

Preparation of amorphous $Ti_{1-x}Cu_x$ ($0.10 < x \leq 0.87$) by mechanical alloying

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We show that amorphous alloy powders of Cu and Ti can be produced over a broad composition range by mechanical alloying of the elemental powders in a high-energy ball mill. The amorphous powders are compared with liquid-quenched amorphous alloys of the same compositions using the techniques of x-ray diffraction and thermal analysis of crystallization. The two types of samples are found to have similar characteristics. Chemical analysis shows that only trace amounts of impurities are introduced in the alloys by the milling process.

INTRODUCTION

For more than 30 years amorphous metallic alloys have been mainly prepared by extreme quenching methods such as vapor condensation¹ or rapid liquid quenching² in the form of thin films, splats, ribbons, or powders. The most commonly utilized industrial techniques are chill block melt spinning for the continuous fabrication of uniform ribbons and other rapid-solidification-rate (RSR) methods for producing metal powders. In research one often employs sputtering, splat quenching, ion implantation, electrodeposition, chemical deposition, laser glazing, and the newly developed process of solid state reaction.³⁻⁵ It was earlier realized that cold working at temperatures in the range of liquid helium (4.2 K) can produce alloying of two metals. It is of interest that alloying of such cold-worked materials was demonstrated by observing an increase of the alloy superconducting transition temperatures.⁶

Intense deformation during repeated mechanical mixing, cold welding, fracturing, and rewelding of ultrafine alloy powders in a dry high-energy ball mill produces mechanically formed alloys. This method has been described by Benjamin⁷ some years ago. Mechanical alloying (MA) can even produce homogeneous alloys of elements which cannot ordinarily be alloyed either by diffusion and sintering or by melting.

In this way it is possible to develop "synthetic" alloys with quite different properties than the corresponding alternative alloys produced by sintering or melting. For example, mechanical alloyed dispersion-strengthened nickel superalloys have, at 1250 K, twice the tensile yield strength of nickel-base superalloys of the same composition prepared by more conventional methods.⁸

Recently, Ermakov *et al.*^{9,10} reported that "amorphous" or partially amorphous structures were obtained when elemental powder mixtures of Y-Cu or Gd-Co were mechanically alloyed. They did not carry out a detailed analysis of the atomic scale structure of the alloys. The first definitive demonstration that structurally amorphous alloys can be prepared by mechanical alloying was reported by Koch *et*

*al.*¹¹ for samples of $Ni_{60}Nb_{40}$. Mechanical alloying has also been applied successfully for the production of amorphous Ni-Ti (Ref. 12) and Nb-Ge, and Nb-Ge-Al.¹³ In this paper we report on the preparation and characterization of amorphous $Ti_{1-x}Cu_x$ alloys over a broad range of composition ($0.1 < x < 0.9$) by the method of mechanical alloying.

EXPERIMENTAL PROCEDURES

For these studies, fine powders of Ti (99.95%, 325 mesh) and Cu (99.95%, $< 63 \mu m$) were used as starting materials. Powder mixtures of appropriate composition were mixed for several minutes using a glass rod in a small vial prior to milling.

The milling was carried out alternatively in a hardened tool steel vial or in a tungsten carbide vial (WC + 6% Co). The volumes of the two vials were identical—80 ml. The balls used for milling were made of WC. Balls of 3, 6, 8, and 10 mm diameter were used. The best results were obtained using balls of 8 and 10 mm diameter. The ball-to-powder weight ratio varied between 3:1 and 10:1. In order to avoid oxidation, the ball mill was sealed under dry argon ($> 99.999\%$) inside of a glove box. For this purpose the respective vials of tool steel or WC were fitted with "O" rings made of Viton. The leakage was checked and found to be less than 5×10^{-9} mbar liter s^{-1} for 1.1 bar of He. The vials were always loaded in the glove box with inside overpressure of 100 mbar argon. In air, it was found that the ground powder had already picked up considerable quantities of oxygen and nitrogen after 5–10 s duration of the grinding process. This could be deduced by the immediate reduction of the pressure during milling in a vial sealed in open air. The milling process was interrupted every hour and, in analogy with the experiments of Koch *et al.*,¹¹ small quantities of mechanically alloyed powder were removed for x-ray diffraction analysis. In addition, small quantities of the alloys were prepared for chemical and powder screening analysis, measurement of superconductivity, metallographic studies, differential thermal analysis (DTA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The tendency of the powder to purf was controlled. When required,

