Relaxation, Crystallization and Consolidation of an Amorphous Pd_<48>Ni_<32>P_<20> Alloy Powder

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Relaxation, Crystallization and Consolidation of an Amorphous $Pd_{48}Ni_{32}P_{20}$ Alloy Powder[*]

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Synopsis
    The influence of applied pressure on the structure relaxation, glass transition, crystallization and consolidation for an amorphous phase was examined by using a typical glassy $Pd_{48}Ni_{32}P_{20}$ alloy in a spherical powder or a ribbon form. The Pd-Ni-P alloy was chosen because of the existence of a wide supercooled liquid region in the temperature range below crystallization temperature (T_x). The relaxation and crystallization are significantly suppressed by the application of compressive load, presumably because of the increase in viscosity and the decrease in diffusivity. As a result, the pressing at a high temperature of $0.97T_x$ is required to produce an amorphous bulk with high relative density. Furthermore, an intermediate annealing between pressings was found to be effective for the reduction of the enhanced viscosity. The multistage pressing treatment consisting of pressing and annealing enabled to produce a highly dense amorphous bulk even at a relatively low temperature near T_g.

I.   Introduction

    Amorphous alloys have been produced in forms of thin sheet, wire with a circular cross section, powder and thin film by using various techniques of melt quenching, vapor condensation, solid state reaction and chemical reduction etc. Furthermore, the alloys have presently been used in various fields by utilizing the combined feature of peculiar material morphologies and unique characteristics resulting from the absence of a periodic atomic configuration over a long range and peculiar alloy components. As typical examples of unique

characteristics for amorphous alloys, one can list up high mechanical strength, high toughness, soft magnetism and high corrosion resistance. In order to extend further the application fields for amorphous alloys, it is important to eliminate the limitation of shape and dimension of amorphous alloys resulting from their glass-forming ability. The elimination seems to be achieved through the following two ways; (1) to find an alloy composition with larger glass-forming ability, and (2) to establish a consolidation process of amorphous powders. A large number of studies have been carried out with the aim of achieving the two ways[1]. This paper is intended to review the influence of applied pressure on the relaxation and crystallization of an amorphous phase and the consolidation behavior under uniaxial compressive stress by using an amorphous $Pd_{48}Ni_{32}P_{20}$ powder with a significant supercooled liquid region before crystallization.

II. Preparation of the Pd-Ni-P Amorphous Powder and its Consolidation Method

A $Pd_{48}Ni_{32}P_{20}$ ingot was prepared by induction melting the sintered compact of pure Pd, Ni and P powders. Spherical amorphous powders were produced by ejecting the molten alloy into stirred cooled water[2] or an in-rotating water layer[3]. The resulting powders had a particle size ranging from 74 to 1190 μm and were used as samples after sieving with meshes. A uniaxial hot-pressing machine was used for the production of a bulky amorphous alloy and the examination on the structural relaxation and glass transition behavior in an evacuated state. The pressing was made at a one-side and the highest applied pressure was 940 MPa. The die and ram were made from a maraging steel and the change in the amount of contraction for the pressed compact with applied pressure, pressing temperature and pressing time was examined with a differential transformer-type strain meter.

