

Letter

Suppression of the glassy solidification of the alloy Pd₇₇Cu₆Si₁₇ by the b.c.c. phase under high pressure

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1. Introduction

Rapid cooling from the melt under high pressure is one of the new methods for forming bulk amorphous alloys. The application of high pressures of 5–8 GPa can reduce the critical cooling rates for glassy solidification by two or three orders of magnitude [1].

However, in some systems, e.g. Au–Si and Au–Ge, new crystalline phases can nucleate in the undercooled melt and suppress glassy solidification under high pressure [2].

In the present paper the easy glass-forming alloy Pd₇₇Cu₆Si₁₇ was chosen as a sample system which allows glassy solidification even at small critical cooling rates of about 10³ K s⁻¹ [3]. Such rates are available in the high pressure cell so the amorphous alloy can be formed at low pressures close to the normal pressure. In this case one can examine the pressure effect on the formation of the amorphous state over the entire available pressure region irrespective of whether or not high pressure suppresses glassy solidification.

2. Experimental procedure

Pure palladium (purity 99.9%) powder, copper (purity 99.9%) powder and silicon (purity 99.99%) were used to prepare the alloy Pd₇₇Cu₆Si₁₇. The components were weighed precisely to give the desired composition. The mixture was alloyed in a rock salt ampoule in the shape of a glass with a lid at a pressure of 3.5 GPa and a temperature of 1500 K for 600 s. For this purpose an opposed cupped anvil apparatus with a working volume of 10 cm³ was used [4]. This procedure made complete alloying possible. The alloy was subsequently homogenized in a fused silica tube under vacuum at a temperature of 1300 K for 6 h and then quenched in water.

High pressure experiments involving rapid cooling from the melt under high pressure were carried out in a toroid-type apparatus [5]. Before the experiments a series of pressure calibration runs were made based on cerium, bismuth and PbTe electrical resistance transitions [6, 7]. Fragments of the alloy were placed in a rock salt pipe ampoule (inner diameter 0.8 mm, length 7 mm) which was put into a catlinite cell. The ends of the heating sample contacted the bulk alloy of the same composition. The alloy was heated directly by a rectangular d.c. pulse at high static pressures from 0.7 to 7.7 GPa. The melting was monitored by the jump in the resistivity. In some experiments an NiCr–NiAl thermocouple was placed in the centre of the alloy. The average cooling rate was about 10⁴ K s⁻¹.

The ingots after the pulse treatment had a smooth surface characteristic of a casting. The rock salt ampoule remained transparent. This indicated that the composition of the alloy did not change during the pulse treatment.

The composition of the ingots was examined by X-ray microanalysis (MAR-1) to an accuracy ±3 at.% Si and ±1 at.% Cu. The analysis showed that the composition of the ingots did not differ from that of the cast alloys.

X-ray transmission diffraction was performed on a DRON-2 diffractometer with monochromated Mo K_α radiation. For these measurements the ingots were mechanically reduced in thickness to 20–30 μm using a set of sandpapers. In addition, the fragments of each ingot were examined by the Debye–Scherrer X-ray technique with Cu K_α radiation. Sodium chloride (*a* = 0.56402 nm) was used as an inner standard.

For direct observation of the structure a JEM-100 C transmission electron microscope was used. Thin foils for electron microscopy were prepared by ion thinning.

Quantitative thermal analysis was performed with a commercial differential microcalorimeter (DSM-2M) from 330 to 770 K at a heating rate of 16 K min⁻¹. The value of the latent heat of crystallization was estimated by means of calibration data based on the heat of fusion of zinc.

3. Results

Both electron and X-ray diffraction analyses showed that the ingots prepared at a pressure of 0.7 GPa were amorphous (Fig. 1). From the area below the crystallization peak a heat of crystallization Δ*H* = 3.4 ± 0.2 kJ

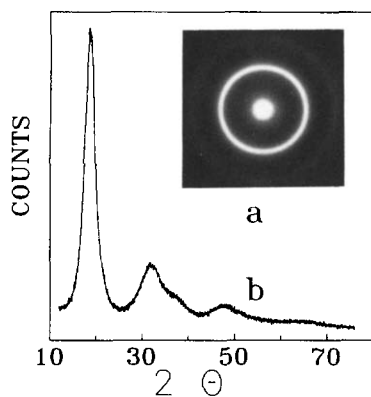


Fig. 1. (a) Electron and (b) X-ray ($a=0.071$ nm for Mo K_{α}) transmission diffraction data of amorphous alloy $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$ formed by rapid cooling at a pressure of 0.7 GPa.

TABLE 1. Measured and calculated d spacings of the new b.c.c. phase

hkl	Intensity ^a	d (meas) (nm)	d (calc) (nm)
110	s	0.2156	0.2156
200	m	0.1522	0.1525
211	m-s	0.1245	0.1245
220	m	0.1078	0.1078
310	w	0.09627	0.09642
222	w	0.08807	0.08802
312	w	0.08149	0.08149

^as, strong; m, medium; w, weak.

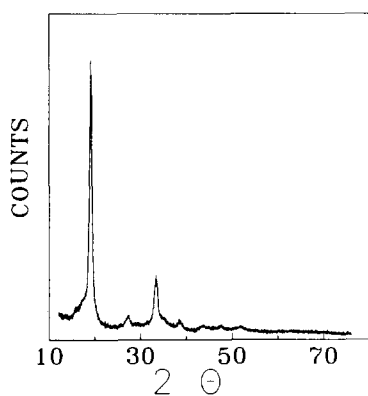


Fig. 2. X-ray transmission diffraction data ($a=0.071$ nm for Mo K_{α}) of alloy $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$ formed by rapid cooling at a pressure of 7.7 GPa.

mol^{-1} was determined, in agreement with previous studies [3]. A small amount of crystalline phases was found in the 0.7 GPa ingots by electron microscope observation. The content of crystalline component was probably less than 1% because it was not observed by means of X-ray diffraction analysis.

A new crystalline phase was observed in the 1.5, 2.5, 5.0 and 7.7 GPa ingots. It was determined to have the b.c.c. structure (Table 1). The comparison of the mea-

sured and calculated d spacings showed good agreement. The lattice parameter of the phase was found to be in the range from 0.304 to 0.305 nm for different ingots. The content of the phase was greater the higher the pressure of preparation. The 7.7 GPa ingots consisted of about 80%–90% of the phase (Fig. 2).

4. Discussion

The amorphous alloy $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ can be formed at cooling rates of about 10^3 K s^{-1} at atmospheric pressure [3]. The phase Pd_3Si is known to nucleate in undercooled $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ liquid at cooling rates of 0.06–23 K s^{-1} [8]. When a pressure of 3.0 GPa is applied, the Pd_3Si nucleation is suppressed but this does not result in glassy solidification at a cooling rate of 10 K s^{-1} [9].

In the present work the amorphous alloy $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$ was prepared by rapid solidification at a pressure of 0.7 GPa at a cooling rate of 10^4 K s^{-1} . A new b.c.c. phase ($a=0.304$ – 0.305 nm) was found to suppress glassy solidification at pressures of over 0.7 GPa. The b.c.c. structure is characteristic for transition metals with an (vanadium, chromium, iron, niobium, molybdenum, tantalum, tungsten) unfilled d electronic subshell. Palladium metal is known to have the f.c.c. structure and its 4d shell ($4d^{10}5s^0$) is filled under normal conditions. One can expect for palladium an unfilled 4d subshell under high pressure, similar to that of nickel and copper [10]. In this case the b.c.c. structure of palladium can be stabilized by the presence of copper and silicon.

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