the agglomeration and sticking of powder on the vial or balls was eliminated or reduced by mechanically scraping the vial and balls.

The material removed was subsequently added again to the grinding process. This troublesome procedure was necessary to ensure homogeneous composition of the final powder with respect to content of Ti and Cu.

Screened MA powders were found to contain particles of size ranging from 2 to 43 μm and larger. X-ray diffraction analysis on particles of size less than 20 μm gave essentially identical results to that on larger particles or agglomerates. The actual x-ray specimens were prepared by applying a layer of screened powder to a Plexiglas sheet using a small amount of silicon grease as a binder. X-ray scans were carried out on a vertical powder diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) without a monochromator. Wet-chemical analysis was carried out on initial powders and selected MA powders.

RESULTS AND DISCUSSION

Figure 1 shows a series of x-ray diffraction patterns taken at 1-h intervals during the ball milling of a $\text{Ti}_{57}\text{Cu}_{43}$ alloy starting from the elemental powder mixture. After 2 h of processing, one notes the appearance of a broad scattering maximum near $2\theta = 41^\circ$. Superimposed on this are relatively sharper Bragg peaks characteristic of the microcrystalline elemental phases. After 4 h of processing, the broad scattering maxima has increased in intensity while the Bragg peaks have nearly disappeared. Finally, after 6 h of processing, only the broad scattering maxima is near $2\theta = 41^\circ$, followed by a still broader but weaker maxima centered near $2\theta = 72^\circ$, are seen.

This pattern is characteristic of an amorphous alloy.

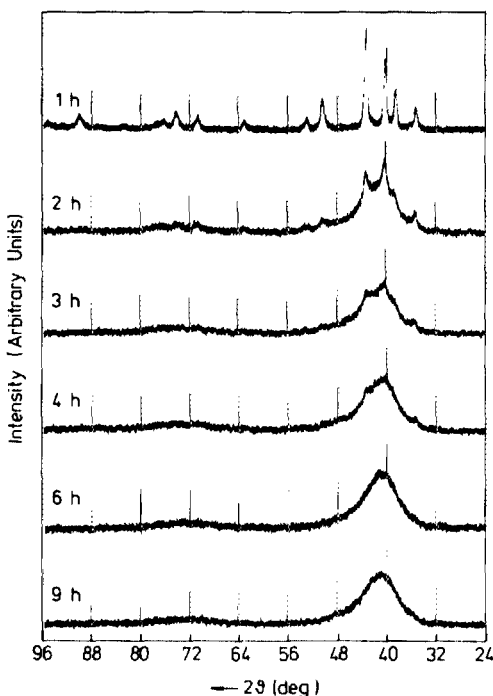


FIG. 1. X-ray diffractograms ($\text{CuK}\alpha$ radiation) of $\text{Ti}_{57}\text{Cu}_{43}$ alloys. With increasing milling time, powder becomes gradually amorphous.

For comparison, a sample of the MA powder was used to produce an amorphous splat quenched alloy. Such splat-quenched amorphous Ti-Cu alloys have been studied previously,¹⁴ the MA powder was remelted and rapidly quenched using a piston and anvil apparatus operated in an argon atmosphere. Foils of thickness 30–40 μm and area $\sim 1\text{--}2/\text{cm}^2$ are produced by the splat quench. The x-ray diffraction pattern of the rapidly quenched sample is compared with that of the MA powder sample in Fig. 2. The two diffraction patterns have similar features. The location of the primary and secondary broad scattering maxima are nearly identical. The half width at half maximum of the primary scattering maximum of the mechanically alloyed sample is about 3% less than that of the corresponding liquid-quenched alloy. Such differences can be attributed to the degree of relaxation of the amorphous structure of the two samples.