III. Influence of Applied Pressure on the Relaxation of Amorphous Powder

Figure 1 shows the thermograms of the $Pd_{48}Ni_{32}P_{20}$ amorphous powders pressed for 1.8 ks at 573 K under an applied pressure of 940 MPa and annealed for 1.8 ks at 573 K without applied load. A large endothermic peak is seen in the temperature range of 570 to 610 K for the annealed sample, while no endothermic peak is seen even in the temperature range above the pressing temperature (T_p) for the hot-pressed sample. The endothermic peak has been thought[4,5] to result
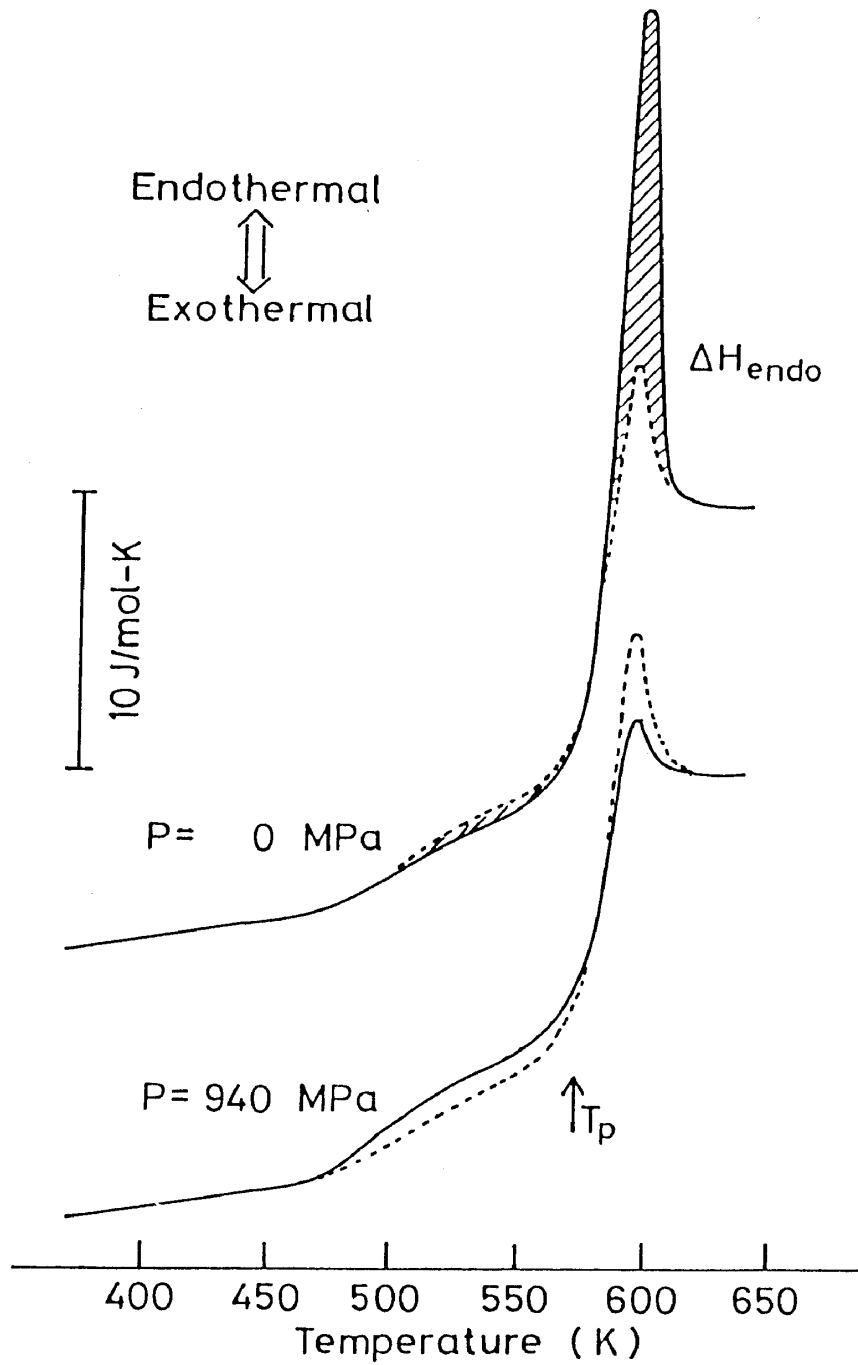
Fig. 1 Change in the relaxation-induced endothermic peak of an amorphous $Pd_{48}Ni_{32}P_{20}$ powder by pressing for 1.8 ks at 573 K. The dotted lines represent the data on the sample annealed for 60 s at 650 K.

from a reversion reaction in which the annealing-induced relaxed structure annihilates upon heating to a temperature higher than the annealing temperature (573 K), acccompanying the absorption of energy. The appropriateness of this concept has also been confirmed[6] from the data obtained by X-ray structure analysis. Accordingly, the absence of the endothermic peak for the hot-pressed sample indicates that the progress of structural relaxation during the hot pressing has almost completely been suppressed by the application of the compressive load. Figure 2 shows the change in the amount of the endothermic heat (ΔH_e) as a function of applied pressure during annealing for the Pd-Ni-P amorphous alloy annealed for 1.8 ks at 573 K. The ΔH_e decreases almost linearly with increasing applied pressure and hence the structural relaxation during annealing is concluded to be suppressed significantly by the application of compressive load.

