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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	26
page range	270-282
year	1976
URL	<a href="http://hdl.handle.net/10097/27857">http://hdl.handle.net/10097/27857</a>

# Viscoelastic Behavior of Amorphous Metals\*

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(Received January 12, 1977)

## Synopsis

The viscoelastic behavior and its rate controlling process of amorphous metals have been examined by extensive experiments of tensile creep and stress relaxation using amorphous Pd-Si, Fe-P-C and Cu-Zr alloys. The differences in creep properties of amorphous and crystalline metals have also been discussed.

Creep curves of all amorphous metals used may be classified into three stages of transient creep, steady-state creep and tertiary creep. The creep strain is composed of recoverable and irrecoverable components and it can be described in terms of viscoelastic elements in rheology. The steady-state creep is controlled by thermally activated process, and seems to be closely related with atomic diffusion in amorphous structure.

## I. Introduction

Recently, amorphous metals have generated a great interest as a new type material having a high strength and toughness<sup>(1)</sup>. In these metals, it has been especially noticed that slip deformations occur inhomogeneously at low temperatures around room temperature and large plastic deformations occur homogeneously at high temperatures near the glass transition temperature  $T_g$ . Quantitative data on the flow characteristics of inhomogeneous deformation at low temperatures are meager because of its occurrence within a localized shear band. On the other hand, the flow character at temperatures near  $T_g$  has been more quantitatively investigated by creep testing<sup>(2)-(5)</sup>. From these creep data it has been pointed out that the creep may be induced by the deformation of viscoelastic origin and that the creep rate is controlled by a thermally activated process probably related with atomic diffusion in amorphous structure. However, a more detailed study is desirable to a better understanding of homogeneous deformation of amorphous metals.

The main purpose of the present study is to obtain the general aspects concerning with the viscoelastic behavior and to clarify the rate controlling process of the creep rate by using three kinds of amorphous metals.

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\* The **1675th** report of the Research Institute for Iron, Steel and Other Metals. Presented at the Second International Conference on Mechanical Behavior of Materials (ICM-II), August, 1976, Boston, Massachusetts, U.S.A.

(1) For example, T. Masumoto and R. Maddin, *Mater. Sci. Eng.*, **19** (1975), 1.

(2) R. Maddin and T. Masumoto, *Mater. Sci. Eng.*, **9** (1972), 153.

(3) H.S. Chen and M. Goldstein, *J. Appl. Phys.*, **43** (1972), 1642.

(4) J. Logan and M.F. Ashby, *Acta Met.*, **22** (1974), 1047.

(5) T. Murata, H.M. Kimura and T. Masumoto, *Scripta Met.*, **10** (1976), 705.

## II. Experimental

Amorphous  $\text{Pd}_{80}\text{Si}_{20}$ ,  $\text{Fe}_{80}\text{P}_{13}\text{C}_7$  and  $\text{Cu}_{60}\text{Zr}_{40}$  alloys were prepared by rapid cooling of melts using centrifugal type<sup>(6)</sup> and roller type<sup>(7)</sup> quenching apparatuses. Specimens obtained were a ribbon shape of about 1 mm in width and 30  $\mu\text{m}$  in thickness. The samples for tensile creep tests, with the gauge length of 10 mm, were prepared by polishing, in width of 0.3 mm, each side of the sample with emery-paper. The creep strain was measured by a Rigaku thermo-mechanical analyser with its specially designed loading adaptor. The strains were detected at the end of quartz glass rods by a differential transformer with sensitivity of 0.1  $\mu\text{m}$ . A stress of about 1  $\text{kg}/\text{mm}^2$ , which is much smaller than the testing stress of 25~50  $\text{kg}/\text{mm}^2$ , was applied to the samples so as to keep the thin sample straight during the time for creep test. Precision of the uniaxial stress applied to the sample was estimated within 2%, and the temperature was controlled to about  $\pm 0.1^\circ\text{C}$ . The creep tests were conducted in vacuum except for the case of measurements of the activation energy for creep. The activation energy for creep of the amorphous Fe-Cr and Fe-Ni base metals was measured in helium atmosphere by the differential test.

## III. Results and discussions

### 1. Creep curves

Figure 1 shows examples of creep curves obtained in amorphous Fe-P-C and Cu-Zr alloys. They exhibit transient and steady-state creep in a manner similar to amorphous Pd-Si alloy<sup>(2)</sup> and some crystalline materials<sup>(8)</sup>. The creep rate of these amorphous alloys decreases at least 1/10 during the course of transient creep. Under the higher stress conditions, tertiary creep takes place and the sample ruptures in the same manner to that of some austenitic alloys<sup>(8)</sup> which exhibit intercrystalline rupture at elevated temperatures.

