

range $\lambda\kappa(0)$ is independent of (d/W) . Therefore,

$$I_c/I_{cu} \approx [1 + \frac{1}{4}(\beta d)^2(l/d - \frac{1}{4})]^{-1}. \quad (\text{A5})$$

Since $\lambda|\kappa(0)|$ must be less than unity in order that Eq. (17) be valid, it is necessary that $(\beta d)^2(l/d - \frac{1}{4}) < 2$

in Eq. (A5). For situations in which (d/W) is not much less than unity, Eqs. (A1) and (A4) are not valid. In these cases the general expressions describing the variation of current density in the films can be used to calculate the critical current.

Amorphous Phase in Palladium-Silicon Alloys*

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By rapid cooling from the melt, an amorphous phase has been obtained in palladium-silicon alloys containing 15 to 23 at.% Si. This phase is stable at room temperature and crystallization cannot be detected after one month at 250°C. With rates of heating greater than 20°C/min, rapid crystallization takes place at 400°C, with a heat release of approximately 1000 cal/mole. The electrical resistivity of an alloy containing 17 at.% Si at room temperature is 2.6 times that of the equilibrium alloy. The resistivity decreases linearly with decreasing temperature and is about 95% of the room-temperature value at 2°K. Various factors involved in the retention of amorphous phases in rapidly quenched liquid alloys are discussed.

INTRODUCTION

BY rapid cooling from the liquid state, amorphous structures have been previously obtained in gold-silicon alloys¹ and in tellurium-base alloys with gallium, indium, and germanium.² The gold-silicon alloy is not stable at room temperature and none of the physical properties have been measured. The tellurium-base alloys are stable up to at least 100°C and electron microscopy studies have shown that crystallization takes place by dendritic growth. A new amorphous phase in palladium-silicon alloys containing from about 15 to 23 at.% silicon is described in the present paper.

EXPERIMENTAL PROCEDURES AND RESULTS

The alloys were prepared by induction melting of the two components in a fused silica crucible under an argon

atmosphere. Within the composition range of interest, a very exothermic reaction takes place (probably due to the formation of the compound Pd₃Si) before the melting point of silicon is reached. The molten ingot does not wet the crucible, and is free from contamination. Rapid cooling from the liquid state was achieved by either the "gun" technique³ or the "piston and anvil" technique.⁴ The foils obtained by the gun technique have very uneven thickness, but can be used for transmission electron microscopy without any mechanical or chemical thinning.^{5,6} Those obtained by the piston and anvil technique are about 25 mm in diameter, have an even thickness of approximately $44 \pm 5 \mu$, and are suitable for electrical resistivity measurements.

The structure of the amorphous alloys was studied by x-ray diffraction, electron diffraction, and electron

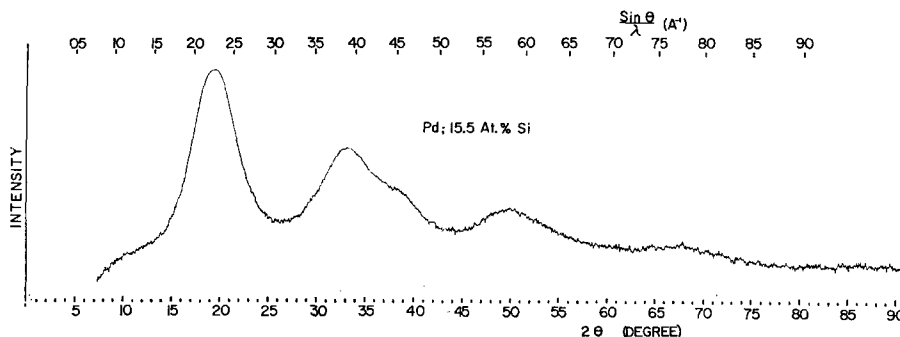


FIG. 1. Microphotometer trace of an x-ray diffraction pattern of a Pd-15.5 at.% Si alloy. Monochromatic Mo $K\alpha$ radiation.

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¹ W. Klement, Jr., R. H. Willens, and Pol Duwez, *Nature* **187**, 869 (1960).

² H. L. Luo and Pol Duwez, *Appl. Phys. Letters* **2**, 21 (1963).

³ Pol Duwez and R. H. Willens, *Trans. Metal AIME* **227**, 362 (1963).

⁴ P. Pietrokowsky, *J. Sci. Instr.* **34**, 445 (1963).

⁵ R. H. Willens, *Proceedings of the Fifth International Meeting for Electron Microscopy* (Academic Press Inc., New York, 1962), Vol. 1, EE-6.

⁶ R. H. Willens, *J. Appl. Phys.* **33**, 3269 (1962).

