

ON THE MECHANISM OF MARTENSITE NUCLEATION

W. KRAUSS, S. K. PABI† and H. GLEITER

Universität des Saarlandes, FB 12.1, Bau 2, D-6600 Saarbrücken, F.R.G.

(Received 16 April 1988)

Abstract—The martensitic transformation in the following two model systems, Fe–30 at. % Ni and In–5.25 at. % Cd, was studied by X-ray diffraction and metallography in order to answer the following question: does the nucleation of martensites occur by a soft mode mechanism or by classical heterogeneous nucleation? The model systems used were sphere shaped single crystals with diameters between 30 and 114 μm . In order to prevent the nucleation of martensite at or near the free surfaces, the Fe–30 at. % Ni and In–5.25 at. % Cd spheres were coated with a thin, coherent Ni-rich or Cd-rich surface layer, respectively. In the Fe–Ni-system, the surface coating suppressed martensite formation in the entire crystal whereas no change was noticed in the In–Cd alloy. This result rules out a soft mode nucleation mechanism for martensite in Fe–Ni and suggests a non-classical (e.g. a soft mode) process in In–5.25% Cd.

Résumé—La transformation martensitique des deux systèmes types Fe–30 at. % Ni et In–5,25 at. % Cd a été étudiée par diffraction des rayons X et par métallographie dans le but de répondre à la question suivante: est-ce que la germination de la phase martensitique se produit par un mécanisme de mode mou ou par la germination hétérogène classique? Les systèmes utilisés sont des monocristaux de forme sphérique dont les diamètres sont compris entre 30 et 114 μm . Pour empêcher la germination de martensite sur ou près des surfaces libres, les sphères de Fe–30 at. % Ni et In–5,25 at. % Cd, ont été recouvertes d'une couche superficielle cohérente riche en Ni et en Cd respectivement. Dans le système FeNi la couche superficielle supprime la formation de martensite dans le cristal entier alors qu'aucun changement n'est remarqué pour le système InCd. Ce résultat rejette un mécanisme de germination par mode mou de la martensite dans Fe–Ni et suggère par contre un mécanisme non classique (par exemple par mode mou) dans In–5,25 at. % Cd.

Zusammenfassung—Mittels Röntgenbeugung und metallografischer Methoden wurde die martensitische Umwandlung in den beiden Modellsystemen Fe–30 At.-% Ni und In–5,25 At.-% Cd untersucht. Folgende Frage sollten geklärt werden: Geschieht die Keimbildung des Martensits über einen Mechanismus mit einer weichen Mode oder liegt klassische heterogener Keimbildung vor? Es wurden kugelförmig ausgebildete Einkristalle mit Durchmessern zwischen 30 und 114 μm benutzt. Um die Keimbildung des Martensits an oder in der Nähe der freien Oberflächen zu vermeiden, wurden die Einkristallkugeln mit einer dünnen Ni-reichen (bei der Fe–Ni-Legierung) oder einer Cd-reichen kohärenten Oberflächenschicht bedeckt. Im Fe–Ni-System unterdrückte diese Schicht die Bildung des Martensits im gesamten Kristall, wohingegen sich im Falle der In–Cd-Legierung keine Änderung ergab. Dieses Ergebnis scheidet Keimbildung des Martensits durch eine weiche Mode für Fe–Ni aus, legt aber einen nicht-klassischen Mechanismus (etwa durch eine weiche Mode) für In–5,25% Cd nahe.

INTRODUCTION

Martensitic transformations are known to occur by nucleation and growth. In most systems, the rate of growth is so high that the transformation kinetic is effectively nucleation controlled. The classical theory of homogeneous nucleation [1] of martensite by heterophase fluctuations has proved to be unsuccessful [2, 3]. Cohen and co-workers [3, 4] attempted to resolve the difficulty by postulating heterogeneous nucleation where preexisting embryos are thought to be “frozen-in” during cooling. The pre-existing embryos are hypothesized to become supercritical below M_s . The rate of nucleation is then controlled entirely by interfacial motion which in turn depends on the formation and motion of interfacial dislocations.