According to the previous works concerning the thermal stability of the structure and the change in creep rate in the course of the crystallization of amorphous alloys, the following experimental facts have been clarified: 1) amorphous alloy changes to a thermodynamically stable one through a sequence of progressively more stable states on annealing<sup>(9),(10)</sup>, 2) the time at which f.c.c. metastable phase begins to appear, is very much decreased by the application of stress to amorphous Pd-Si alloy<sup>(2)</sup>, 3) Pd-Si alloy having the structure of f.c.c. shows a 0.1 fold smaller steady-state creep rate than that of the sample in

(6) T. Masumoto and S. Tomizawa, Seminar of Japan Inst. Metals, (1972), 184, No. 71.

(7) H.S. Chen and C.E. Miller, Rev. Sci. Instr., **41** (1970), 1237.

(8) For example, F. Garofalo, *Fundamentals of Creep and Creep-Rupture in Metals*, Macmillan, (1965).

(9) T. Masumoto and R. Maddin, Acta Met., **19** (1971), 725.

(10) T. Masumoto, Y. Waseda, H.M. Kimura and A. Inoue, Sci. Rep. RITU, **A26** (1976), 21.

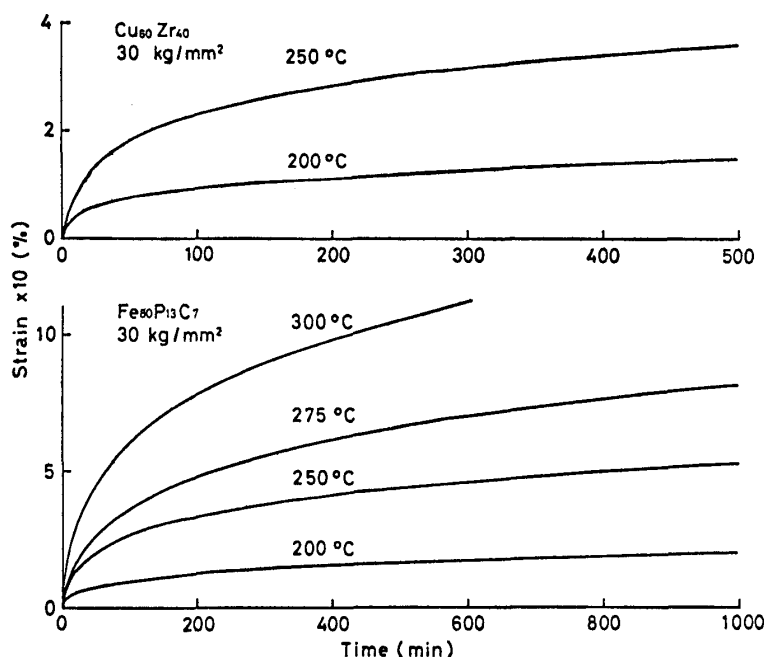


Fig. 1. Creep curves of amorphous Cu-Zr and Fe-P-C alloys.

amorphous state<sup>(2)</sup>. In the present work, however, there is little difference between the X-ray diffraction patterns taken from the crept and uncrept samples as shown in Fig. 2. This fact suggests that the decrease in creep rate during transient creep is not caused by the gradual formation of the crystalline phase in amorphous matrix, but by the essential nature of amorphous state.

## 2. Transient creep

A decrease in creep rate during transient creep of crystalline materials is attributed to an increase in resistance against the creep deformation.<sup>(8)</sup> Similar to crystalline materials, amorphous alloys do not exhibit any transient creep, if the stress is removed at the stage of steady-state creep and applied again to the sample after the removal of the stress during 10 sec. As is seen from Fig. 3, the transient creep, however, takes place with the same feature as the initial one by applying the stress again after a prolonged isothermal aging at the same temperature under the condition where the testing stress is nearly zero. The saturated amount of recovery ( $\epsilon_{rt}$ ) is estimated to be nearly equal to the transient creep strain as shown in Fig. 4. The amount of the creep recovery is measured repeatedly by using a single specimen. The saturated amount of the recovery is plotted against time in the lower figure. The irrecoverable creep strain obtained by subtraction of  $\epsilon_{rt}$  from  $\epsilon_t$  is also plotted in these figures. The gradient of the irrecoverable strain is nearly equal to the steady-state creep rate under the same experimental condition. This experimental fact shows that transient and steady-state components of the creep strain can be described in terms of visco-elastic elements such as Maxwell