Figure 3 shows the change in the ΔH_e as a function of pressing temperature for the Pd-Ni-P amorphous alloy pressed for 1.8 ks under no applied load and an applied load of 940 MPa. The ΔH_e in the absence of applied load as well as in the applied load state increases significantly with increasing T_p, shows maximum values of 216 Jmol^{-1} at 573 K in the absent load and 169 Jmol^{-1} at 603 K in the applied load and then decreases rapidly with further increasing T_p. As shown in Fig. 3, the maximum ΔH_e value is smaller by about 20 % in the pressed state and the subsequent decrease in ΔH_e in the higher temperature region is also considerably smaller. This difference indicates that the applied load causes an increase in the glass transition temperature from an amorphous solid to a supercooled liquid as well as the suppression of atomic rearrangement to an internal equilibrium state in the supercooled liquid state. The significant suppression effect on the atomic rearrangement caused by the applied load in the range from T_g to the supercooled liquid region results in the increase in viscosity and the suppression of viscous flowability as described later. The atomic rearrangement in the supercooled liquid region is known to occur through atomic diffusion via free volume[7]. However, under an applied load, the free volume decreases and the atomic diffusivity via free volume is also suppressed, in addition to the load-induced difficulty in the movement of constituent atoms themselves. The load-induced reduction of the atomic mobility is concluded to result in the suppression of the structural relaxation to an internal equilibrium state in the region from the amorphous solid to the supercooled liquid.
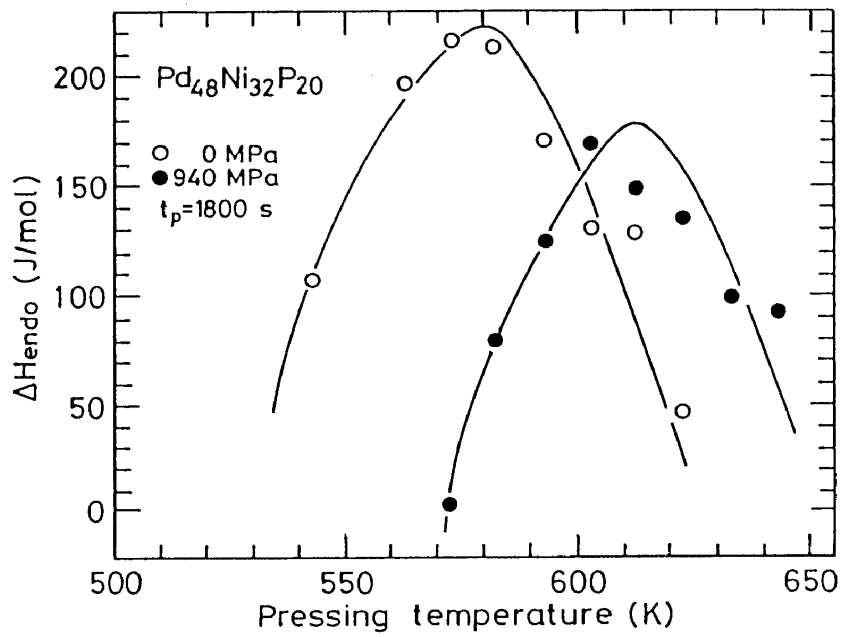
Fig. 2 The heat of relaxation-induced endothermic reaction (ΔH_{endo}) as a function of applied pressure for an amorphous $Pd_{48}Ni_{32}P_{20}$ powder pressed for 1.8 ks at 573 K.

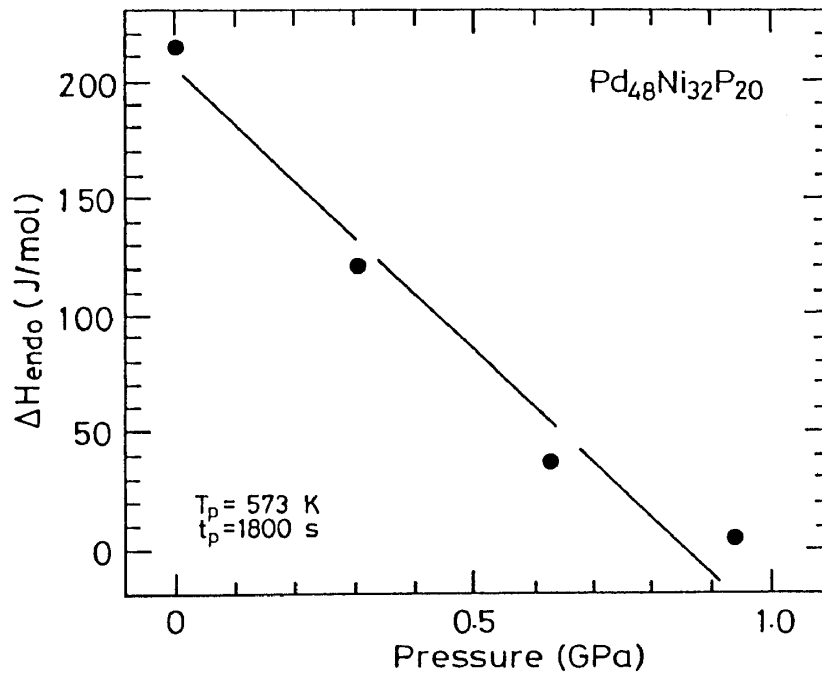Fig. 3 The ΔH_{endo} as a function of pressing temperature (T_p) for 1.8 ks for an amorphous $Pd_{48}Ni_{32}P_{20}$ powder. The data of the unpressed powder are also shown.