Figure 3 shows a second example of a series of x-ray diffraction patterns taken at 1-h intervals during the synthesis of a $\text{Ti}_{30}\text{Cu}_{70}$ amorphous alloy by ball milling. One again notes a progression similar to that seen in the earlier case. An entirely amorphous product is again obtained after 6 h of milling. We note that the primary scattering maxima of the amorphous phase is shifted to higher scattering angles for the more Cu-rich alloy. This characteristic is observed in general as the Cu content of the alloys is increased. Figure 4 shows x-ray diffraction patterns of the amorphous product obtained for six alloys of progressively increasing Cu content and illustrates the gradual shift of the primary scattering maximum. It is found that the primary maximum shifts maximum from $2\theta = 39.4^\circ$ for $\text{Ti}_{90}\text{Cu}_{10}$ to $2\theta = 43.2^\circ$ for $\text{Ti}_{13}\text{Cu}_{87}$. This can be attributed to a progressive decrease of the nearest neighbor distance as the Cu content is increased. The metallic radius of Cu ($r_{\text{Cu}} = 1.28 \text{ \AA}$) is smaller than that of Ti ($r_{\text{Ti}} = 1.47 \text{ \AA}$) and thus nearest-neighbor Cu pairs have smaller separation than nearest-neighbor Ti pairs with Cu-Ti pairs expected to have an intermediate value.

On the basis of the above x-ray data, we believe that amorphous alloys of Cu-Ti are formed over the range from 10 to 87 at. % Cu during ball milling. To determine what, if any, impurities are introduced into the alloys by the ball milling process, wet chemical analysis was carried out on the amorphous alloy products. It was found that the typical product powders contain less than 1000 ppm O_2 , 300 ppm N_2 ,

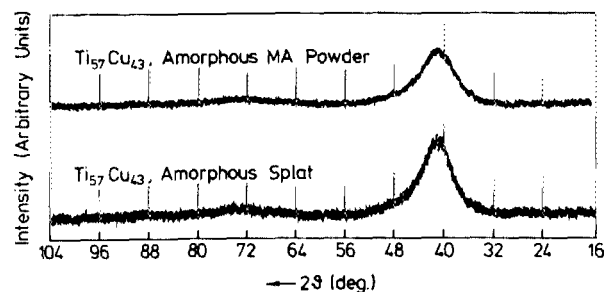


FIG. 2. Comparison of x-ray diffractograms ($\text{CuK}\alpha$ radiation) of amorphous $\text{Ti}_{57}\text{Cu}_{43}$ MA powder (milled 6 h) with amorphous $\text{Ti}_{57}\text{Cu}_{43}$ prepared by splat quenching.

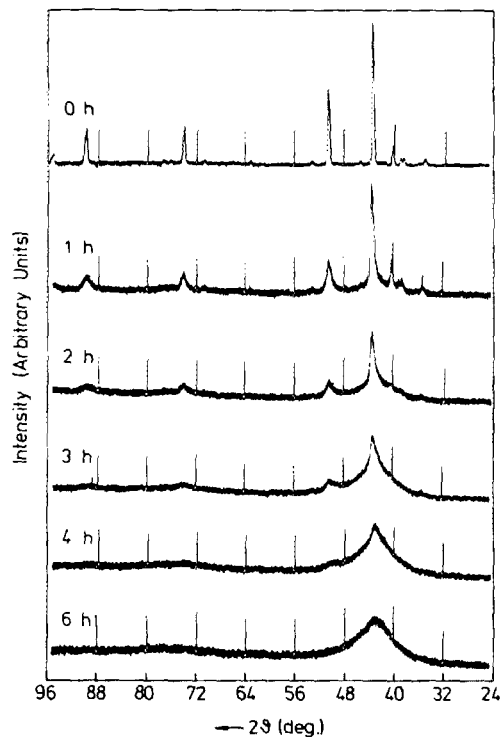


FIG. 3. X-ray diffractograms ($\text{CuK}\alpha$ radiation) of $\text{Ti}_{30}\text{Cu}_{70}$ alloys. After 6 h of grinding, a completely amorphous structure was observed.