Although the notion of “frozen-in” martensitic embryos remained popular for some 20 years, the origin of embryo formation remained unsettled. Attempts to affect the embryo distribution in the parent phase by applying hydrostatic pressure [5, 6] or magnetic fields [7] at high temperatures were unsuccessful. A detailed model by Olson and Cohen [7–10] attempts to account for this failure by postulating the parent crystal to be formed by closely spaced groups of austenite stacking faults which develop from existing crystal defects. These groups of faults become unstable during cooling and undergo a spontaneous transformation into the product structure. The resulting embryos will adjust in size to the variation of the chemical driving force of the martensitic transformation [10]. The model seems to be applicable primarily to f.c.c. \rightarrow b.c.c. and f.c.c. \rightarrow h.c.p. transformations in steels [11].

While all the models mentioned so far assume a classical nucleation path where the nucleus forms

†Present address: Department of Metallurgical Engineering, Indian Institute of Technology, Kharagpur 721302, India.

from perturbations of a fixed amplitude (composition or structure) and varying size, a nonclassical path involving perturbations of varying amplitude may also lead to the formation of martensites [10]. For example, lattice softening and soft mode phonons have been observed above M_s temperature in various alloys [12–18], and this has led to a “soft-mode” model for martensite nucleation. A soft mode phonon is proposed to “condense”, resulting in the displacement of the atoms in the parent phase into a lattice configuration of the martensitic product phase [14, 19]. The theory postulates a homogeneous nucleation of martensite and suggests the absence of pre-martensitic embryos. The “soft-mode” theory, however, cannot account for heterogeneous nature of martensite nucleation demonstrated, for example, by small particle experiments [20, 21] and the martensitic transformation in coherent γ -iron precipitates [22]. Moreover, various diffraction experiments in traditional soft mode systems have revealed a “central peak” phenomenon which seems inconsistent with a simple soft mode mechanism.

Clapp [23] proposed a “localized soft mode” nucleation model, i.e. as one or several of the elastic constants approach zero, the strain near lattice defects may form strain-spinodal regions in crystals, where the amplitude and the period of the lattice vibrations are larger than in the perfect lattice. However, the elastic behaviour of most ferrous alloys except those which become ferromagnetic prior to martensitic transformation, do not show any unusual changes above M_s [24]. In order to assess the question, whether martensitic nucleation in different systems occurs by similar mechanisms, the formation of martensite in the following two model systems was investigated. Indium rich In–Cd alloys undergo a diffusionless structural transition from f.c.c. to f.c.t. by a thermoelastic martensitic mechanism [14, 25, 26]. The shear modulus $c' = \frac{1}{2}(c_{11} - c_{12})$ in this system tends to a very small value in both phases manifesting the softening of the acoustic phonon mode as the transition temperature is approached. Reduction in c' has also been observed in Fe–Ni alloys [15–17] prior to martensitic transformation for Ni concentrations greater than 29 at.% in which M_s is less than the Curie temperature, and this softening seems magnetoelastic in origin [16, 17]. On the other hand the martensitic transformation in Fe–Ni (30%) is of the non-thermoelastic type involving a large transformation hysteresis.

The experiments reported are based on the following idea. In Fe–Ni and In–Cd systems, the M_s temperatures decrease sharply with an increase of the Ni and/or the Cd content, respectively [12, 25, 27]. Hence, if small single crystals of an In–Cd or a Fe–Ni alloy with compositional gradients at their free surfaces are generated by coating and diffusion of Cd or Ni, respectively, into the microcrystals, the Cd- or Ni-enriched free surface region of the crystals would have a lower M_s temperature than the interior

(Fig. 1). As a consequence, the particle surfaces cannot be effective nucleation sites unless the temperature approaches the M_s temperatures of the surfaces, M_{s0} . Thus, the martensite nucleation process in the microcrystals remains the same irrespective of a compositional gradient at the free surface, if the nucleation is predominantly homogeneous. However, if nucleation is heterogeneous, a comparison between the nucleation characteristics of small crystals with and without concentration gradients at their free surfaces would reveal the role of the free surface for the martensite nucleation process.

