

intact, diffuse preferably into an oxygen precipitate growing area during a heat treatment at 1000 °C.

Oxygen precipitate growth involves emission of silicon self-interstitials (I_{Si}) into the surrounding silicon matrix.¹¹ The high diffusivity of C_s , compared with that of I_{Si} , in silicon and I_{Si} -enhanced C_s diffusion⁸ may reasonably lead carbon atoms to an oxygen precipitate growing area. As a next step, these I_{Si} may interact with the diffused C_s resulting in the formation of $C_s I_{Si}$ (Ref. 12). The formation of $C_s I_{Si}$ may reduce the interfacial energy of oxygen precipitates. Consequently, the enhancement effect of carbon on oxygen precipitation at 1000 °C is explained primarily with a catalytic role by modifying the interfacial energy or the point defect ambient at the oxygen precipitate surface. On the other hand, the carbon role of heterogeneous seeding sites for oxygen precipitation³ is dominant at a low temperature, e.g., 750 °C, since the carbon diffusivity in silicon at such a low temperature ($D \sim 10^{-15}$ cm²/s) is much smaller than that at 1000 °C ($D \sim 10^{-12}$ cm²/s).¹³

In summary, direct evidence for the co-aggregation of oxygen and carbon in a CZ silicon slice subjected to a heat treatment at 1000 °C has been shown for the first time by

means of a SIMS technique. In conjunction with IR data, the carbon enhancement effect on oxygen precipitation at 1000 °C has been explained by a catalytic mechanism.

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Melting of Ni₄₀Pd₄₀P₂₀ glass

H. W. Kui and D. Turnbull

Division of Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, Massachusetts 02138

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Upon reheating, most glassy metal alloys crystallize at a temperature not far removed from the glass temperature T_g and far below the liquidus temperature T_l . We have reported that the alloy Ni₄₀Pd₄₀P₂₀, which exhibits a scaled glass temperature ~ 0.68 , has been melt quenched, under a flux of dehydrated B₂O₃, to glass at rates as low as 1°/s. Here we report experiments in which some specimens of this alloy, when similarly fluxed during reheating, have been reheated to temperatures within 50° of T_l and 280° above T_g at rates $\sim 2.5^\circ$ /s, and then cooled again to T_g , without crystallization. From this behavior we infer that the steady frequency of homogeneous nucleation of crystals in the alloy is $< 10^{-1}$ cm⁻³ s⁻¹.

In earlier studies we showed that molten Ni₄₀Pd₄₀P₂₀ alloy could be cooled in bulk form (1–4 g masses) to the glass state at rates as low as 1°/s when special care was taken to remove heterophase nucleants from the alloy. In one procedure,¹ chemical treatments of the alloy surface were used to remove the nucleants. Later we found² that continued fluxing of the alloy in dehydrated B₂O₃ was a more effective denucleating technique. With this technique we prepared a massive (4 g, ~ 1 cm thick) specimen of alloy glass free of any detectable internal or superficial crystallinity. This behavior indicated that the frequency I of homogeneous crystal nucleation in the alloy could hardly have exceeded 0.1 cm⁻³ s⁻¹. However, it is possible that the nucleation resistance reflected a long transient period in the approach to a steady-state level of I well in excess of 0.1.

Upon reheating most glasses crystallize at some tem-

perature, "kinetic crystallization temperature," T_{kc} , well below the liquidus T_l . This crystallization may be initiated by homogeneous or heterogeneous nucleation. In metallic glass studies the available reheating rates are generally much lower in magnitude than the quench rates required to form the glass. However, there is no difficulty in achieving heating rates of the low magnitude used in quenching Ni₄₀Pd₄₀P₂₀ to a glass. We report results of studies of the crystallization behavior of this alloy upon reheating.

Specimens (0.2–0.5 g) of the alloy were prepared as described earlier.² In the experiment, the alloy was submerged in molten dehydrated B₂O₃, prepared as before, contained in an evacuated fused silica tube heated by an oxygas torch mounted at the specimen level. Temperature was measured by a chromel-alumel thermocouple (TC), sheathed by Al₂O₃, placed in a capillary channel under the specimen which was

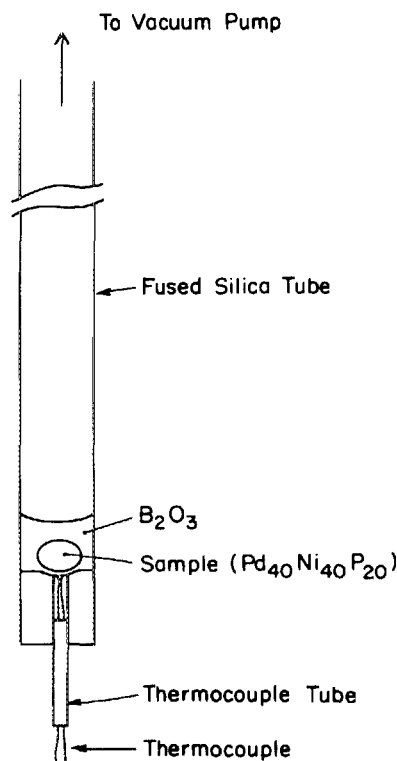


FIG. 1. Schematic diagram of the apparatus used for heat treatments.

separated from the TC junction by a thin silica layer (see Fig. 1). The temperature recorded was up to 20° above that of the flux as measured, in separate tests, by a TC immersed directly at various positions in the flux.

