JOURNAL OF MATERIALS SCIENCE 17 (1982) 3045–3051

Morphological aspects of crystallization of chalcogenide glasses obtained by rapid cooling from the liquid state

MIECZYSŁAW KACZOROWSKI
Metal Casting Section Institute of Metal Forming, Welding and Casting, Warsaw Technical University, Narbutta 85, 02-524 Warsaw, Poland

The results of a study of growth morphology during crystallization of amorphous tellurium alloys are presented in this paper. By comparison with a process of precipitation from a supersaturated solid solution it was shown that a number of common features exist between the crystallization of amorphous materials and that from the liquid phase. It is proposed in the discussion that glass-to-crystal transition is an intermediate transition between the crystallization from the liquid phase and the non-coherent precipitation from supersaturated solid solution. It was also shown that the magnitude of the elastic strain energy $n \cdot \Delta g_s$ depends mainly on the differences between the density of amorphous phase and that of the crystal and may be described by means of an equation of the type:

$$\Delta g_s = A \cdot \ln \left(\frac{\rho_c}{\rho_a}\right)$$

1. Introduction

A method elaborated in 1960 of rapid cooling from the liquid state [1] enabled phases of unconventional structure to be obtained. Among these, the non-crystalline materials deserve particular attention. These materials, frequently referred to as amorphous or liquid-like, in many cases possess specific properties which are interesting from the practical point of view and owing to this they have been the subject of numerous investigations [2–5]. These investigations are aimed, amongst other things, at the determination of non-crystalline phases formation, discovery of the pattern reliably describing their structure, and determination of their thermal stability and of the transition path from the amorphous state to the crystalline state.

The latter question seems to be particularly interesting, as a detailed recognition of changes accompanying the crystallization process may add essential information to the phase transition theory.

From amongst many publications on this subject [6–15] the publications of Köster [16], and Suryanaryana and Anantharaman [17] deserve particular attention as they report a detailed analysis of decomposition of amorphous phases, based on considerations of a hypothetical scheme of their free energies. According to these schemes, three type of crystallization of amorphous phases are possible:

(i) polymorphic crystallization;
(ii) eutectoidal crystallization;
(iii) primary crystallization of one of the phases.

It is the opinion of these authors [16, 17], that the type of reaction which results in an equilibrium crystalline state depends on the free surface energy of crystals, the energy of deformation and diffusion activation energy. However, the deciding factor is the difference in free energy between the initial and the final states. It must be stressed here, that the authors use the two terms *polymorphic crystallization* or *eutectoidal crystallization* to suggest that they treat the glass-to-crystal transformation as a transformation of the solid state of a precipitation reaction type.

0022–2461/82/103045–07$03.34/0

Contrary to these authors, Kowamoto [19] uses the terminology applied for the description of liquid-to-crystal transformation; for example, the "eutectic reaction".

Therefore, the question arises: "What type of transformation results in the crystallization of amorphous phases?" In spite of appearances, the answer to this question is not evident, and for this reason the present paper has been dedicated to this matter.

As opposed to the quoted papers [16–18], the results of our investigation on the growth morphology of crystals formed in an amorphous matrix have been used for the analysis of this problem.

2. Experimental details

Tellurium alloys from a group of so-called chalcogenide glasses of the following compositions: Te–20 at.% Sn, Te–20 at.% Pb, Te–15 at.% Ge, Te–40 at.% Cu, and Te–25 at.% Pb were used as materials for investigation.

The non-crystalline state specimens were obtained by the splat-cooling method. The supersaturated solid solution of Sn–10 at.% Sb alloy which was to be used for comparative investigations was obtained by the same method. The alloys were further heated in order to initiate a transformation in which the first crystals appeared (in amorphous alloys), or precipitates (in the Sn–10 at.% Sb alloy).

Because the most essential information in this investigation is of a morphological nature, observations were made using a transmission electron microscope (TEM).

3. Results

Microscopic observations were carried out using the Philips EM 300 transmission electron microscope at a voltage of $U_a = 100\,\text{kV}$.

The initial stage of crystallization of the amorphous alloy Te–20 at.% Sn is shown in Fig. 1a. It can be seen that at this stage single spherical crystals are uniformly distributed in the amorphous matrix form. Sometimes they form agglomerates consisting of two or more crystals, probably resulting from the fact that the surface of an early formed grain is a preferred site for heterogeneous nucleation and growth of further crystals. Frequently observed specific differentiation of contrast within such agglomerates suggests that the crystals are twinned in the growth plane. Detailed structural investigations proved that the crystals are of a two-phase structure. One of the regular phases has the primitive cubic structure of $P_0\alpha$ type with a lattice parameter $a_0 = 0.32\,\text{nm}$, while the other has a hexagonal structure with lattice parameters $a_0 = 0.445\,\text{nm}$ and $c_0 = 0.585\,\text{nm}$ [19].

