 77.
10. G. D. SANDROCK, A. J. PERKINS and R. F. HEHEMANN, *ibid.* **2** (1971) 2769.

Received 10 March
and accepted 12 November 1986