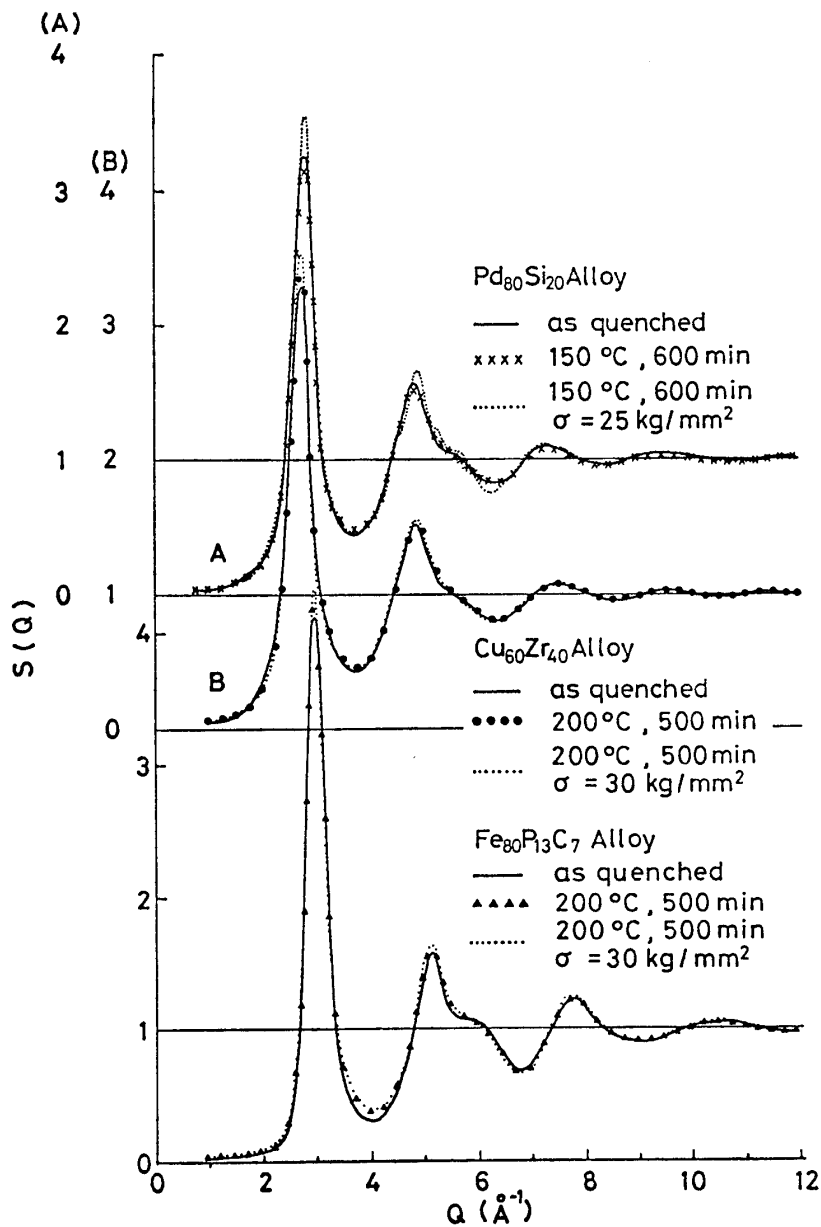


Fig. 2. Differences in the X-ray diffraction patterns taken from the uncrept and crept samples.  $S(Q)$ : structure factor,  $Q=4\pi \sin \theta/\lambda$ .

and Voigt elements. In general, this situation can not be applicable to the creep properties of crystalline materials.

Figure 5 shows the variation of Vickers hardness at room temperature with creep strain of crystalline Pd and amorphous Pd-Si alloy. As seen from this figure, there is no variation in hardness of the crept sample within the experimental errors in contrast with case of crystalline Pd. This result means that there is a difference between the strengthening factors for amorphous alloy and crystalline Pd. The mechanism of the strengthening in amorphous metals can not be clarified, unless the changes in structure and internal stress are extensively studied.

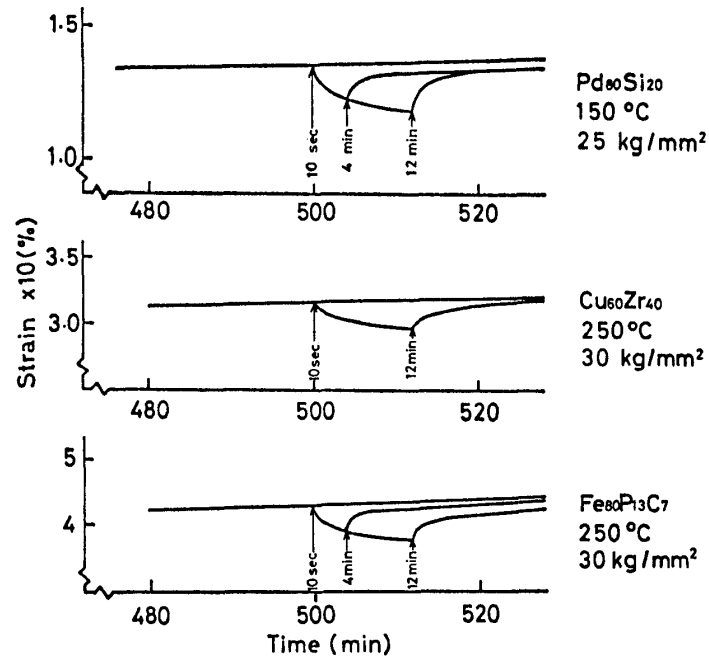


Fig. 3. Anelastic creep recovery of amorphous Pd-Si, Cu-Zr and Fe-P-C alloys. The sample which is crept up to the steady-state region (500 min), is subjected to the recovery test during the time up to 12 min. The stress is applied again at a point indicated by a direct line.