EXPERIMENTAL

About 100 g of a Fe–30 at.% Ni alloy (called alloy A) was prepared by melting 99.99% pure Fe and Ni in a high purity alumina crucible under a reducing atmosphere ($\sim 15\%$ H_2). The alloy was remelted twice and homogenized at 1170 K for 2 days in the reducing atmosphere. The compositional homogeneity of the alloy was confirmed by elemental analysis in a scanning electron microscope.

An In-rich alloy containing 5.25 at.% Cd (alloy B) was prepared from 99.999% pure In and Cd. The melt was thoroughly shaken prior to solidification. The homogeneity was carried out in silicone oil at 390 K for about 4 days.

A polycrystalline powder of the alloy A was generated by filing. Single crystal spheres of the alloy A were produced by the “drop-tube” technique [28, 29], where the filings were melted and solidified during free fall through a 3 m long quartz tube under protective atmosphere. The spheres were single crystals, 48–104 μm in diameter, having the same Ni-content as the bulk. For studying the effect of particle size on the martensitic transformation in alloy A, the spheres were sieved in four groups, namely grade 1 with diameters ranging from 104 to 85 μm , grade 2 with 84 to 75 μm , grade 3 with 72 to 62 μm and grade 4 with 61 to 48 μm .

In order to produce single crystal spheres of alloy B, small droplets (diameter 30–45 μm) were prepared by emulsifying [30] the melt in oil. The droplets of the emulsion were cooled from 480 K to room temperature at a rate 10 K/h. The resulting spheres were washed repeatedly with water and acetone prior to drying at room temperature. Crystals larger than 45 μm were discarded by sieving.

A portion of the spheres of alloy A of every grade was coated on all sides with pure (99.99%) Ni by sputtering. The thickness of the coating was 0.3 μm . Some spheres of alloy B were completely coated (2–5 μm) with Cd (99.999%) by vapour deposition. By subsequent annealing, the atoms of the coatings were diffused into a surface region of the crystals (Fig. 1). The concentration profile of the surface region was estimated [31] from diffusion data available in literature [32, 33]. Usually, the width of the diffusion profile was too narrow to be measured in

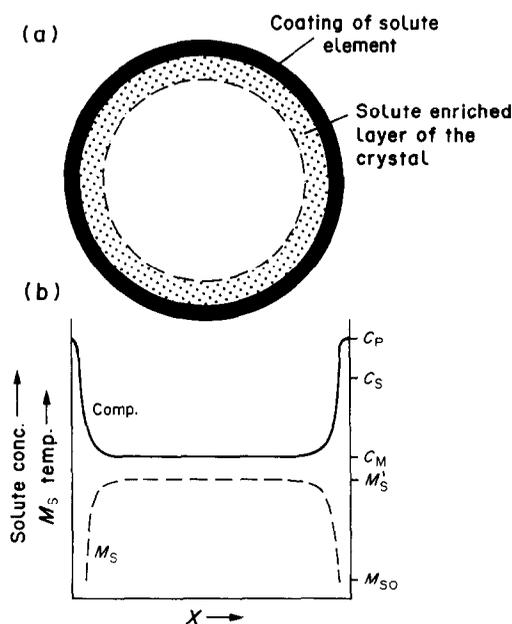


Fig. 1. Schematic illustration of (a) the cross section through the Fe-Ni or In-Cd microcrystals coated with Ni or Cd followed by controlled diffusion to generate a solute enriched coherent surface layer and (b) the corresponding solute concentration C as well as the M_s temperatures. The C_p , C_s and C_M represent the concentrations in the coating, at the surface, between coating and crystal and inside of the microcrystal where solute enrichment has not occurred. The corresponding M_s temperatures are M_{s0} (at the free surface) and M_s' (in the center of the microcrystal). X is the distance measured from the center of the microcrystal.