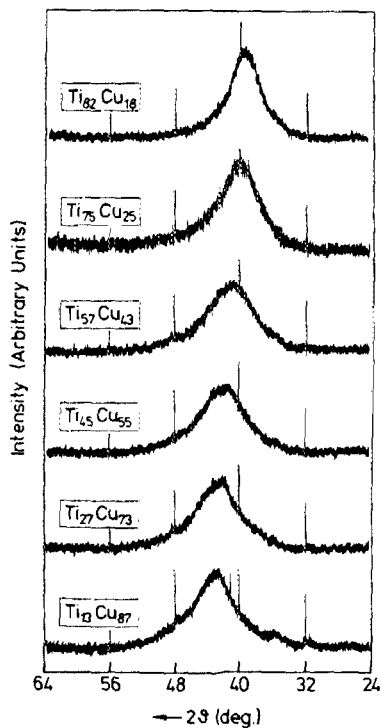


FIG. 4. X-ray diffractograms ($\text{CuK}\alpha$ radiation) of $\text{Ti}_{1-x}\text{Cu}_x$ alloys. The first peak, representing the contribution of the nearest-neighbor atoms, shifts to higher 2θ values with increasing Cu concentration.

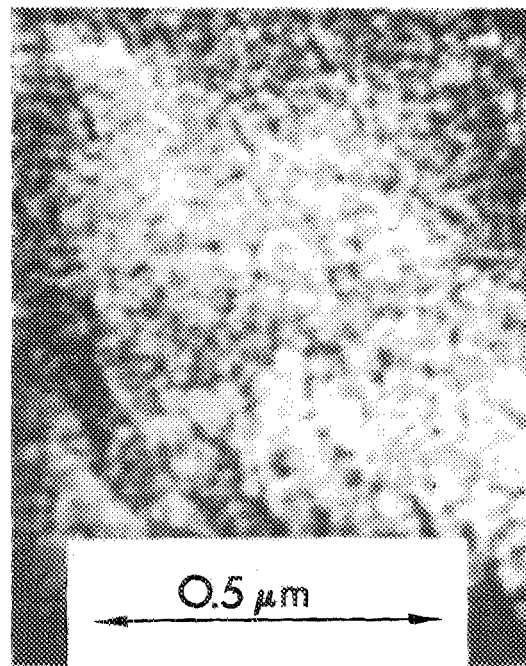


FIG. 5. SEM micrograph of $\text{Ti}_{30}\text{Cu}_{70}$ MA microcompacts. The white spots are Ti-Cu particles.

320 ppm Fe, 50–200 ppm Co, 200–500 ppm W, and less than 300 ppm C. The residual gas levels (O_2 , N_2) were found to be no greater than that obtained by wet chemical analysis of the starting powders, while the Fe, Co, W, and C impurities are presumably attributed to the milling process (which employs Co-bonded WC balls). As a means of characterizing the micromorphology of the powder, individual grains were examined using scanning electron microscopy (SEM). Figure 5 shows an SEM micrograph of a sample of $\text{Ti}_{30}\text{Cu}_{70}$ following 2 h of ball milling. The sample exhibits a fine texture on a scale of the order of several nm. The individual domains are presumably produced by progressive refinement of the original powder mixtures as milling proceeds.