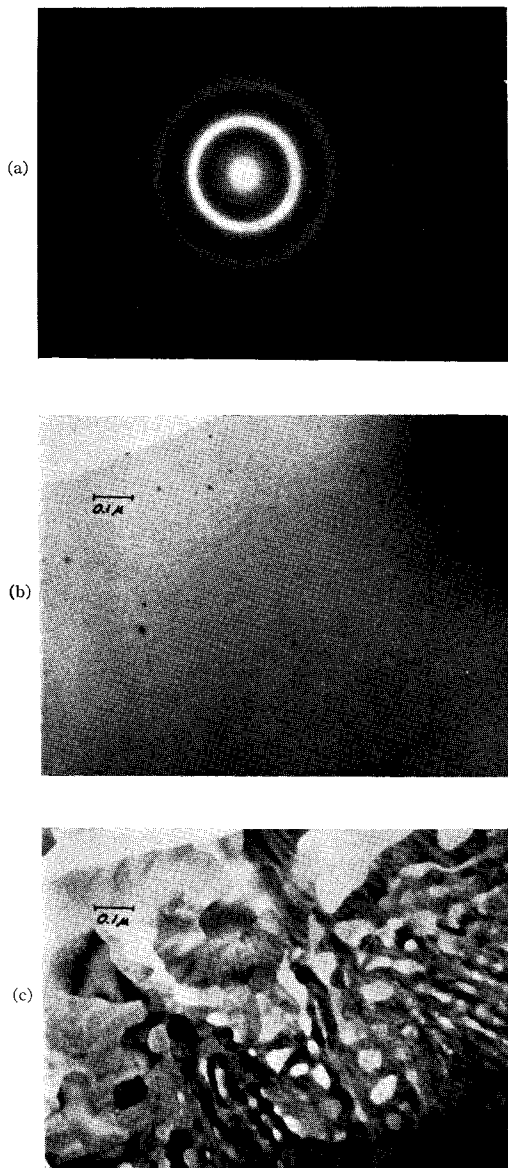


FIG. 2. (a) Transmission electron diffraction pattern (100 kV) of amorphous Pd-20 at.%Si alloy. (b) Transmission electron micrograph of same alloy. (c) Same area as (b), showing crystalline structure after heating the specimen in the microscope.

microscopy. The x-ray diffraction patterns were obtained with a 114.6-mm-diam Debye-Scherrer camera, using Mo $K\alpha$ radiation monochromatized by the (200) reflection of a calcium fluoride crystal. A typical microphotometer trace of a pattern of an alloy containing 15.5 at.%Si is shown in Fig. 1. The general shape of this pattern is typical of an amorphous structure. Electron diffraction and microscopy confirmed the amorphous structure. A typical electron diffraction pattern and the corresponding electron micrograph are shown in Figs. 2 (a) and (b). It is quite obvious that the electron diffraction pattern does not have sharp Bragg-type diffraction maxima, in spite of the very short wave-

length of the electrons (0.037 Å). In addition, transformation of the amorphous foil to a crystalline state was observed within the microscope by heating the specimen to an estimated temperature of about 400°C, and the resulting structure is shown in Fig. 2(c). The structure seems to be equiaxed and, contrary to what was observed previously in tellurium-base amorphous alloys,⁶ no dendritic growth can be detected. This observation gives support to the argument, advanced in Ref. 6, by which the poor thermal conductivity of the tellurium-base alloy gave rise to temperature gradients during the dendritic growth. Such temperature gradients are probably absent in the present case, since as shown in the next paragraph, the amorphous Pd-Si alloys have a high electrical conductivity and their thermal conductivity can, therefore, be expected to be also quite high.

The electrical resistivity of an amorphous Pd-Si alloy containing 17 at.%Si was measured between 2° and 373°K and compared with the resistivity of the same alloy in its crystalline equilibrium state. The results are shown in Fig. 3. As expected the room-temperature resistivity of the amorphous alloy is greater than that of the crystalline one (about 2.6 times). The resistivity decreases linearly with temperature down to 2°K, and the temperature coefficient between 2° and 300°K is 0.00017/°C.⁷ Evidently the electrical conductivity is mainly governed by polyvalent scattering, the phonon scattering having a very small contribution.⁸

The temperature stability of amorphous foils has been studied by both thermal analysis and differential thermal analysis. Within a range of heating rates from about 20 to 10 000°C/min, a very sharp exothermic

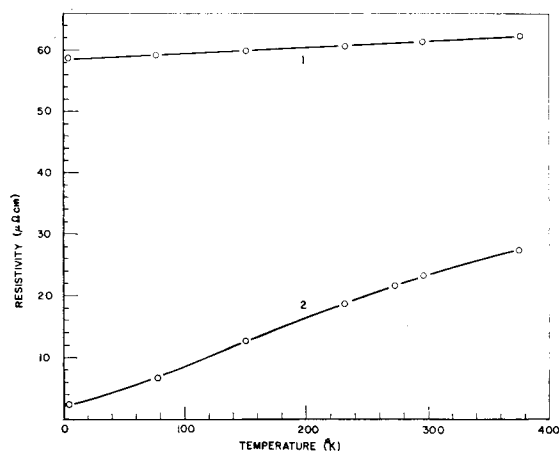


FIG. 3. Temperature dependence of the electrical resistivity of a Pd-17 at.%Si alloy in the amorphous (1) and crystalline state (2).