Fig. 1b shows the initial stage of crystallization of the amorphous alloy Te–20 at.% Pb. The single crystals shown in the photograph have a polyhedral shape and a hexagonal structure with lattice parameters $a_0 = 0.449\,\text{nm}$ and $c_0 = 0.585\,\text{nm}$ [20].

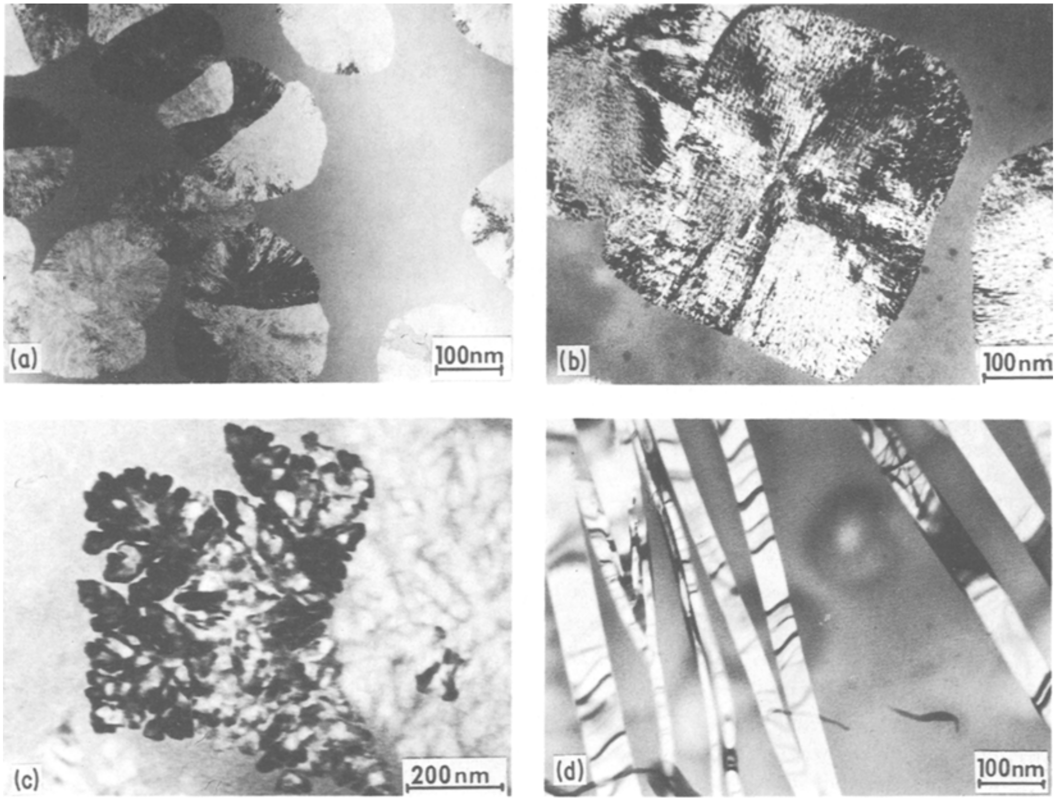
The contrast observed inside the crystals results from the decomposition of supersaturated solid solution, which takes place simultaneously with the crystal growth process. The crystallization morphology of the amorphous alloy Te–15 at.% Ge is presented in Fig. 1c. The electron micrograph shows dendritic growth of the crystal in this alloy, which is also described by Willens [21]. Dendrites which form are almost pure tellurium and consequently are of a hexagonal structure with slight deformation in relation to the structure of tellurium. Similarly, during crystallization of the amorphous alloy Te–20 at.% Cu crystals of Te(Cu) form which have a hexagonal structure and lattice parameters slightly differing from the lattice parameters of pure tellurium. In case of the Te–40 at.% Cu alloy, the crystals are acicular or elongated platelet shape, which is clearly shown in Fig. 1d.

The crystallization morphology of the Te–25 at.% Pb alloy is shown in Fig. 1e. This figure suggests that the growth of crystals takes place by displacement of the crystallization boundary, similar to discontinuous reaction.

