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Elastic properties of Pd₄₀Cu₃₀Ni₁₀P₂₀ bulk glass in supercooled liquid region

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In situ ultrasonic measurements for the Pd₄₀Cu₃₀Ni₁₀P₂₀ bulk glass in three states: Glassy solid, supercooled liquid, and crystalline, have been performed. It is found that velocities of both longitudinal and transverse waves and elastic moduli (shear modulus, bulk modulus, Young's modulus, and Lamé parameter), together with Debye temperature, gradually decrease with increasing temperature through the glass transition temperature as the Poisson's ratio increases. The behavior of the velocity of transverse wave vs. temperature in the supercooled liquid region could be explained by viscosity flow, rather than the two different crystallization processes in the region, suggested in the literature. No decomposition was detected at a temperature only 5 K below the crystallization temperature. © 2001 American Institute of Physics. [DOI: 10.1063/1.1359490]

In the last decade, many multi-component glass forming alloy systems with a large supercooled liquid region were discovered.^{1,2} These materials possess an extremely high glass forming ability, and high thermal stability against crystallization. For example, a cooling rate of merely 0.1 K/s is required to suppress crystallization, and to form a metallic glass sample with diameter up to 72 mm for the Pd₄₀Cu₃₀Ni₁₀P₂₀ alloy.³ Measurements of viscosity,⁴ crystallization,⁵ diffusion,⁶ density,⁷ thermal expansion,⁸ electron transport,⁹ structure,¹⁰ and specific heat capacity,¹¹ have been performed on bulk Pd₄₀Cu₃₀Ni₁₀P₂₀ glass. Recently, Wang *et al.*,¹² performed ultrasonic measurements at ambient temperature for as-cast bulk Pd₃₉Cu₃₀Ni₁₀P₂₁ glass and samples annealed at various temperatures for 1.5 h, and found that two different crystallization processes are likely to exist in the supercooled liquid region. No decomposition process in the supercooled liquid region,¹³ at a temperature 35 K below the crystallization temperature of a eutectic reaction,^{3,14} was reported for the bulk Pd₄₀Cu₃₀Ni₁₀P₂₀ glass. We report here the results on *in situ* ultrasonic measurements for Pd₄₀Cu₃₀Ni₁₀P₂₀ bulk glass in three states: Glassy solid, supercooled liquid, and crystalline.

A master alloy ingot with composition Pd₄₀Cu₃₀Ni₁₀P₂₀ was prepared by arc melting a mixture of pre-alloyed Pd₆₀P₄₀, Pd, Ni, and Cu of purity ranging from 99.9 to 99.999 at. %, together with a B₂O₃ flux medium in a purified argon atmosphere. A glassy rod-shaped sample with a diameter of 15 mm was prepared by the water quenching method described in Ref. 3. The amorphous nature of the as-quenched rod was confirmed by x-ray diffraction and transmission electron microscopy. Thermal analysis was performed in a differential scanning calorimeter (DSC). The *in*

situ ultrasonic measurements were performed by an ultrasonic pulse ring-around method,¹⁵ in the temperature range 294–675 K at a heating rate of 5 K/min under a flow of purified argon.

Figure 1 shows the DSC trace of bulk Pd₄₀Cu₃₀Ni₁₀P₂₀ glass at a heating rate of 5 K/min under a flow of purified argon. The glass exhibits an endothermic event characteristic of the glass transition at $T_g = 561$ K, followed by one exothermic event indicating a eutectic crystallization process at $T_x = 635$ K, and $\Delta T = T_x - T_g = 74$ K. Figure 2 shows the longitudinal and transverse acoustic velocities, V_l and V_s , as functions of temperatures up to 675 K. The calorimetric glass transition temperature, and the onset crystallization temperature of the glass, are marked in Fig. 2 indicating the supercooled liquid region. At 294 K $V_l = 4.51$ km/s, while $V_s = 1.89$ km/s. With increasing temperature, velocities of both waves gradually decrease at a slope of 0.362 m/(sK) for the longitudinal wave (294–530 K), and a slope of 0.356 m/(sK) for the transverse wave (294–520 K). V_l decreases with increasing temperature in the range 580–640 K at a

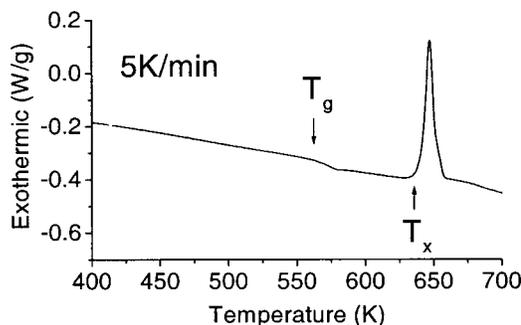


FIG. 1. DSC trace of Pd₄₀Cu₃₀Ni₁₀P₂₀ bulk glass at a heating rate of 5 K/min under a flow of purified Ar. The positions of T_g and T_x are indicated.