IV.   Influence of Applied Pressure on Crystallization

Figure 4 shows the change in the normalized resistance of the $Pd_{48}Ni_{32}P_{20}$ amorphous ribbon measured under applied loads of 0.5, 3.7 and 6.8 GPa with pressing temperature. The application of the high pressures was made by using a hexagonal pressing machine and the measurement of sample temperature was made through a thermo-electrical power calibrated as a function of applied pressure. As shown in Fig. 4, the resistance decreases rapidly upon crystallization and hence one can detect accurately the change in crystallization temperature (T_x) with applied pressure. T_x thus measured for the $Pd_{48}Ni_{32}P_{20}$ amorphous alloy increases almost linearly with increasing applied load and the rise in T_x per 1 GPa is evaluated to be 15 K from the slope. It is thus concluded that the application of compressive load to the Pd-Ni-P amorphous alloy causes an increase in the difficulty of crystallization, in addition to the rise of T_g and the suppression of the relaxation to the internal equilibrium state in the supercooled liquid. A similar rise of T_x with increasing applied pressure has also been observed for other amorphous alloys of $Pt_{60}Ni_{15}P_{25}$[8] and $Ni_{80}P_{20}$[8].

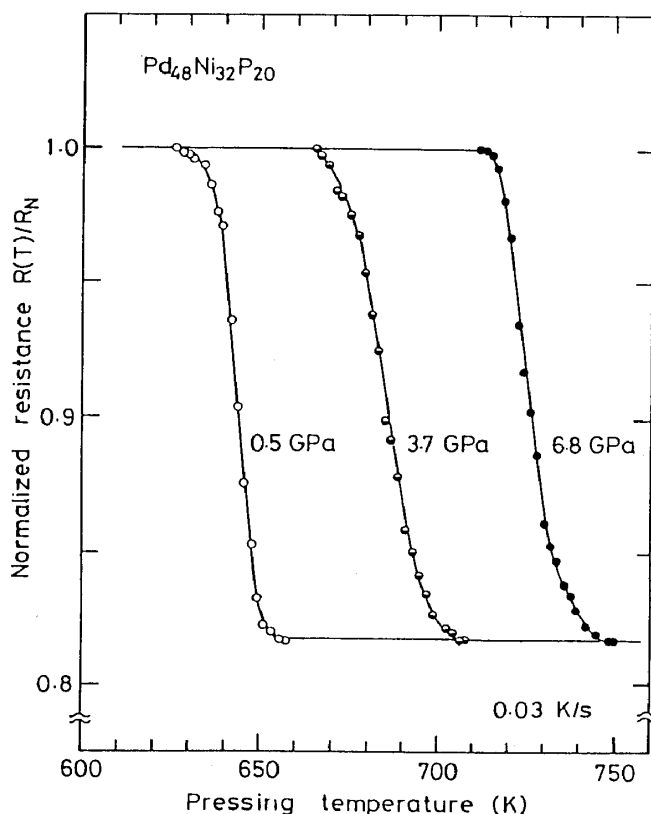Fig. 4   Normalized electrical resistance as a function of T_p for an amorphous $Pd_{48}Ni_{32}P_{20}$ ribbon pressed at different applied pressures.