⁷ We are indebted to Professor Mathias and his collaborators of the University of California at San Diego, who made measurements below 2°K. The amorphous alloy is not superconducting at 0.3°K.

⁸ C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, *Phil. Mag.* 7, 865 (1962).

reaction takes place at $400^{\circ}\pm 10^{\circ}\text{C}$. A typical time-temperature curve obtained by heating a small alloy foil (about 1×1 cm and $50\ \mu$ thick) in a vacuum of 10^{-4} Torr or better is shown in Fig. 4. From the temperature rise resulting from the amorphous-to-crystalline transition (about 160°C), the heat evolved in the process can be estimated to be of the order of 1 cal/mole. These results do not lead to the conclusion that the amorphous-to-crystalline transition takes place at a sharply defined temperature. In fact, preliminary experiments indicate that the transformation takes place by nucleation and growth at 300°C . However, the amorphous phase appears to be stable indefinitely at 200°C .

An analysis of the x-ray diffraction pattern of the alloy after transformation indicates that the broad diffused band characteristic of the amorphous structure is still present, but is reduced in intensity. The Bragg peaks in the pattern do not correspond to those of the two phases predicted by the presently accepted phase diagram (a mixture of Pd and Pd_3Si).⁹ It is possible that the crystalline phase (or phases) resulting from the transformation of the amorphous structure at temperatures not exceeding 400°C is a transition nonequilibrium crystalline structure.

DISCUSSION

The various factors which promote the formation of amorphous phases in binary alloys rapidly quenched from the melt are not well understood. The occurrence of an amorphous structure in gold-silicon alloys (unstable at room temperature) was discussed by Cohen and Turnbull.^{10,11} They pointed out that the composition of the alloy is located near the eutectic concentration. In addition the eutectic temperature in the gold-silicon system is relatively low, and the liquidus curve from pure gold to the eutectic has a very steep slope. According to Cohen and Turnbull, these factors are conducive to glass formation. Similar conditions are found in the present case of palladium-silicon alloys.⁹ The eutectic composition is about 15.5 at.% and, as previously stated, amorphous alloys can be obtained

⁹ M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

¹⁰ M. H. Cohen and D. Turnbull, *Nature* **189**, 131 (1961).

¹¹ D. Turnbull, *Trans. Metal. Soc. AIME* **221**, 422 (1961).

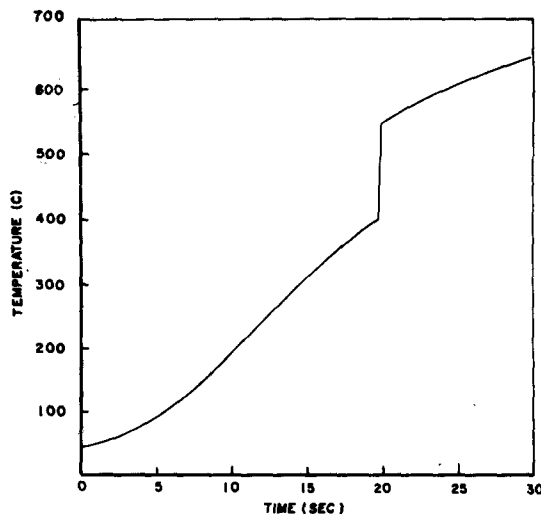


FIG. 4. Temperature-vs-time curve of an amorphous foil of Pd-20 at.%Si alloy.

from about 15 to 23 at.% silicon. The eutectic temperature (about 800°C) is also low compared with the melting point of palladium (1552°C).

Other important factors, such as the viscosity of the melt, and the tendency for the melt to undercool, are involved in preventing crystallization. No measurements have been made of viscosity in palladium-silicon alloys, so the effect of this factor is difficult to evaluate. It has been observed, however, that within the range of composition leading to amorphous structures, palladium-silicon alloys can be appreciably undercooled. This fact has already been mentioned in the first paper published on the equilibrium diagram,¹² and studies underway at this laboratory indicated that without taking any special precautions, such as reducing the molten globule size below approximately $50\ \mu$,¹³ relatively large ingots (about 10 g) of Pd-Si alloys containing 20 at.%Si can be undercooled as much as 300°C . If a better understanding of these various factors could be gained, it might be possible to find other alloys in which amorphous phases can be obtained by rapid cooling from the melt.

¹² P. Lebeau and P. Jolibois, *Compt. Rend.* **146**, 1028 (1908).

¹³ R. E. Cech and D. Turnbull, *Trans. AIME J. Metals* **191**, 242 (1951).