As was suggested in an earlier paper [22], the crystals show a tendency to form a superlattice. This is not unexpected if the composition of the alloy, which may be written A_3B, is taken into account.

Fig. 2 shows the process of precipitation from the solid solution obtained as a result of ultrarapid cooling of Sn–10 at.% Sb alloy. This solution produces crystals of a tetragonal structure with lattice parameters $a_0 = 0.582\,\text{nm}$ and $c_0 = 0.318\,\text{nm}$ [23].

During isothermal ageing at a temperature of 373 K, precipitates of SnSb form in a linear arrangement. These precipitates are coherent to the matrix and are acicular in shape. The crystallographic relations between the precipitates and the matrix are as follows:



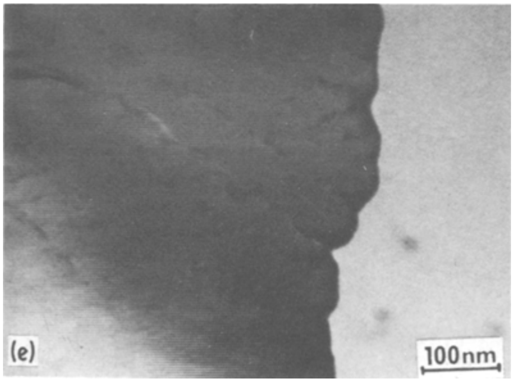


Figure 1 The early stage of crystallization of amorphous alloys: (a) Te–20 at.% Sn; (b) Te–20 at.% Pb; (c) Te–15 at.% Ge; (d) Te–20 at.% Cu; (e) Te–25 at.% Pb.

$$\langle 0\,2\,0\rangle_{\mathrm{SnSb}} \parallel \langle 0\,2\,0\rangle_{\mathrm{Sn}}$$

and

$$\{2\,0\,2\}_{\mathrm{SnSb}} \parallel \{2\,0\,1\}_{\mathrm{Sn}}$$

The close crystallographic relationship between the precipitation lattice and the matrix lattice must be stressed. Such a relationship occurs often during reaction in the solid state, resulting from reasons described in detail in papers on the theory of phase transitions in the solid state [24].

4. Discussion and conclusions

Examples of the crystallization process of the alloys shown in Fig. 1 allow one to distinguish four morphological types:

(i) crystals of spherical or polyhedral morphology (Te–20 at.% Sn and Te–20 at.% Pb alloys);

(ii) large crystals, the growth of which occurs by displacement of the crystallization boundary deep in the amorphous matrix (Te–25 at.% Pb alloy);

(iii) crystals of acicular or platelet morphology (Te–40 at.% Cu);

(iv) dendritic growth (Te–15 at.% Ge alloy).

In spite of considerable differences among these morphologies, their common feature is their independence of crystal structure from the matrix structure. This is evident and fully understandable in view of one "definition" of amorphous materials, according to which "they have a structure without structure".

If the alloys investigated were recognized as microcrystalline, then the hypothetical size of

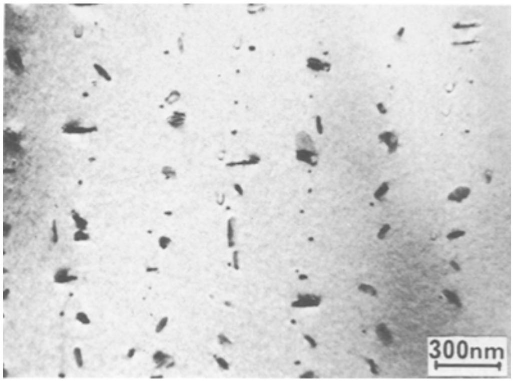


Figure 2 The precipitates of SnSb compound in a supersaturated Sn (Sb) matrix.

microcrystals as calculated from Scherrer's formula [25] on the grounds of broadening of the diffraction maximum would be ~ 1.5 nm. Then if one of the microcrystals became the place for nucleation and "forced" a crystal to grow in a particular crystallographic direction resulting from the relationship between the microcrystal "lattice" and the lattice of the crystal growing on it, such relations between the lattice of the crystal and other microcrystals could not be expected during growth. This results from mutual disorder among microcrystals.