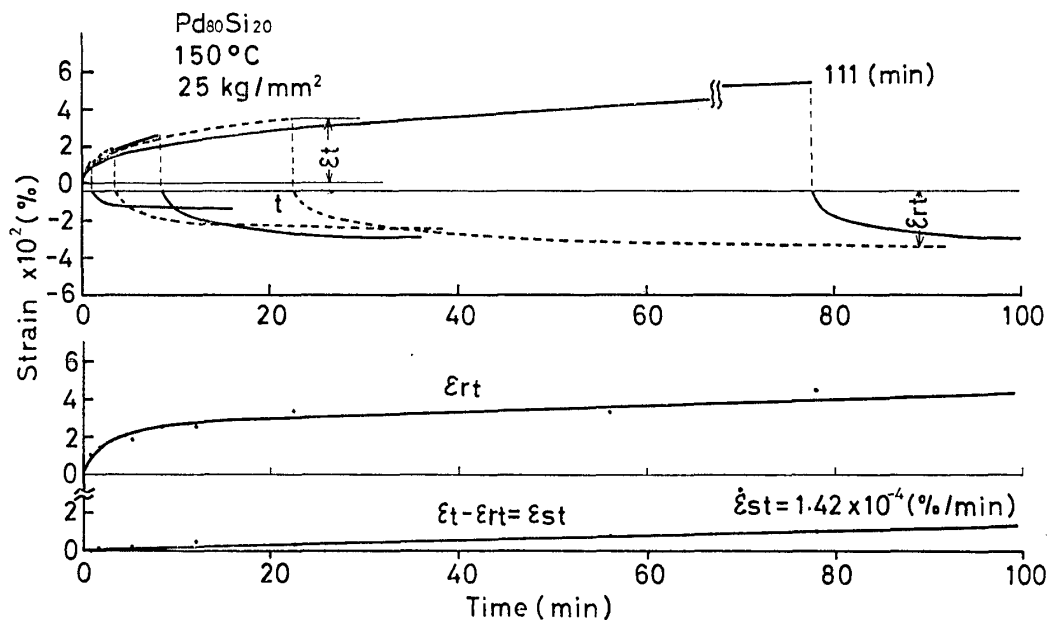


Fig. 4a. Anelastic creep recovery curves obtained after the creep tests up to the various creep strain levels using a single sample of amorphous Pd-Si alloy (above). The time dependence of the saturated amount of the creep recovery ( $=\epsilon_{rt}$ ) and the difference between the creep strain  $\epsilon_t$  and  $\epsilon_{rt}$  (below).

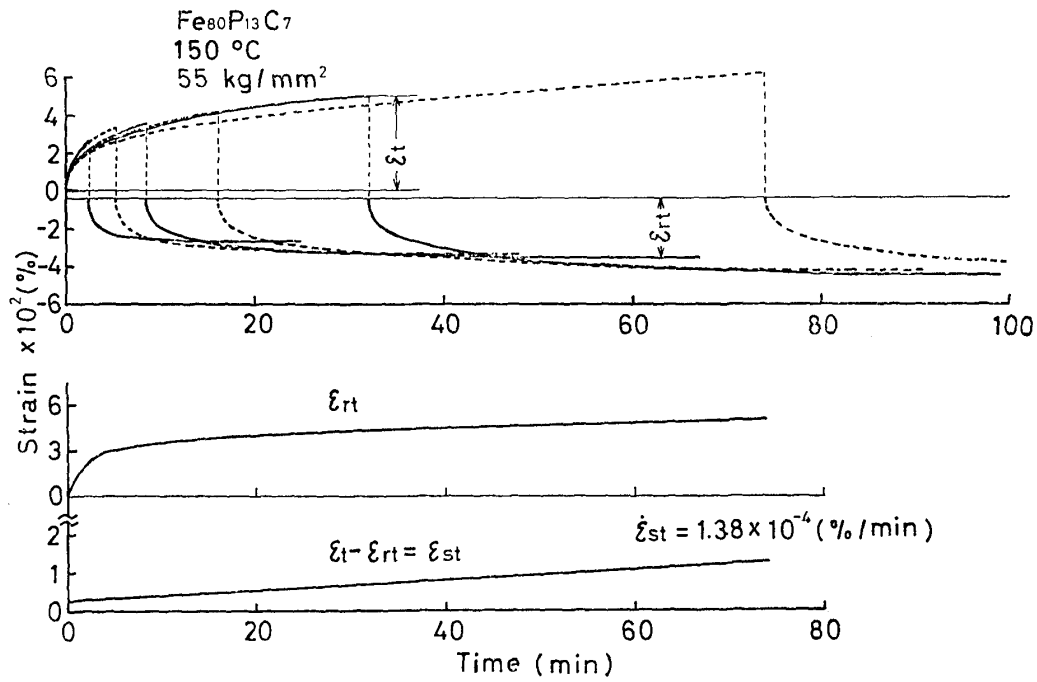


Fig. 4b. Anelastic creep recovery curves obtained after the creep tests up to the various creep strain levels using a single sample of amorphous Fe-P-C alloy (above). The time dependence of the saturated amount of the creep recovery ( $=\epsilon_{rt}$ ) and the difference between the creep strain  $\epsilon_t$  and  $\epsilon_{rt}$  (below).