V. Consolidation of Amorphous Alloy Powders

1. Temperature dependence of viscosity

It is well known that amorphous alloys become remarkably soft in the temperature region between T_g and T_x. The softening phenomenon is due to the glass transition from an amorphous solid to a supercooled liquid and the deformation mode also changes from an inhomogeneous shear type to a homogeneous viscous flow type. Figure 5 shows the temperature dependence of viscosity (η) which is evaluated from the creep behavior under different stresses in the supercooled liquid region. It is seen that η decreases very significantly from about 10^{12} Pa.s near T_g to 10^8 Pa.s near T_x. Even when water changes to a supersaturated water vapor at 373 K, the change in η is only one order (about 1/23)[9]. This indicates clearly that the deformation of the amorphous alloy becomes easy drastically in the narrow temperature region from T_g to T_x.
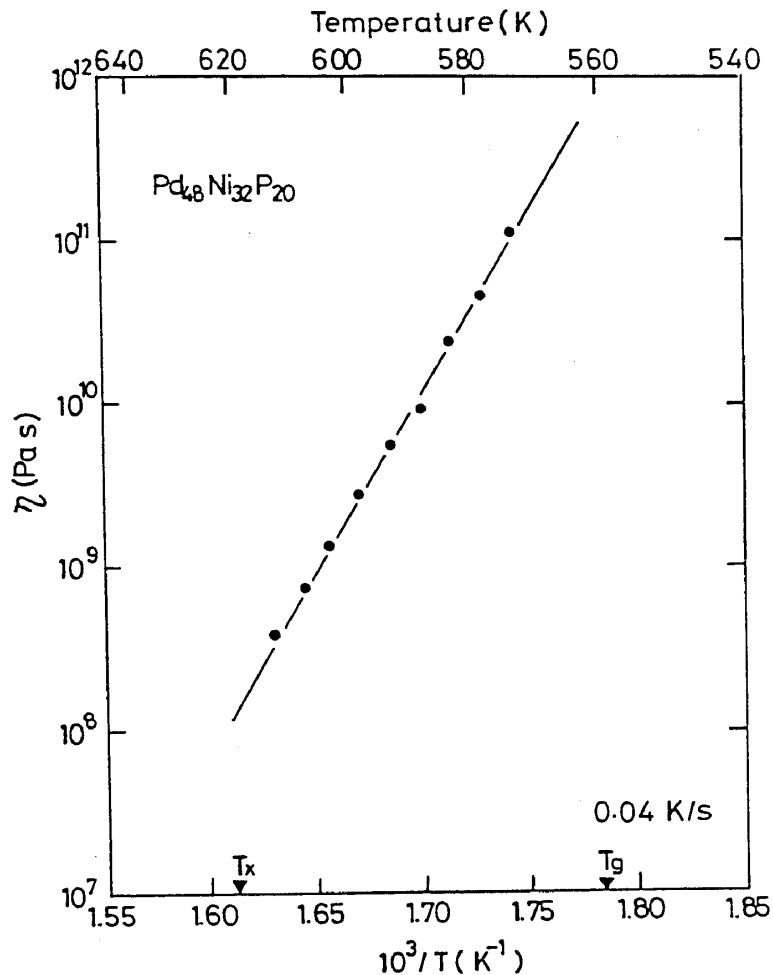

Fig. 5 Temperature dependence of viscosity (η) for an amorphous $Pd_{48}Ni_{32}P_{20}$ ribbon.

2. Temperature and time regions for formation of bulky amorphous solids

We investigate the possibility that a bulky amorphous solid without crystalline phase is produced by hot-pressing the Pd-Ni-P amorphous powder through the remarkable softening phenomenon in the region from T_g to the supercooled liquid. The investigation requires the data on T_g and T_x at the same heating rate as that (0.03 K/s) in the hot-pressing treatment. Figure 6 shows the DSC curve of the $Pd_{48}Ni_{32}P_{20}$ amorphous powder heated at a rate of 0.03 K/s. The T_g and T_x are 560 and 620 K, respectively. Furthermore, as shown in Figs. 5 and 6, η is of the order 10^{12} Pa.s at T_g and 10^8 Pa.s at T_x, indicating that the significant change in η reaching four orders takes place in the supercooled liquid region of 60 K between T_g and T_x.