To further investigate whether the mechanically alloyed amorphous samples are similar to those prepared by liquid quenching, thermal stability studies using DTA and DSC have been carried out. Figure 6 shows the DTA results for the two different amorphous $\text{Ti}_{57}\text{Cu}_{43}$ alloys for comparison. Case (a) is an MA powder after 6 h milling time and case (b) is a sputter of 40- μm thickness which has been produced by rapid quenching under argon (in a piston and anvil sputter cooling apparatus). The DTA samples have been heated in Al_2O_3 crucibles with the rate of 40 K min^{-1} under a flowing helium atmosphere. Al_2O_3 powder was used as reference material. The onset of crystallization has been found for amorphous sputters at 649 K and for MA amorphous powder at 670 K. DSC results gave essentially the same crystallization behavior. A detailed analysis of absolute heats of crystallization has not yet been carried out. We also note that DTA and DSC experiments have also shown evolution of small quantities of argon gas from amorphous $\text{Ti}_{1-x}\text{Cu}_x$ MA powders. This evolution of argon generally occurred at temperatures ranging from between 50 and 250 K below the

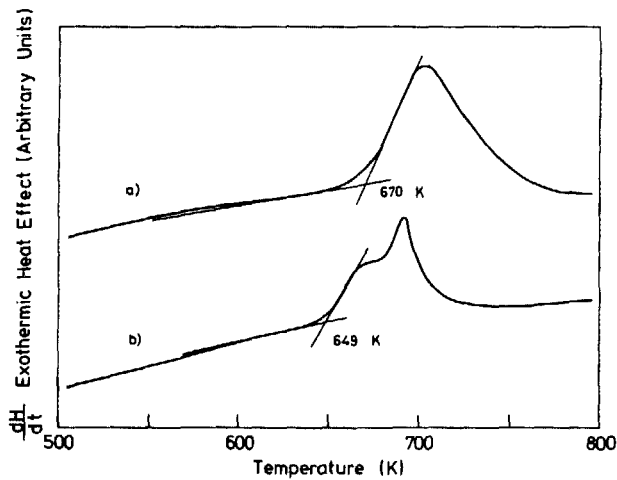


FIG. 6. DTA curves show the crystallization peaks for amorphous $Ti_{57}Cu_{43}$ MA powder (a), and amorphous $Ti_{57}Cu_{43}$ MA prepared by splat quenching (b).

temperature T_x , where crystallization was observed. Some samples did however show traces of argon evolution even above T_x . Evolution of such trapped argon occurs gradually and does not give a well-defined exotherm (as does crystallization). These calorimetric experiments show that our MA $Ti_{1-x}Cu_x$ powders exhibit crystallization at a temperature range close to that observed in amorphous splat-quenched foils.

The observed heats of crystallization per unit mass are also comparable for the two cases. One might argue that trapped gas could stabilize a nanocrystalline structure such

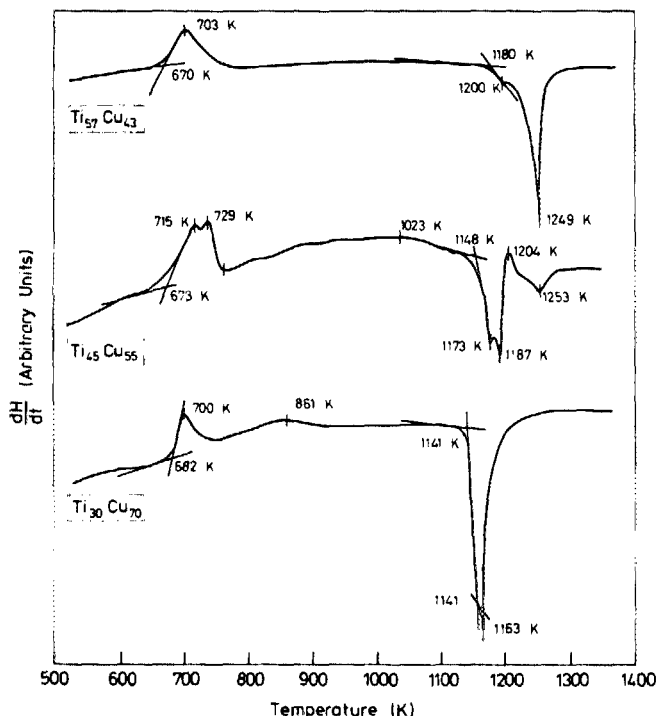


FIG. 7. DTA curves from $Ti_{57}Cu_{43}$, $Ti_{45}Cu_{55}$, and $Ti_{30}Cu_{70}$ amorphous MA powders.