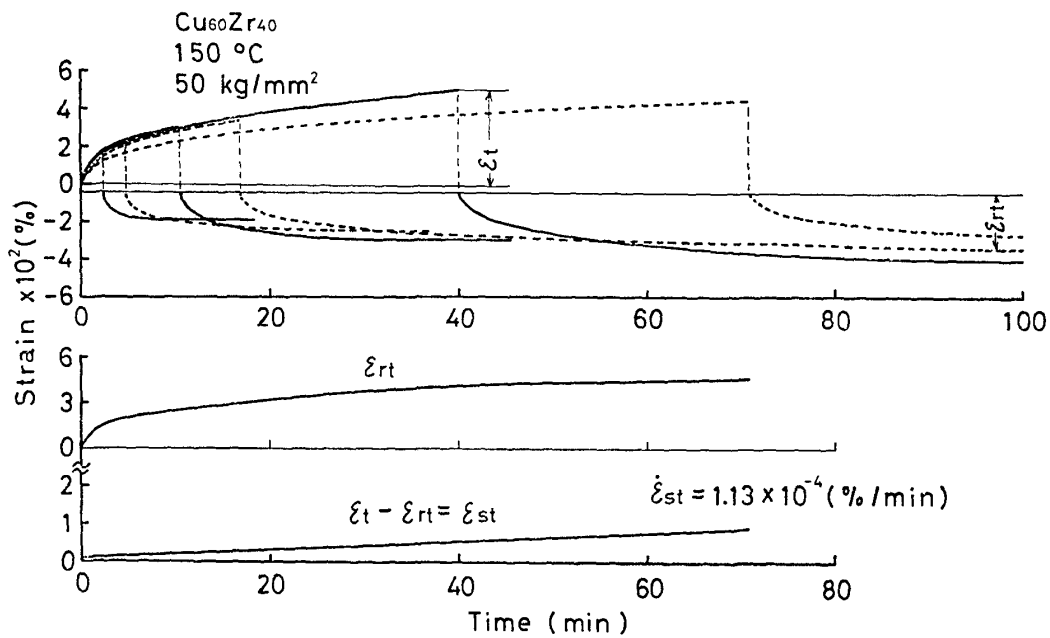


Fig. 4c. Anelastic creep recovery curves obtained after the creep tests up to the various creep strain levels using a single sample of amorphous Cu-Zr alloy (above). The time dependence of the saturated amount of the creep recovery ( $=\epsilon_{rt}$ ) and the difference between the creep strain  $\epsilon_t$  and  $\epsilon_{rt}$  (below).

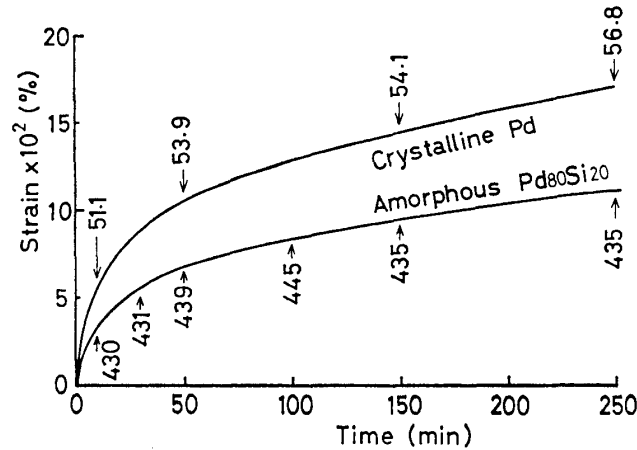


Fig. 5. Variation of Vickers hardness at room temperature with creep strain of crystalline Pd metal and amorphous Pd<sub>80</sub>Si<sub>20</sub> alloy crept at 370°C, 3 kg/mm<sup>2</sup>, and 150°C, 25 kg/mm<sup>2</sup>, respectively.

### 3. Steady-state creep

Table 1 shows the activation energy and the stress exponent of the amorphous metals together with the values of the respective major elements in the crystalline and liquid phases. The activation energies of the amorphous metals are smaller

Table 1. Stress exponent and activation energy for steady-state creep of amorphous Pd-Si, Fe-P-C and Cu-Zr alloys together with the values of the respective major elements in the crystalline and liquid phases.