In the formation of a highly dense amorphous bulk from amorphous powders by utilizing the significant increase in viscuous flowability caused by the rapid decrease in η, the pressing for longer times at higher temperatures is generally thought to be more favorable. However, an amorphous alloy crystallizes upon the long-time annealing at a temperature near T_g. It is therefore necessary for the production of a bulky amorphous alloy to choose an appropriate combination of pressing temperature, pressing time and applied
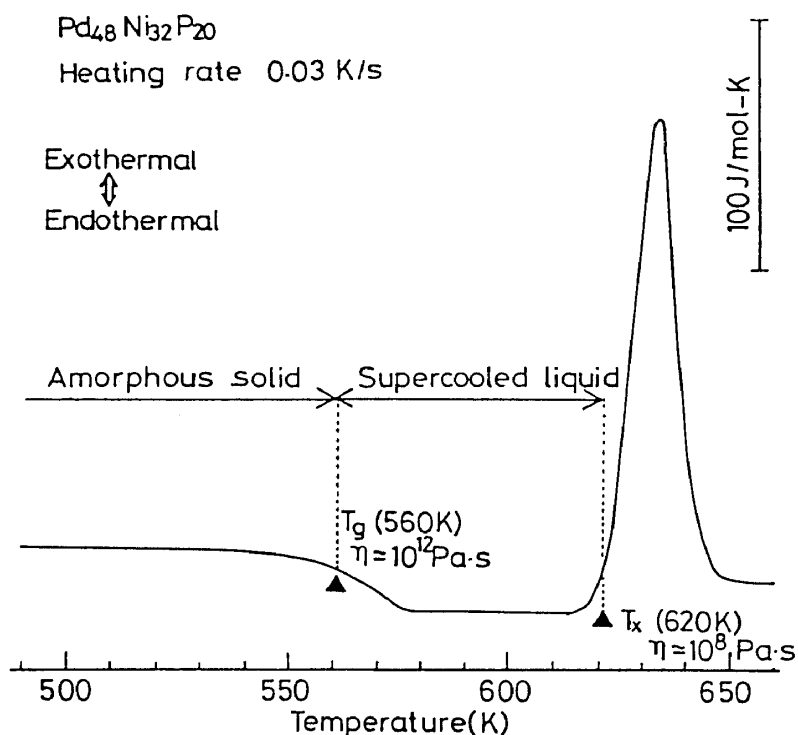

Fig. 6 Differential scanning calorimetric curve of an amorphous $Pd_{48}Ni_{32}P_{20}$ ribbon. The data of η are also shown for reference.

pressure. From the isothermal temperature-time-transformation diagram for the transition from amorphous to crystalline phase under no applied pressure, it is expected that a highly dense amorphous bulk is obtained by hot pressing for a short time near T_x or for a long time near T_g. However, unexpectedly, the actual pressing temperature-time region for the formation of a highly dense amorphous bulk is limited to the temperature range from 600 K to 620 K corresponding to 0.97 T_x to 1.0 T_x, which is different from the expected region, as shown in Fig. 7. That is, the region is strongly dependent only on the pressing temperature. It is furthermore notable in Fig. 7 that the crystallization does not occur even after a long time pressing of 10.8 ks. As an example, Fig. 8 shows an optical micrograph revealing the cross sectional structure of the $Pd_{48}Ni_{32}P_{20}$ amorphous bulk produced by hot-pressing for 3 s at 613 K under an applied load of 630 MPa. It is seen that a highly dense bulk without any appreciable voids along grain boundaries and at the triple point of grain boundaries is produced even by hot pressing for a short time of 3 s. The relative density of the amorphous bulk obtained in the pressing temperature region shown in Fig. 7 is in the range of 97.4 to 99.2 %. There is a tendency for the relative density to increase with increasing pressing temperature (T_p), while there is no appreciable change in the density with pressing time (t_p) and applied pressure.
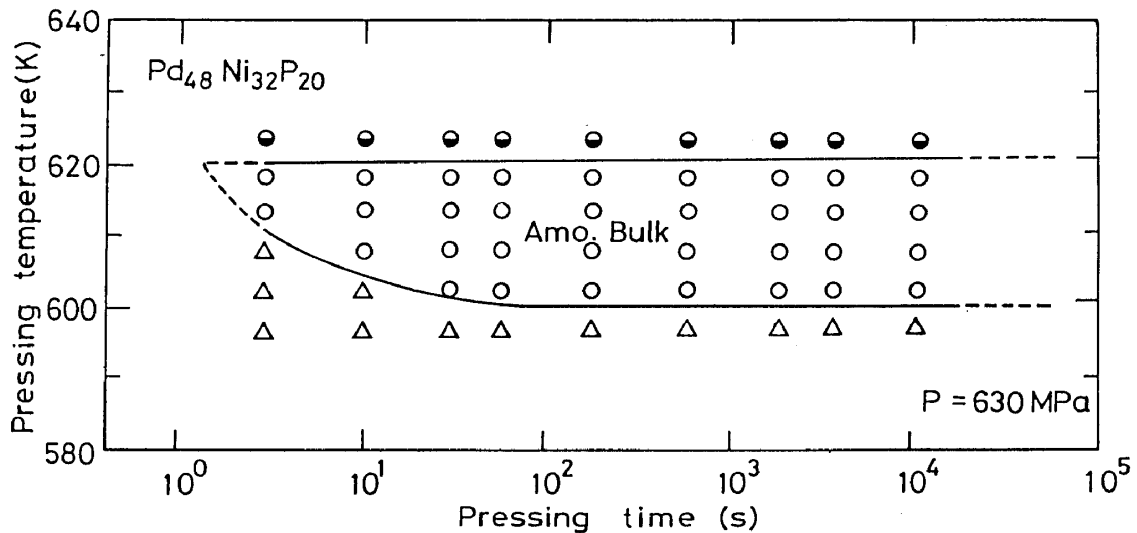