the scanning electron microscope. The diffusion/heat treatment for the alloy B was carried out in vacuum. The crystals of alloy A were sealed in quartz tubes filled with a protective atmosphere prior to the diffusion treatment. It is known [25, 34] that in Fe-30 at.% Ni alloys martensite starts forming on cooling below 215 K. In order to initiate martensite formation in the coated specimens, cooling below ambient temperature was carried out in two ways: (i) by dipping the sealed quartz tube into liquid nitrogen and (ii) by means of a refrigerator cooling the spheres at a rate of $3 \text{ K} \pm 0.5 \text{ K/min}$ up to 78.7 K, thereafter the rate being 0.5 K/min to 16.5 K.

The martensitic transformation in all alloys was studied by X-ray diffraction with MoK_α radiation. The "integrated intensity" method of Averbach and Cohen [35] was applied to estimate the volume fraction of martensite formed. The error in the estimate [20, 35] was about 2%. The peaks examined in alloy A were: f.c.c.: (111), (200), (220), (311); b.c.c.: (110), (200) and (211).

In alloy B splitting of the (220) diffraction peak during the f.c.c. \rightarrow f.c.t. transition was utilized. The X-ray diffractometer stage used for this alloy was capable of controlling the temperature within $\pm 0.2 \text{ K}$ between 390 and 140 K. Moreover, the room tem-

perature was maintained at $298 \text{ K} \pm 1 \text{ K}$ to prevent compositional changes in the specimen during the diffractometer alignment. Transformation in alloy A was also studied metallographically by mounting batches of 10–100 crystals in a cold setting resin. The crystals were mechanically polished and etched first with a glycerin-aqua regia mixture to reveal the grain structure. Subsequently an aqueous solution of sodium disulphate was used to produce the required colour contrast between the martensite and the retained austenite [36].

RESULTS

Fe-Ni system

The program for the various experiments is displayed schematically in Fig. 2. The M_s , M_f , A_s and A_f temperatures of bulk Fe-30 at.% Ni polycrystalline are [3, 27, 37] 215, 130, 640 and 670 K, respectively. This large transformation hysteresis allows all metallographic and X-ray examinations to be conducted at room temperature. The spheres obtained from the drop-tube had a f.c.c. structure (cf. experiment 1, Fig. 2) with lattice parameter $a = 0.3578 \text{ nm}$. On quenching the uncoated spheres to liquid nitrogen (cf. experiment 2), martensite formed with a lattice constant of $a = 0.2335 \text{ nm}$. These lattice parameters agree with the numbers quoted in literature [35, 38].

The percentage of martensite formed in experiments 2 to 5 are summarized in Table 1. In experiments 2 and 5, the martensite formed during quenching in liquid nitrogen (LNQ). An increase of the sphere size had only limited influence. No martensite formed in spheres coated on all sides with Ni (cf. Table 1, experiment 3). The metallographic observations agreed with the X-ray diffraction data.

In experiment 4 (Fig. 2) the uncoated microcrystals were cooled slowly in a refrigerator to temperatures well below M_f . Metallography and X-ray diffraction revealed no martensite (Table 1). At the end of experiment 4, the spheres were removed carefully from the X-ray diffractometer stage, washed thoroughly in acetone, dried, sealed in a quartz capsule and subsequently quenched in liquid nitrogen (Fig. 2, experiment 5). X-ray and metallographic studies revealed $\sim 57\%$ martensite, which agrees with the results of the direct quench in liquid nitrogen (cf. Table 1, experiments 2 and 5).