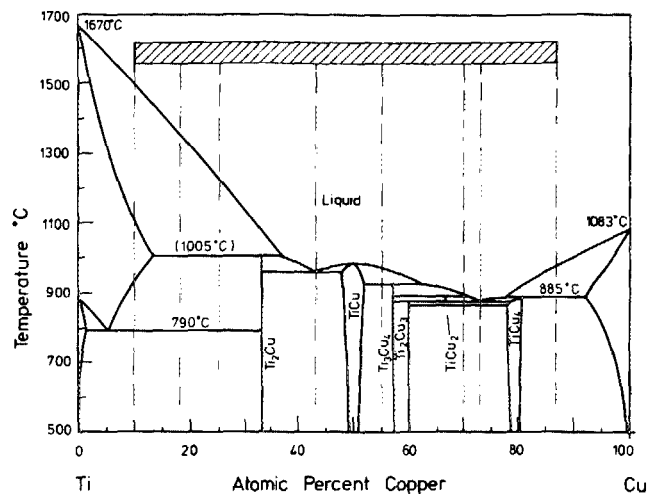


FIG. 8. Binary alloy phase diagram of the Ti-Cu system¹⁶ showing the composition range of amorphous $Ti_{1-x}Cu_x$ alloys formed by mechanical alloying.

as that obtained when ultrafine powders of dimension 1–10 nm are consolidated.¹⁵ However, the x-ray patterns obtained here do not exhibit the gaslike diffraction pattern seen for such nanocrystalline matter. Furthermore, the trapped gas (argon in the present case) is evolved at temperature below T_x showing that the amorphous structure observed does not require the trapped gas for stabilization.

Figure 7 illustrates the DTA graphs of three MA Ti-Cu powders over a broad temperature range. Exothermic heat peaks refer to crystallization events whereas the endothermic peaks were found to correspond to alloy melting. Similar to liquid-quenched amorphous splats and ribbons, several temperatures of crystallization are shown by some alloys, e.g., $Ti_{30}Cu_{70}$. The melting points in the calorimetric studies correspond quite well to the existing eutectic and solidus-liquidus curves given by the binary Ti-Cu phase diagram¹⁶ (Fig. 8). The broken lines mark the compositions of our Ti-Cu alloys. Figure 9 illustrates the measured T_x onsets and the T_x midpoints for six different amorphous MA Ti-Cu alloys in comparison with T_x data of amorphous splats and amorphous ribbons.¹⁶ These results demonstrate that amor-

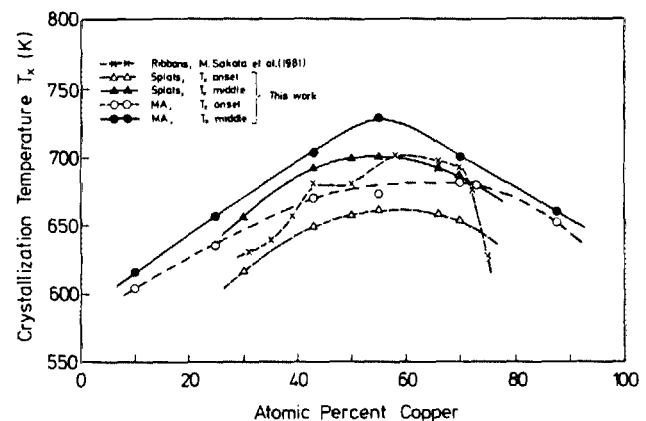


FIG. 9. Crystallization temperature T_x vs composition of $Ti_{1-x}Cu_x$ alloys.

phous MA powders prepared over a wide range of compositions exhibit crystallization temperatures similar to those seen for amorphous ribbons and splats prepared by melt spinning and splat cooling over the same range of compositions.