	Stress exponent, n			Activation energy, kcal/mol		
	Pd <sub>80</sub> Si <sub>20</sub>	Fe <sub>80</sub> P <sub>13</sub> C <sub>7</sub>	Cu <sub>60</sub> Zr <sub>40</sub>	Pd <sub>80</sub> Si <sub>20</sub>	Fe <sub>80</sub> P <sub>13</sub> C <sub>7</sub>	Cu <sub>60</sub> Zr <sub>40</sub>
Creep (Amorphous)	1.6 <sup>a)</sup>	1.1 <sup>b)</sup>	1.1 <sup>b)</sup>	9.4-11.5 <sup>a)</sup>	9.8-10.8 <sup>b)</sup>	9.2~11.4 <sup>b)</sup>
Creep (Crystalline)	4.4 <sup>b)</sup>	5.5-6.6 <sup>c)</sup>	4.8 <sup>d)</sup>	42 <sup>b)</sup>	58-62 <sup>c)</sup>	48 <sup>d)</sup>
Diffusion (Molten met.)	—	—	—	—	15.7 <sup>e)</sup>	9.7 <sup>f)</sup>

a) R. Maddin and T. Masumoto, "The Deformation of Amorphous Palladium-20 at. % Silicon," *Mater. Sci. Eng.*, **9** (1972), 153.

b) Present work.

c) Values for alpha iron in ferromagnetic state. For example, T. Murata and Y. Imai, "Effects of Temperature and Stress on Transient Creep Behavior of Alpha Iron," *Trans. JIM*, **17** (1976), 43.

d) Values for copper. For example, C.R. Barrett and O.D. Sherby, "Steady-State Creep Characteristics of Polycrystalline Copper in the Temperature Range 400°-950°C," *Trans. Met. Soc. AIME*, **230** (1964), 1322.

e) Value for Fe-10.7 at.%C. L. Yang, M.T. Simnad and G. Derge, "Self-Diffusion of Iron in Molten Fe-C Alloys," *J. Metals*, **8** (1956), 1577.

f) Value for copper. J. Henderson and L. Yang, "Self-Diffusion of Copper in Molten Copper," *Trans. Met. Soc. AIME*, **221** (1961), 72.



than those of the crystalline metals and are nearly equal to the values in the liquid phase. The creep rate is proportional to the  $n$ -th power of the applied stress, which is nearly equal to unity.

As is well known, the steady-state creep rate of pure crystalline metals is closely related with self-diffusion of the constituent atoms<sup>(8)</sup>, because the activation energy for creep changes with the same feature as that of self-diffusion in the vicinity of the Curie temperature<sup>(11)</sup>. Figure 6a shows the comparison of the

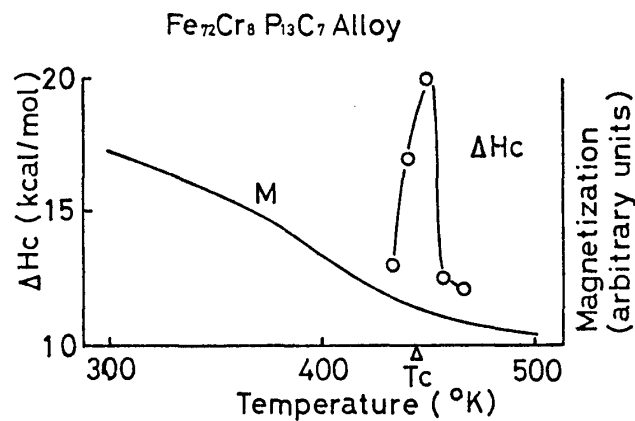


Fig. 6a. Anomaly of activation energy for steady-state creep in the vicinity of the Curie temperature of amorphous Fe-Cr-P-C alloys.