In-Cd system

The small transformation hysteresis ($\sim 25 \text{ K}$) in this system [12, 39] precludes a metallographic study of the martensitic reaction. The results obtained from X-ray diffraction experiments may be summarized as follows.

1. Spheres of alloy B transform from f.c.t. to f.c.c. structure at 338 K on heating, while on cooling the f.c.t. structure reverts at 313 K. These observations are in agreement with available data from bulk specimens [12]. Apparently, the small size of the

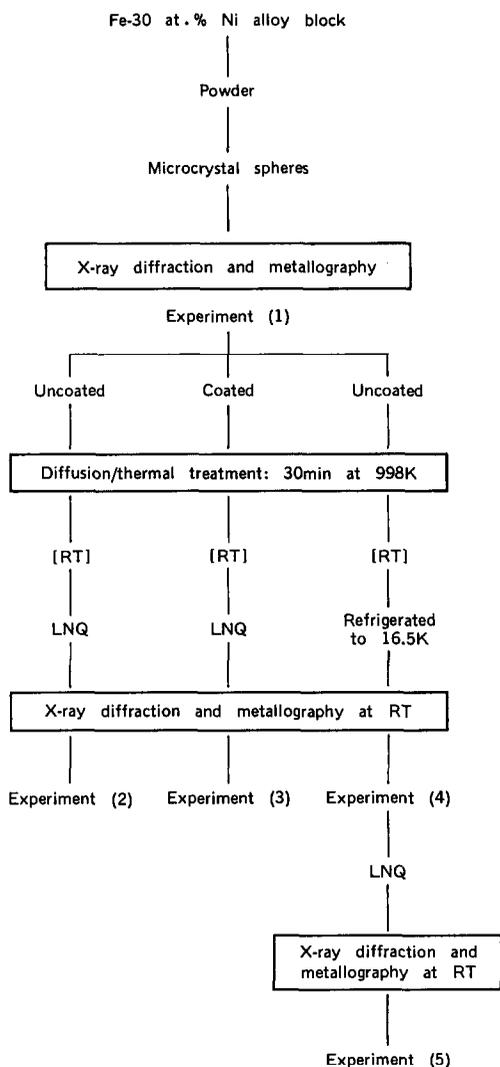


Fig. 2. The scheme of the experiments 1–5 with the Fe–Ni alloy. LNQ signifies liquid nitrogen-quenched; RT means room temperature.

microcrystals has not influenced the transformation characteristics.

2. Alloy B crystals coated with Cd and homogenized for 2 days at $298\text{ K} \pm 0.1\text{ K}$ were fully f.c.c. at 298 K. The crystals were homogenized for another 20 days and the f.c.c. to f.c.t. transition was complete on

cooling to 251 K. The equilibrium solubility [39] of Cd in In at 298 K is 6.1 at.%. For this composition, the phase transition should start at 280 K and complete at about 253 K [12]. In other words, Cd enrichment of the In rich matrix up to the equilibrium solubility limit (i.e. 6.1 at.% at 298 K) seems to have taken place in coated microcrystals by diffusion from the Cd coating and any conceivable oxide layer on the In rich crystals did not impede the diffusion.

3. Alloy-B coated with Cd and homogenized for 22 days at $298\text{ K} \pm 0.1\text{ K}$ was heated for 30 min at 308 K and the temperature was brought down to 263 K at a rate of 15 K/min; thereafter the cooling rate was slowed down to about 1 K/min. The martensite structure appeared at 250 K and the reaction seems to be complete at 233 K. The diffusion treatment at 308 K would bring down the M_{50} to 130 K [12, 39] making the surface region of the spheres ineffective for martensite nucleation at 233 K.

DISCUSSION

The early work of Cech and Turnbull [20] on Fe–30 at.% Ni small particles has revealed that if transformation starts in a particle, the degree of transformation is independent of particle size but depends on temperature. Moreover, at any given temperature, either the transformation in a particle proceeds up to a definite degree or the particle fully retains its f.c.c. structure. Present metallographic studies also support this trend.