Let us consider the question of crystallization of the amorphous phase on the grounds of the solid state transformation theory. Initially it would be necessary to recognize an amorphous body as a supersaturated solid solution of a structure characterized by the lattice-order within an area of approximately 1 nm radius. In this case the formation of the first crystals would be by precipitation from a supersaturated solid solution, then according to [26] the overall change of free energy, ΔG, would be:

$$\Delta G = n \cdot (g^{\beta} - g^{\alpha}) + \eta \cdot n^{2/3} \cdot \sigma + n \cdot \Delta g_s \quad (1)$$

where n is the number of atoms in the crystal nucleus; g^{β} and g^{α} are the free energies per atom, for the β-phase (crystalline phase nucleus) and the α-phase (amorphous phase), respectively; $\eta \cdot n^{2/3}$ is the nucleus surface, wherein η is a geometric factor depending on nucleus shape; $n \cdot \Delta g_s$ is the elastic strain energy caused by formation of the β-phase nucleus in an α-matrix; and σ is the surface tension.

From the point of the matter under investigation, the third element is of the most importance and its magnitude considerably affects the geometrical shape of the forming precipitates. The magnitude of $n \cdot \Delta g_s$ depends mainly on whether the forming precipitate has a structure similar to the matrix structure to such a degree that coherence between their crystal lattice is possible or not, and on the degree of lattice incoherence. When lattice coherence occurs, Δg_s is high, and then the precipitates take the form of thin platelets or acicular shapes which grow up in precisely determined so-called "soft" directions (for example, [1 0 0] for the f c c and b c c lattice) [27].

If the precipitates are incoherent, Δg_s is small, because of the stresses on the grain interface; or, the incoherence of the precipitate lattice and the matrix are accommodated by dislocations. In this case the shape of the precipitates is determined mainly by the magnitude of $\eta \cdot n^{2/3} \cdot \sigma$. Because every system tends to the state of minimum free energy, this element will reach its minimum when the precipitates take the form of the smallest surface. This form is a sphere or a relatively regular polyhedron.

From the above considerations it can be concluded that from the view-point of morphology of the crystallizing phases in an amorphous matrix, this transformation may be classified as a process of formation of incoherent particles precipitating from a supersaturated solid solution. The lack of crystallographic relations between the precipitation lattice and the matrix lattice results from the lack of coherence between these phases, and the latter from the disordered distribution of crystal elements in the matrix structure.

This statement would seem fully justified were it not for the fact that the dendritic growth during precipitation from a supersaturated solid solution has not been proved so far. Thus the dendritic growth morphology of amorphous Te–15 at.% Ge alloy, observed by the author and others [28–32], also during the crystallization of amorphous alloys of Co, Ni and Fe, undermines the soundness of the present conclusion.

Dendritic growth results from constitutional supercooling at the crystallization boundary between the crystal and the liquid surrounding it [30] and belongs to the most standard casting structures. Therefore, the following question must be thought over: "What factors are in favour of considering the glass-to-crystal transformation on the grounds of the theory of crystallization from the liquid phase?"

The first factor is that the structure of the amorphous phase is more similar to that of a liquid than to that of a perfect crystal. It is testified to by the fact that both the liquid and amorphous body structures are described by means of the same function – a radial distribution function (RDF). The second factor, resulting from the first, is that the crystals forming in a matrix of such a structure take the shape which only slightly depends on the matrix. This is demonstrated (similar to crystallization of initial phases in the liquid phase) by taking crystals of the form which minimize the total free energy of the system by minimizing the surface free energy. Crystals thus formed are round, as seen in Fig. 1a. It is often the case that during growth the initial crystals develop growth-preferred surfaces, for example {1 0 0}, forming crystals of polyhedral shape (Fig. 1b). During crystallization of the phases which feature anisotropy of their physico-chemical properties (for example a considerable difference in thermal diffusivity in various crystallographic directions) crystals form in the liquid which are elongated platelets or needle-shaped. An example of such a growth morphology is crystallization in the Te–40 at.% Cu alloy (Fig. 1d). According to earlier studies [33] the growth of Te crystals takes place mainly in directions parallel to the direction of maximum heat removal rate, i.e. in the basal plane (0 0 1) of the unit cell of hexagonal tellurium. A dendritic growth is observed under conditions of constitutional supercooling on the crystallization boundary, and as already mentioned, this is a typical casting structure (Fig. 1e).

In spite of the examples quoted above, it seems to be little probable that the crystallization of amorphous phases may be considered on the grounds of a classic theory of liquid crystallization (solidification) because the crystal formation process takes place in the solid state.