Fig. 7 Pressing temperature and time ranges for the formation of an amorphous bulk by pressing an amorphous $Pd_{48}Ni_{32}P_{20}$ powder at 630 MPa.

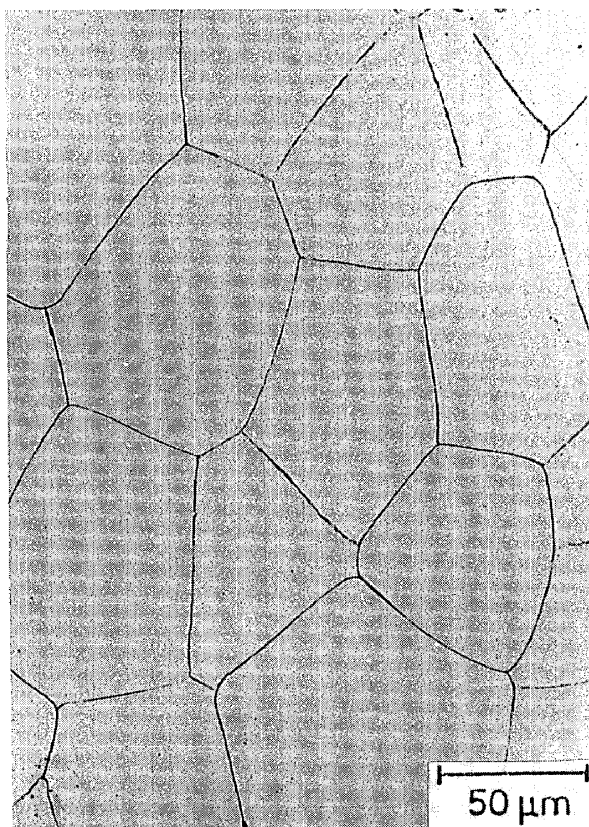Fig. 8 Optical micrograph of an amorphous bulk produced by pressing an amorphous $Pd_{48}Ni_{32}P_{20}$ powder under 630 MPa for 3 s at 613 K.

3. Deformation mode of the amorphous powder under applied loads

In order to investigate the densification behavior of the Pd-Ni-P amorphous powder by hot pressing, the change in η as a function of applied pressure and pressing time was examined. As a result, η at $T_p=613$ K in the supercooled liquid region increases rapidly from 8.6×10^8 Pa.s to about 10^{11} Pa.s after $t_p=100$ s. The t_p value leading to the increase in η decreases with increasing T_p, because the relaxation time for atomic rearrangement caused by applied pressure becomes short with increasing temperature. Furthermore, η increases significantly by the application of compressive load. For instance, as shown in Fig. 9, the η value for $t_p=300$ s at $T_p=593$ K is 2×10^{11} Pa.s under an applied load of 160 MPa, 5×10^{11} Pa.s under 310 MPa and 1×10^{12} Pa.s under 630 MPa. Such an increase in η with compressive
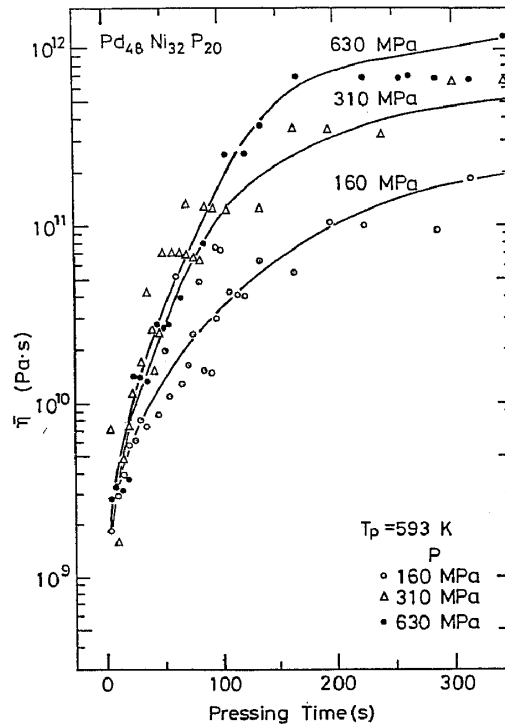
Fig. 9   Change in η of an amorphous $Pd_{48}Ni_{32}P_{20}$ powder with pressing time at different applied pressures.