In another investigation on the transformation in Fe–Ni alloy spheres, Huizing and Klostermann [40] have observed that for Ni content higher than 29 at.% no surface martensite is formed and the transformation occurs by a burst only. The results reported here have clearly indicated that the surface coating on Fe–30 at.% Ni microcrystals tends to suppress the martensite transformation. If the solute enriched outer layers extend up to 700 nm at the end of diffusion treatment, the volume fraction of the microcrystal enriched in Ni is about 0.09 and 0.04 for spheres of 50 and 100 μm diameters, respectively. The remarkable effect of the thin surface coating (cf. Table 1) obviously emphasizes the importance of surfaces in the martensite nucleation. This agrees

Table 1. Percentage of martensite in Fe–30 at.% Ni microcrystals measured in different experiments (cf. Fig. 2) by X-ray diffraction

Experiment No.	Surface condition ^a	Type of cooling ^b	Percentage martensite in different grades			
			Grade 1 $\varnothing = 85\text{--}114\ \mu\text{m}$	Grade 2 $\varnothing = 73\text{--}74\ \mu\text{m}$	Grade 3 $\varnothing = 62\text{--}72\ \mu\text{m}$	Grade 4 $\varnothing = 48\text{--}61\ \mu\text{m}$
2	UC	LNQ	56	56	54	53.5
3	C	LNQ	0	0	0	0
4	UC	R, 16.5	0	0	—	—
5	UC	R, 16.5 K then LNQ	57	57.5	—	—

^aUC = uncoated, C = coated.

^bLNQ = liquid nitrogen quenched to 78.7 K; "R, 16.5 K" signifies cooling in a refrigerator to 16.5 K.

with a recent observation [41] that grain boundaries provide nucleation sites for martensite, but only certain types of grain boundaries are qualified to be potential nuclei. An investigation on the martensitic transformation of small fully coherent γ -precipitates in ϵ -copper matrix [22] has also shown that localized particle/matrix decohesion resulting from vacancy condensation tends to trigger the transformation. Moreover, these studies [4, 22] have also revealed that lattice dislocations themselves do not act as favourable nucleation sites for ferrous martensite.

The reluctance of microcrystals to form martensite with the decreasing size of the crystals was noted in a number of Fe-base alloys [20, 42, 45]. It is often attributed to the stabilization of austenite in small particles [25]. The absence of martensite in slowly cooled Fe-Ni crystals observed in the present study (experiment 4), however, seems not due to a change in the austenite structure, because the amount of martensite obtained on quenching, (cf. experiment 2, Table 1). These experiments seem to emphasize the importance of quenching stresses in initiating the martensitic transformation. The amplitude of these stresses should decrease with decreasing particle size. It is not understood whether the stress has dominating influence on the formation or on the migration of embryo-matrix interface.

Lattice softening and soft mode phonons as well as the premartensitic phenomenon have been observed in Fe-Ni and In-based alloys [12-17, 42, 43] in the vicinity of M_s . An X-ray diffraction study on a Fe-30.5 at.% Ni single crystal also revealed a softening of long wave length (100) [100] longitudinal modes as the sample temperature approached M_s . However, for Fe-Ni systems the distinctly heterogeneous nature of the martensitic nucleation observed in the present study as well as in earlier investigation [20] precludes the applicability of the simple soft mode nucleation theory. Nucleation by localized soft modes at lattice dislocation or vacancies seems inadequate for explaining the remarkable effect of surface coating. On the other hand, the ability of the surface to act as nucleation site depends on the cooling rate (cf. Table 1, experiments 2 and 4) while the lattice instability is a function of temperature and not of cooling rate; hence localized soft mode at the free surface cannot account for the observed nucleation. It appears, therefore, that martensite in Fe-30 at.% Ni alloy forms via a classical nucleation path where the surfaces (interfaces) are effective nucleation sites. In In-Cd systems, attempts to suppress the nucleation of martensite by a surface coating were unsuccessful. Thus, in contrast to the markedly heterogeneous nature of nucleation in Fe-Ni systems, martensite in In-Cd alloys seems to form by a homogeneous nucleation process.