The specimens were initially held in the flux for 2 h at 1050°C and were brought to this temperature and held for 5 min between successive thermal treatments, which were as shown schematically in Fig. 2. That is, the alloy was cooled from 1050°C to a temperature near the glass temperature ($T_g \sim 320^\circ\text{C}$) and then reheated ($B \rightarrow C$) to one ($\sim 600^\circ\text{C}$) somewhat below the liquidus but well into the regime where crystal growth is very rapid ($>$ several cm/s). If, to this point, there was no evidence of crystallization, the alloy was cooled again ($C \rightarrow D$) and reheated ($D \rightarrow E$). Crystallization was noted visually from the movement of an interface across the specimen with concomitant surface roughening. When these effects were noted, we concluded that the specimen had remained liquid to that point. No conclusion on the state of the specimen was drawn if there was no visual manifestation of crystallization.

Crystallization occurred only rarely in the $A \rightarrow B$ stage of the treatment. Upon reheating at rates of 2° – $5^\circ/\text{s}$, we found that the T_{kc} were distributed, depending on the specimen and trial, along the path $BCDE$. Most were between B and C at or only a few degrees above 480°C (about 150°C above T_g) which would have been the T_{kc} normally recorded. However, about ten of the approximately 50 specimens investigated exhibited in certain trials, usually the later ones, crystallization only after the CDE section of the path was reached; that is, the specimens remained liquid to temperatures only 50° below the liquidus. In 20 of these trials, T_{kc}

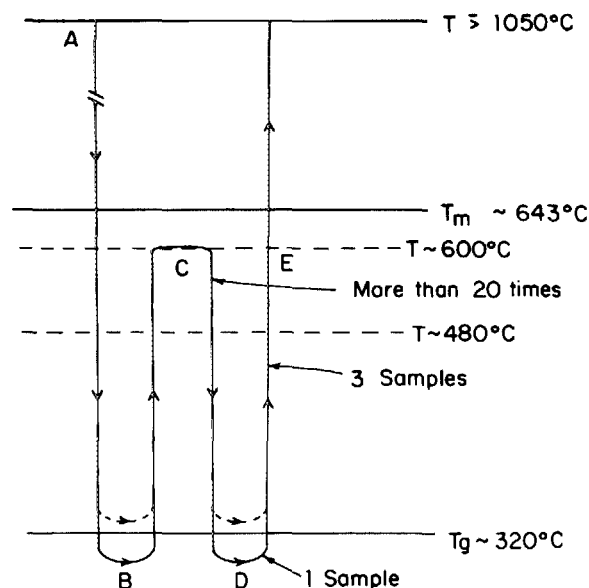


FIG. 2. Temperature history of the specimens in cooling and reheating experiments. The ordinate is temperature.

was between 600 and 490°C on the $C \rightarrow D$ part of the path. Four specimens, in single trials, reached point D without crystallization; three of these crystallized during heating from $D \rightarrow E$. The fourth, weighing 0.415 g , after reaching D was cooled to 30°C and then removed from the tube and examined. Its surface was entirely smooth and etching revealed no superficial crystallinity. Upon heating to $T > T_g$, it began to flow and flatten, in response to gravity, and then it crystallized. This specimen had been heated from B to C at an average rate of $2.5^\circ/\text{s}$.

We have noted that the incidence of trials in which crystallization was delayed to point C or beyond along the $B \rightarrow C \rightarrow D$ path was quite low. However, it is likely that crystallization, when it occurred, was initiated, in each specimen, from a single nucleus. This nucleus could have formed from a heterogeneity or as a result of vibration ("dynamic" nucleation). Either of these processes might be favored by convective currents in the flux arising from nonuniform heating. However, of greater significance are the trials in which the specimens remained liquid over the entire $B \rightarrow C \rightarrow D$ path and beyond. Here the times spent appear to be much longer than the transient times required to reach steady-state nucleation. From this we infer that the frequency of steady-state homogeneous nucleation in this alloy cannot be greater than $0.1\text{ cm}^{-3}\text{ s}^{-1}$. This high resistance to homogeneous nucleation correlates with the exceptionally high scaled glass temperature, $(T_g/T_l) \sim 0.68$, exhibited by this alloy.

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