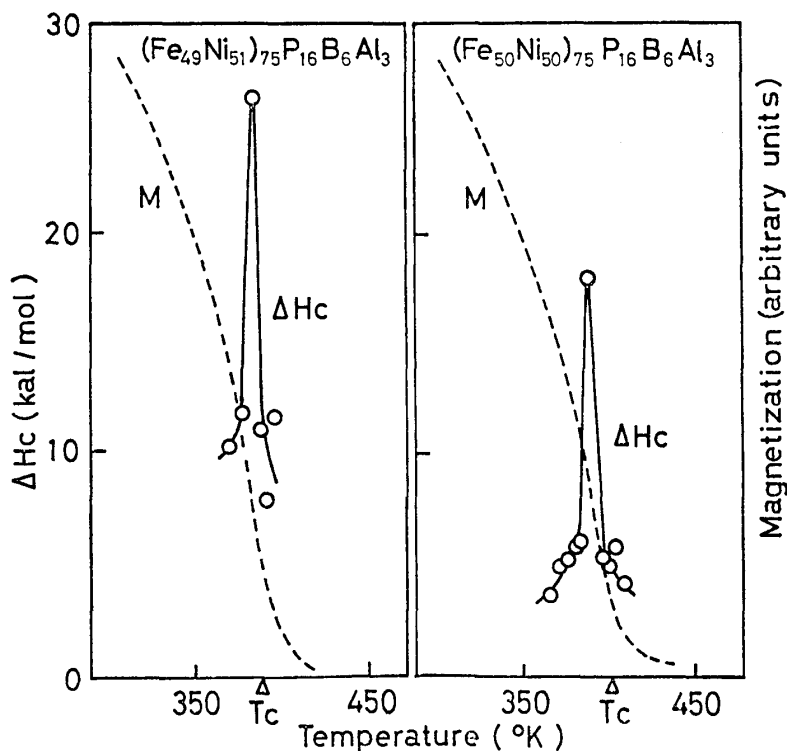


Fig. 6b. Anomaly of activation energy for steady-state creep in the vicinity of the Curie temperature of amorphous Fe-Ni-P-B-Al alloys.

(11) For example, Y. Imai and T. Murata, Sci. Rep. RITU, **A17** (1965), 306.

magnetization and the activation energy for creep of amorphous Fe-Cr base alloy. Here the tail of the magnetization about the Curie temperature is an art effect due to the applied field. The activation energy for creep shows a maximum at temperature where the temperature dependence of the magnetization becomes maximum. The same result is again observed in Fe-Ni base amorphous metals as shown in Fig. 6b. This phenomenon is the same to the case of crystalline metals,<sup>(11)</sup> and is considered to be an experimental evidence showing that the creep rate of these alloys is controlled by atomic diffusion in amorphous phase.

#### 4. Tertiary creep and rupture

Amorphous metals do not exhibit a pronounced tertiary creep as compared with that of pure metals in crystalline state, and creep rupture occurs suddenly at the beginning of the tertiary creep as seen in Fig. 7. Figure 8 shows the relationship between the rupture time and the initial stress in creep tests. The gradient of these curves at higher stress level is nearly equal to -1, and however the experimental points obtained under a lower stress level, deviate very much from these straight lines. The experimental points with an arrow denote the result that no rupture takes place at this stress level after the creep time of 200 min or more, at which crystallization takes place. Figure 9 shows the fractured surface obtained under the experimental condition of 220°C and 67 kg/mm<sup>2</sup>. As is clearly seen, the so-called vein pattern exists on this surface. This pattern is much simpler than that<sup>(12)</sup> obtained by the tensile test at room temperature. From the morphology of

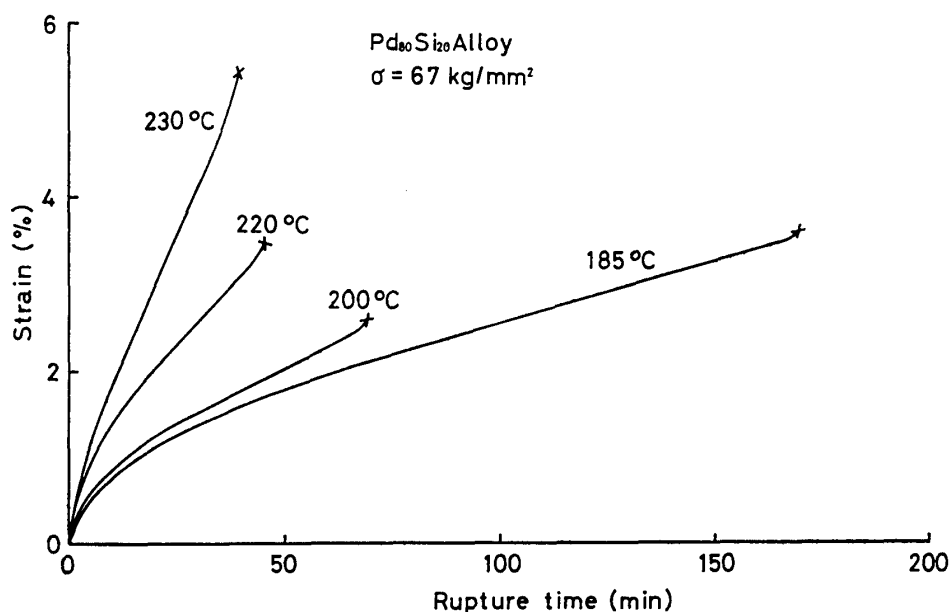


Fig. 7. Creep rupture curves of amorphous Pd-Si alloys at various temperature under 67 kg/mm<sup>2</sup>.

(12) H.J. Leamy, H.S. Chen and T.T. Wang, *Metal. Trans.*, **3** (1972), 699.