In summary, the present investigations illustrate that soft modes may not always play a significant role in the nucleation of martensite. In consequence, it

appears that a unified mechanism for martensitic nucleation in all alloy systems may not exist.

CONCLUSIONS

1. Nucleation of martensite in Fe-30 at.% Ni microcrystals is heterogeneous. Surfaces have great potency as nucleation sites. Other lattice defects (dislocations, vacancies) seem to have less pronounced influence on the nucleation frequency.

2. Martensite formation in Fe-30 at.% Ni microcrystals is completely suppressed by slow cooling. Possibly quenching stresses play an important role in the nucleation of ferrous martensites.

3. "Soft mode nucleation" or "localized soft mode nucleation" theories seem at variance with the observed nucleation characteristics of martensite in Fe-30 at.% Ni alloys.

4. Surface and lattice dislocations have little influence in the diffusionless f.c.c. \rightarrow f.c.t. transition of In-Cd alloys. The nucleation process here is predominantly homogeneous, which may be explained by the soft-mode nucleation theory.

5. Lattice softening may not in all systems be crucial for the martensitic nucleation process.

Acknowledgements—The authors would like to thank Professor J. H. Perepezko, University of Wisconsin, Madison, Wisconsin, U.S.A., for providing the drop-tube facilities. Several helpful suggestions by Professor L. Delaey, University of Leuven, Belgium, in planning the experiments are gratefully appreciated. One of the authors (S.K.P.) acknowledges the financial support of the Alexander von Humboldt Foundation.

REFERENCES

1. J. C. Fischer, J. H. Hollomon and D. Turnbull, *Trans. Am. Inst. Min. Engrs* **105**, 691 (1949).
2. C. L. Magee, in *Phase Transformations*, p. 115. Am. Soc. Metals Park, Ohio (1970).
3. L. Kaufman and M. Cohen, *Prog. Metal Phys.* **7**, 165 (1958).
4. V. Raghavan and M. Cohen, *Acta metall.* **20**, 333 (1972).
5. S. V. Radcliffe and M. Schatz, *Acta metall.* **10**, 201 (1962).
6. M. K. Korenko and M. Cohen, *Scripta metall.* **8**, 751 (1974).
7. G. B. Olson and M. Cohen, *Metall. Trans.* **7A**, 1897 (1976).
8. G. B. Olson and M. Cohen, *Metall. Trans.* **7A**, 1905 (1976).
9. G. B. Olson and M. Cohen, *Acta metall.* **27**, 1007 (1979).
10. G. B. Olson and M. Cohen, in *Proc. Int. Conf. Solid \rightarrow Solid Phase Transformations* (edited by H. I. Aaronson, D. E. Laughlin, R. F. Sekerka and C. M. Wayman), p. 1145. Am. Inst. Min. Engrs, New York (1982).
11. C. M. Wayman, *ibid*, p. 1119.
12. M. R. Madhava and G. A. Saunders, *Phil. Mag.* **38**, 777 (1977).
13. N. G. Pace and G. A. Saunders, *Proc. R. Soc. A* **326**, 521 (1972).
14. N. Nakanishi, *Prog. Mater. Sci.* **24**, 143 (1980).