The viscosity of amorphous materials is practically the same as that of crystalline bodies, and the density of crystalline materials is about 2% higher. In spite of an insignificant difference in density, the amorphous structure is, however, much "looser" – less compact. Thus it has a higher ability to accommodate possible stresses which may develop during the crystallization process. Because of the lesser degree of space packing, it should be undoubted that the diffusion coefficient of amorphous bodies is higher than that of crystalline bodies [34], but lower than that of a liquid in which connection movements and only transitory stability of close-order complexes considerably raise its diffusivity. According to the theory of solid state diffusion, the most important mass transport mechanism is the vacancy mechanism. From the standpoint of physical chemistry, glass is a supercooled liquid, so it has an uncomparably higher number of structural defects than a crystalline body, including point defects.

According to Górecki [35] the equilibrium concentration of vacancies at the melting temperature is described for metals by the formula:

$$c_v^e = \exp(4.1 - E_f/kT_m) \qquad (2)$$

where T_m is the absolute melting temperature, and 4.1 is an entropy figure at the melting point, as suggested by Kraftmakher [37] and Strelkov [36].

It follows from comparative calculations carried out by the authors [38] for aluminium, that the equilibrium concentration of vacancies at the melting point is one order of magnitude higher than that at ambient temperature. If a cooling rate of about 10^6 to 10^8 deg sec^{-1} for the splat-cooling method is taken into consideration, it is unprobable that a considerable change in the concentration of vacancies may take place during the liquid solidification process.

For this reason the amorphous body is supersaturated with vacancies. If a vacancy mechanism of diffusion is assumed for an amorphous body, it should be expected that the rate of phase transformation controlled by diffusion (for example, amorphous-phase crystallization) should be noticeably higher than the rate of precipitation from supersaturated crystalline solid solutions. Confirmation of the above statement is given by the results of tests carried out by Mader and Nowick [39], who calculated that the diffusion activation energy during crystallization of the amorphous phase is higher only by one order of magnitude than the activation energy of crystallization of pure metals from a liquid. Summarizing the above considerations it seems to be a reasonable statement that for amorphous materials the significance of the expression $n \cdot \Delta g_s$ in Equation 1 is relatively small, in comparison with its significance in the case of precipitation of coherent matrix phases.

In spite of this, contrary to the liquid state, the equation describing the total change of free energy of a system resulting from the formation of a particle of the new phase, should include an element which takes into account the change in elastic strain energy. However, in this case the value of $n \cdot \Delta g_s$ is determined mainly by stresses resulting from differences between the specific volume of the precipitated particle and that of the amorphous matrix. When the average difference of specific volume amounts to about 2%, the linear contraction factor amounts to about 1.26%, assuming uniform change of volume in all directions. Stresses connected with such small changes of volume, i.e. strains, also should not be great, the more so, because, as was mentioned earlier, the amorphous phase lattice possesses great ability to accommodate stresses. Nevertheless, in the case of some alloys, changes of volume are much greater [40] and then the element $n \cdot \Delta g_s$ may take essential values. In this case the ratio of the amorphous phase density to that of the crystalline phase ρ_a/ρ_c determines the value of Δg_s.

If the value of Δg_s is determined by the difference between the density of an amorphous phase ρ_a and that of a crystalline phase, ρ_c, then when $\rho_a/\rho_c \simeq 1$, Δg_s should be negligible. Assuming that for $\rho_a/\rho_c = 1$ the value $\Delta g_s = 0$, this function should take the form:

$$\Delta g_s = A \cdot \ln\left(\frac{\rho_a}{\rho_c}\right) \tag{3}$$

where A is a constant depending on the interactions between atoms on the crystal–amorphous matrix interface.

In the light of these considerations, the following conclusions may be proposed:

(1) from the morphological standpoint, the crystallization of amorphous phases may be considered as an intermediate transition between the liquid-to-crystal transition and the precipitation of non-coherent particles from supersaturated solid solution;

(2) the expression $n \cdot \Delta g_s$ is considerably affected by differences between the density of the amorphous phase and that of the crystal;

(3) a function describing the dependence between Δg_s and the differences in densities of the crystalline and amorphous phases may take the form: $\Delta g_s = A \cdot \ln(\rho_c/\rho_a)$.

Acknowledgement

The author wishes to thank Professor H. Matyja for helpful comments and discussion. This work was supported by the US National Science Foundation under Grant GF 42176.