load is concluded to result in the increase of T_g shown in Fig. 3. The significant change in η of the supercooled liquid with applied load suggests that the viscous deformation becomes difficult within a short time after the pressing because of the decrease in free volume[7] leading to the significant decrease in η in the supercooled liquid region.

4.   Multistage hot-pressing

It was described in section 5-3 that the remarkable increase in η by applied pressure was attributed to the peculiar structure of an amorphous alloy. It is therefore expected that the control of the structural change in an amorphous alloy by the hot-pressing condition enables us to suppress the increase in η, leading to the formation of an amorphous bulk even in a low temperature range. Figure 10 shows the change in the relative density of the $Pd_{48}Ni_{32}P_{20}$ amorphous powder by the thermo-mechanical treatment consisting of pressing-annealing-pressing. When the hot pressing is made under a pressure of 630 MPa at a low temperature of 593 K where no dense amorphous bulk is obtained even after hot-pressing for long periods, the densification is stagnated immediately after the pressing started and the relative
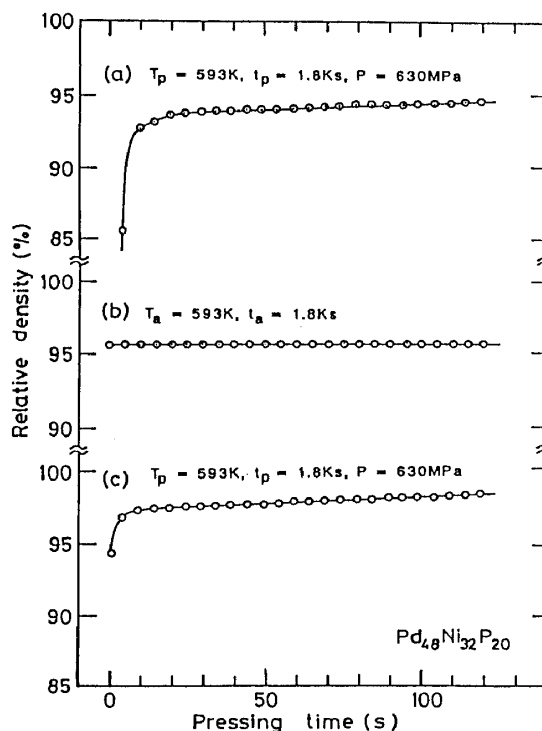
Fig. 10 Change in the relative density of an amorphous $Pd_{48}Ni_{32}P_{20}$ powder by a multistage pressing treatment.

density at this stage is 96.5 %, as shown in Fig. 10. However, by the subsequent sequent treatment of the elimination of the pressing, annealing for 1.8 ks at 593 K under no applied load and then pressing at 593 K under a load of 630 MPa, the relative density increases significantly to 98.2 %. The significant increase in the density caused by the multistage pressing treatment is presumably because the viscosity raised by pressing decreases through relaxation during annealing. The 100 cyles of the sequent treatment consisting of pressing under an applied load of 630 MPa and annealing without applied pressure at a time interval of 60 s enabled the formation of a highly dense amorphous bulk even at a low temperature of 583 K (=1.04 T_g). This result indicates that the repetition of the short-time pressing and annealing causes a significant acceleration of the densification of the amorphous green compact as compared with that for the single long-time pressing treatment.

VI. Conclusion

The influence of an applied compressive load on the structural relaxation and crystallization of an amorphous alloy and the

correlation between the influence and the densification behavior of the amorphous powders were examined for a typical glassy $Pd_{48}Ni_{32}P_{20}$ alloy with a significant supercooled liquid region before crystallization. It has been shown that the relaxation and crystallization of the amorphous alloy are significantly suppressed by the applied load and hence the hot-pressing at a high temperature such as $0.97T_x$ is necessary for the formation of a highly dense amorphous bulk. It has further been clarified that the multistage thermo-mechanical treatment including an intermediate annealing leading to the decrease in viscosity raised by the previous pressing treatment causes the formation of the amorphous bulk with a high packing density even at a relatively low temperature near T_g.

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