Finally, we mention that we have attempted to consolidate (by cold pressing and sintering) the amorphous MA powders produced in this study. We have observed that the MA powder has excellent flowing and pressing characteristics. With small pressures (of 100–200 bar/cm²), it is possible to produce bulk pellets of diameter 10 mm and height 8 mm, having a relatively high density (> 95% bulk density). The pellets have good mechanical integrity. We are carrying out additional studies of such consolidation by sintering at elevated temperatures. Results will be reported in a future publication.

CONCLUSION

We have shown that amorphous powders can be produced by mechanical alloying of elemental Cu and Ti powders in a high-energy ball mill over a broad range of alloy compositions. The powders were studied by x-ray diffraction and thermal analysis and compared with amorphous samples prepared by liquid quenching. The two types of alloys have similar atomic scale structure and crystallization behavior. Chemical analysis has shown that the ball milling process produces only limited contamination by impurities. Future work will be directed toward determining the more general applicability of this method of producing amorphous alloys. The consolidation characteristics of such alloys may prove promising in efforts to produce bulk amorphous metal structures.

ACKNOWLEDGMENTS

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- ¹W. Buckel and R. Hilsch, *Z. Phys.* **132**, 420 (1952).
- ²P. Duwez, R. H. Willens, and W. Klement, *J. Appl. Phys.* **31**, 1136 (1960).
- ³X. L. Yeh, K. Samwer, and W. L. Johnson, *Appl. Phys. Lett.* **42**, 242 (1983).
- ⁴R. B. Schwarz and W. L. Johnson, *Phys. Rev. Lett.* **51**, 415 (1983).
- ⁵L. Schultz, in *Amorphous Metals and Non-Equilibrium Processing, Proceedings of the Materials Research Society—Europe Meeting*, Strasbourg, June 1984, edited by M. Von Allmen (Les Editions de Physique, Les Zolis Cedex, France, 1984), p. 135.
- ⁶G. Bergmann, R. Hilsch, and G. v. Minnigerode, *Naturforschung* **19**, 580 (1964).
- ⁷J. S. Benjamin, *Metall. Trans.* **1**, 2943 (1970).
- ⁸P. S. Gilman and J. S. Benjamin, *Annu. Rev. Mater. Sci.* **13**, 279 (1983).
- ⁹A. E. Ermakov, E. E. Yurchikov, and V. A. Barinov, *Fiz. Metal. Metalloved.* **52**, 1184 (1981).
- ¹⁰A. E. Ermakov, V. A. Barinov, and E. E. Yurchikov, *Fiz. Metal. Metalloved.* **54**, 935 (1982).
- ¹¹C. C. Koch, O. B. Cavin, C. G. McKamey, and J. O. Scarbrough, *Appl. Phys. Lett.* **43**, 1017 (1983).
- ¹²R. B. Schwarz, R. R. Petrich, and C. K. Saw, *J. Non-Cryst. Solids* **76**, 281 (1985).
- ¹³C. Politis, *Proceedings of the International Conference on the Materials and Mechanisms of Superconductivity*, Ames, Iowa, May 29–31, 1985 (in press).
- ¹⁴S. F. Bartram, in *Handbook of X-Rays*, edited by E. F. Kaelble (McGraw-Hill, New York, 1967), Vol. 17-1.
- ¹⁵H. Gleiter and P. Marquardt, *Z. Metallkd.* **75**, 263 (1984).
- ¹⁶J. L. Murray, *Bull. Alloy Phase Diagrams* **4**, 81 (1983).
- ¹⁷M. Sakata, N. Cowlam, and H. A. Davies, *Proceedings of the IV International Conference on Rapidly Quenched Metals*, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Tokyo, 1982), p. 327.