References

1. P. DUWEZ and R. H. WILLENS, *Trans. AIME* **227** (1963) 362.
2. T. R. ANANTHARAMAN and C. SURYANARAYANA, *J. Mater. Sci.* **6** (1971) 1111.
3. P. MAINTREPIERRE, *J. Appl. Phys.* **41** (1970) 498.
4. R. HASEGAWA, *Phys. Lett.* **36A** (1971) 425.
5. H. S. CHEN and T. T. WANG, *J. Appl. Phys.* **41** (1970) 5338.
6. A. BARNA, P. B. BARNA and J. F. POCZA, *J. Non-Cryst. Solids* **8** (10) (1972) 36.
7. B. G. BAGLEY and D. TURNBULL, *Acta Met.* **18** (1970) 857.
8. M. SHIOJIRI, *J. Phys. Soc. Japan* **21** (1966) 335.
9. K. L. CHOPRA and S. K. BAHL, *J. Appl. Phys.* **40** (1969) 4171.
10. A. L. ASEEV, O. J. VASIN and S. J. STENIN, *Phys. Stat. Sol. (a)* **10** (1972) 297.
11. M. R. ANSEAU, *Phys. Lett.* **43A** (1) (1973) 57.
12. T. MASUMOTO and R. MADDIN, *Acta Metal.* **19** (1971) 725.
13. P. DUHAJ, V. SLADEK and P. MRAFKO, *J. Non-Cryst. Solids* **13** (1974) 341.
14. F. VASILIU and F. GLODEANU, *Rev. Romm. Phys.* **18** (1973) 3.
15. T. TAKAMORI, R. ROY and G. J. McCARTHY, *Mater. Res. Bull.* **5** (1970) 529.
16. U. KÖSTER, *Acta Metal.* **20** (1972) 1361.
17. C. SURYANARAYANA and T. R. ANANTHARAMAN, *J. Mater. Sci.* **5** (1970) 992.
18. U. KÖSTER, "Advances in Colloid and Interface Science", Vol. 10 (Elsevier, Amsterdam, 1979) p. 129.
19. M. KACZOROWSKI, J. KOZUBOWSKI, B. DĄBROWSKI and H. MATYJA, *J. Mater. Sci.* **13** (1978) 1105.
20. *Idem, ibid.* **13** (1978) 407.
21. R. H. WILLENS, *J. Appl. Phys.* **33** (1962) 3269.
22. M. KACZOROWSKI, B. DĄBROWSKI and H. MATYJA, *Mat. Sci. Eng.* **29** (1977) 189.
23. M. KACZOROWSKI and H. MATYJA, *J. Mater. Sci.* **14** (1979) 2887.
24. J. W. CHRISTIAN, "The Theory of Transformation in Metals and Alloys" (Pergamon Press, Oxford, London, 1965).
25. B. D. CULLITY, "Podstawy Dyfrakcji Promieni Rentgenowskich" (WNT, Warszawa, 1964).
26. W. A. TILLER, "Physical Metallurgy", edited by R. W. Cahn (North-Holland, Amsterdam, 1965) Ch. 9, p. 385.
27. M. KACZOROWSKI and J. BINDAS, *Z. Metallkde* **72** (1981) 582.
28. M. KACZOROWSKI, *Proc. ITB* **6** (1981) 74.
29. S. C. MOSS and J. P. NEUFVILLE, *Mat. Res. Bull.* **7** (1972) 423.
30. P. K. RASTOGI and P. DUWEZ, *J. Non-Cryst. Solids* **5** (1970) 1.
31. P. DUWEZ, *Trans. ASM* **60** (1967) 607.
32. W. A. TILLER, "The Art and Science of Crystal Growing" (Wiley, New York, 1962) Ch. 15.
33. M. KACZOROWSKI, B. DĄBROWSKI and H. MATYJA, *Mat. Sci. Eng.* **29** (1977) 155.
34. H. SCHMALZRIED, "Solid State Reaction" (Verlag Chemie, GmbH, Weinheim, 1974) p. 129.
35. T. GÓRECKI, *Z. Metallkde* **65** (1974) 426.

36. A. SEEGER, D. SCHUMACHER, W. SCHILLING and J. DIEHL, (Eds), "Vacancies and Interstitials in Metals" (North-Holland, Amsterdam, 1970).
37. J. A. KRAFTMAKHER and P. G. STREILKOV, *Fiz. Tverdego Tela* 8 (1966) 1049.
38. M. KACZOROWSKI and R. SZOSTAK,
39. S. MADER and A. S. NOWICK, *Acta Metal.* **15** (1967) 215.
40. M. KACZOROWSKI, unpublished results.

Received 15 January
and accepted 22 February 1982