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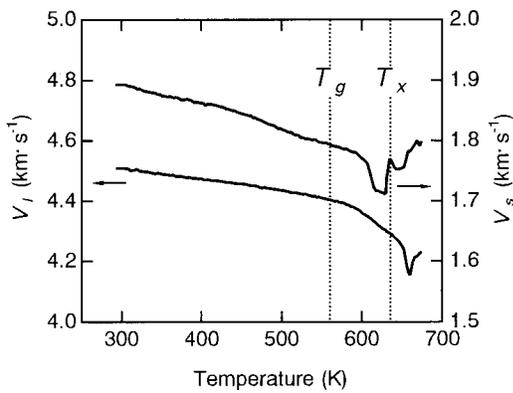


FIG. 2. Velocities of longitudinal (V_l) and transverse waves (V_s) vs. temperature for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ bulk glass at a heating rate of 5 K/min under a flow of purified Ar. T_g and T_x are indicated.

slope of 1.890 m/(sK). However, between T_g and T_x , V_s rapidly drops from about 1.792 km/s at 580 K to 1.719 km/s at 614 K. It has a constant value of roughly 1.712 km/s around 630 K, followed by a rapid increase to 1.771 km/s at 635 K. Above T_x , the temperature dependence of both waves is complex. The sample first consists of crystalline phases and residual amorphous alloy, and then crystallizes completely above about 660 K. Using the density data of $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ bulk glass versus temperature reported in Ref. 8, the temperature dependences of the elastic moduli (shear modulus, Young's modulus, Lamé parameter, and bulk modulus), together with Debye temperature and Poisson's ratio, can be found in Figs. 3 and 4. At 300 K, the shear modulus, Young's modulus, Lamé parameter, bulk modulus, Debye temperature, and Poisson's ratio are 33.4, 93, 123, 145.3 GPa, 270 K, and 0.393, respectively. These values are similar to those for $\text{Pd}_{39}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{21}$ bulk glass.¹² With increasing temperature the shear modulus, Young's modulus, Lamé parameter, bulk modulus, and Debye temperature decrease, while the Poisson's ratio increases. At T_g , there is no dramatic change of any of these parameters, although the slope of specific volume vs temperature changes from $5.457 \times 10^{-3} \text{ m}^3/(\text{gK})$ below T_g to $8.785 \times 10^{-3} \text{ m}^3/(\text{gK})$ above T_g .⁸ Note that a significant change in shear modulus at T_g was suggested for ZrTiCuNiBe bulk glasses.¹⁶ In the supercooled liquid region, it is experimentally found that the temperature dependences of all the elastic

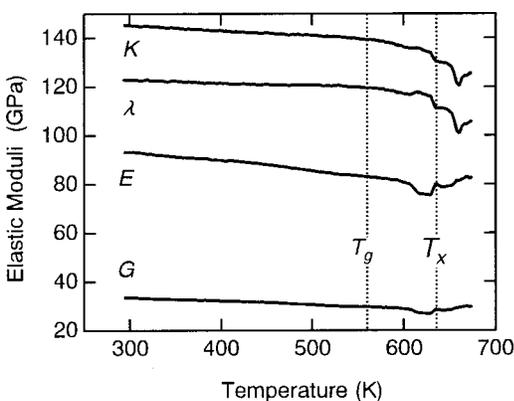


FIG. 3. Temperature dependences of the elastic moduli [shear modulus (G), bulk modulus (K), Young's modulus (E)] and Lamé parameter (λ), for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ bulk glass. T_g and T_x are indicated.