15. K. Salama and G. A. Alers, *J. appl. Phys.* **39**, 4857 (1968).
16. H. Hausch and H. Warlimont, *Acta metall.* **21**, 401 (1973).
17. Y. Endoh and Y. Noda, *J. Phys. Soc. Japan* **46**, 806 (1970).
18. R. J. Comstok, J. B. Cohen and H. R. Harrison, *Acta metall.* **33**, 423 (1985).
19. N. Nakanishi, Y. Muvabami and S. Kachi, *Scripta metall.* **5**, 433 (1971).
20. R. E. Cech and D. Turnbull, *Trans. Am. Inst. Min. Engrs* **206**, 124 (1956).
21. C. L. Magee, *Metall. Trans.* **2**, 2419 (1971).
22. C. H. Li, D. A. Porter and K. E. Easterling, *Acta metall.* **33**, 317 (1985).
23. P. C. Clapp, *Physica status solidi (b)* **57**, 561 (1973).
24. H. Warlimont, G. Hauschi, A. Prsetyo and F. Reyraud, in *New Aspects of Martensitic Transformation, Suppl. Trans. Japan Inst. Metals* **17**, 153 (1976).
25. Z. Nishiyama, *Martensitic Transformation*, Chaps 2, 4 and 5. Academic Press, New York (1978).
26. C. M. Wayman, in *Physical Metallurgy* (edited by R. W. Cahn and P. Haasen), Vol. 2, 3rd edn, p. 1031. North Holland, Amsterdam (1983).
27. L. Kaufman and M. Cohen, *Trans. Am. Inst. Min. Engrs* **206**, 1393 (1956).
28. Y. Ujiiie, Master thesis, Univ. of Wisconsin, Madison (1986).
29. L. L. Lacy, M. B. Robinson and T. J. Rathz, *J. Cryst. Growth* **51**, 47 (1981).
30. J. H. Perepezko, *Mater. Sci. Engng* **25**, 125 (1981).
31. B. Karlsson and L. E. Larsson, *Mater. Sci. Engng* **20**, 161 (1975).
32. J. Askill, in *Handbook of Physics and Chemistry* (edited by R. C. Weast), 66th edn, p. F46. CRC Press, Florida (1986).
33. A. D. Romig, J. R. and J. J. Goldstein, *Metall. Trans. A* **12A**, 243 (1981).
34. D. A. Mirzayev, *Physica Metall. Metallogr.* **56**, 596 (1983).
35. B. Averbach and M. Cohen, *Trans. Am. Inst. Min. Engrs* **176**, 401 (1948).
36. I. Becket, I. Klemm, *Handbuch der Metallogr., Ätzverfahren*, p. 159. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig (1962).
37. M. Hansen, *Constitution of Binary Alloys*, p. 667, McGraw Hill, New York (1958).
38. *Powder Diffraction File, Inorganic Materials 1979*, p. 379, ICPDS (1979).
39. F. A. Shunk, *Constitution of Binary Alloys*, 2nd Suppl., p. 214. McGraw Hill, New York (1963).
40. R. Huizing and J. A. Kolstermann, *Acta metall.* **14**, 1685 (1966).
41. S. Kajiwara, *Metall. Trans.* **17A**, 1693 (1986).
42. S. Nagashima and Z. Nishiyama, *J. Japan Inst. Metals* **23**, 728 (1959).
43. Y. Kachi, Y. Bando and S. Higuchi, *Japan J. appl. Phys.* **1**, 307 (1962).
44. Y. Bando, *Trans. Japan Inst. Metals* **5**, 135 (1964).
45. Y. A. Klyachko and G. K. Baranova, *Physica Metall. Metallogr.* **25**, 569 (1968).
46. M. Simotomai, R. Hasiguti and K. Karaswas, in *New Aspects of Martensitic Transformation, Suppl. Trans. Japan Inst. Metals* **17**, 129 (1976).
47. S. W. Wilkins, M. S. Lehmann, T. R. Finlayson and T. F. Smith, in *Proc. Int. Conf. on Solid → Solid Phase Transformations* (edited by H. I. Aaronson, D. E. Laughlin, R. F. Sekerka and C. M. Wayman), p. 1235. A.I.M.E. Philadelphia, Pa (1982).