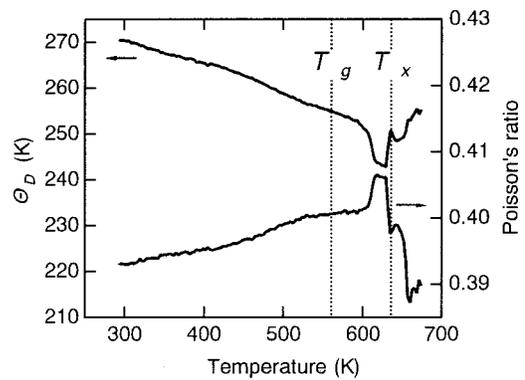


FIG. 4. Temperature dependences of the Debye temperature (θ_D) and Poisson's ratio for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ bulk glass. T_g and T_x are indicated.

moduli, the Debye temperature, and Poisson's ratio, are strongly correlated with the temperature dependence of the velocity of transverse waves. The Debye temperature drops from about 252 K at 600 K to 243 K at 625 K, indicating that interatomic interactions become weaker. This is also reflected in the shear modulus and Young's modulus. On the other hand, Poisson's ratio increases from 0.402 to 0.406, while bulk modulus and Lamé parameter have a maximum around 610 K. At the crystallization temperature, T_x , a kink is detected for all elastic constants. Above T_x , the temperature dependence of all elastic constant is complicated due to the sample microstructure.

To explain the behavior of the velocity of transverse wave vs. temperature in the supercooled liquid region, microstructures of samples annealed at 615, 630, and 650 K were investigated by high-resolution transmission electronic microscopy (HRTEM). Some examples are shown in Fig. 5. The samples were heated in the DSC at a rate of 5 K/min to the given temperature. After annealing for less than 5 s, the samples were then quenched to room temperature. It was found that after annealing at 615 and 630 K respectively, the materials were still in the amorphous state. No decomposition was detected in samples annealed at 615 and 630 K, while the material partially crystallized after the annealing at 650 K. Longitudinal waves are readily propagated in gases and liquids, as well as in elastic solids. The gradual decrease of the velocity of longitudinal waves with temperature in Fig. 2 is a result from the softening of the interatomic inter-

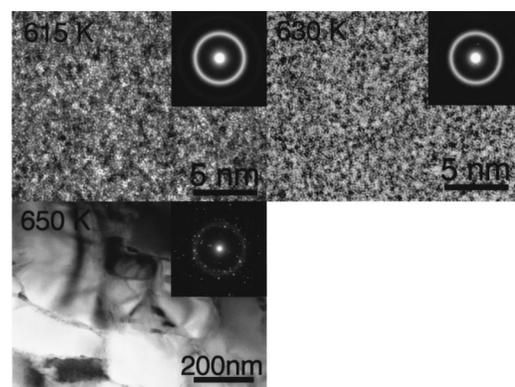


FIG. 5. High-resolution transmission electron microscopy images and their corresponding selected area diffraction patterns of samples heated at a rate of 5 K/min to 615, 630, and 650 K, respectively, and annealed for less than 5 s before being quenched to room temperature.

action. No kink was observed at T_g and T_x , while V_l has a minimum at about 658 K where the sample is completely crystallized. Unlike longitudinal waves, transverse waves are not supported by elastic collisions of adjacent atoms. For the propagation of transverse waves, it is necessary that each atom attracts its neighbors strongly so that during movement it pulls its neighbors with it, thus causing the sound to move through the material. Consequently, in gases, the forces of attraction between molecules are too small for shear waves being transmitted. The same is true for liquids, unless it is particularly viscous. Nishiyama and Inoue have investigated the viscosity of $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ bulk glass and found that it drops from 10^{12} to 10^8 Pa s in the supercooled liquid region, and rapidly increases when approaching the crystallization temperature.⁴ Thus, viscous flow in the supercooled liquid region from 580 to 620 K, and the crystallization reaction at 635 K, could explain the observed behavior of transverse wave velocity vs. temperature in the 580–635 K region.¹⁵

In situ ultrasonic measurements for bulk $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ glass in three states: glassy solid, supercooled liquid, and crystalline, have been carried out. From the results of viscosity versus temperature,⁴ it appears quite probable that the observed temperature dependency of both the longitudinal and the transverse wave velocity in the supercooled liquid region results mainly from viscous flow. No evidence of the two different crystallization processes suggested in the literature was observed in the supercooled liquid region, and there are no dramatic changes in the elastic moduli (the shear modulus, bulk modulus, Young's modulus, and Lamé parameter), and in the Debye temperature and Poisson's ratio at the glass transition temperature. Furthermore, no decomposition was detected in a sample annealed at a temperature just 5 K below the crystallization temperature.

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