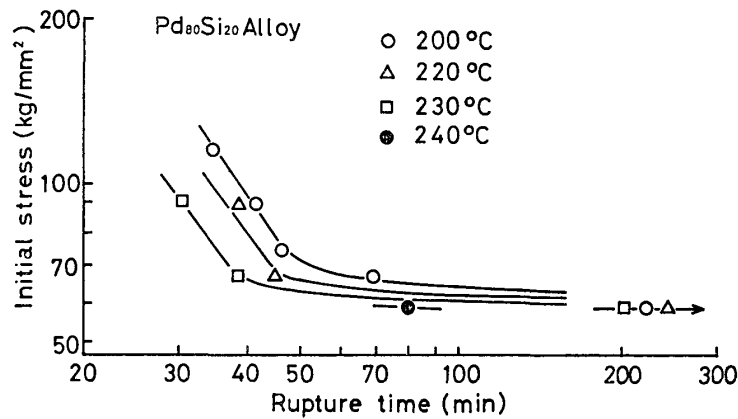


Fig. 8. Relationship between the rupture time and the initial stress in creep tests of amorphous Pd-Si alloys.

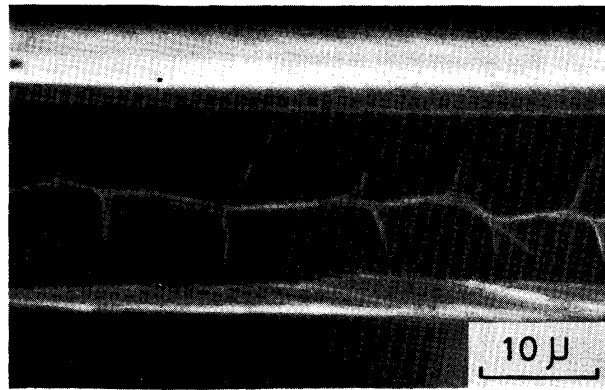


Fig. 9. Fracture surface of amorphous Pd-Si alloy crept under the condition of 220°C and 67 kg/mm<sup>2</sup>. (Pd<sub>80</sub>Si<sub>20</sub> alloy, T=220°C,  $\sigma=67$  kg/mm<sup>2</sup>).

pattern, it is considered that the creep rupture of this kind occurs when the stress exceeds the tensile stress at the testing temperature due to the gradual decrease in the cross sectional area of the sample during the creep test. To examine the detailed properties of the creep rupture, especially the initiation of fracture is the matter of problem.

##### 5. Consideration based on viscoelasticity

Amorphous metals deform in a viscoelastic manner, because the stress exponent of the steady-state creep rate is nearly equal to unity and the creep strain is considered to be separated into the transient and the steady-state components. Therefore, two components can be represented approximately by the Voigt and Maxwell elements, respectively, as indicated in Fig. 10, where  $K_1$  is the value calculated by using the elastic constant of the amorphous sample,  $\eta_1$  is the value reflecting the viscous nature of this sample, which can be derived from the evaluation of the stress dependency of the steady-state creep rate,  $K_2$  is the spring

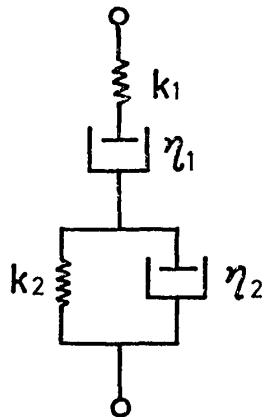


Fig. 10. Rheological model for explanation of creep behavior of amorphous metals.

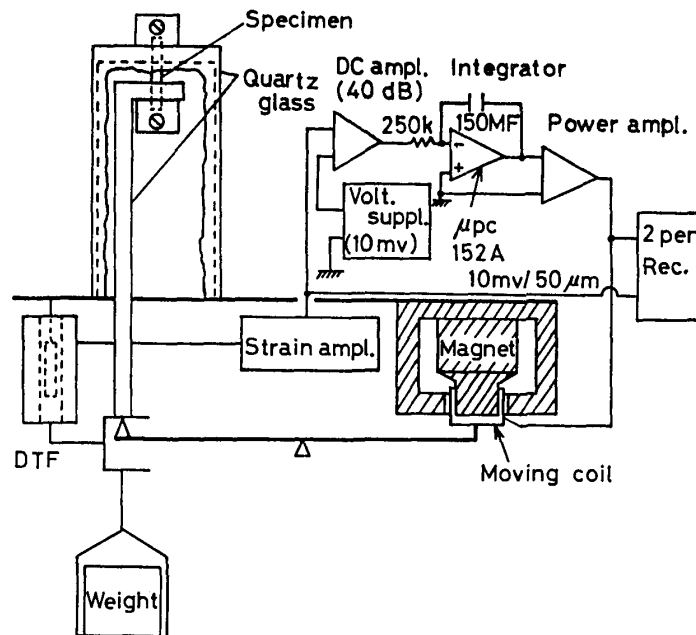


Fig. 11. Systematic diagram of equipment for stress relaxation test.

constant calculated from the ratio of the transient creep strain to the instantaneous creep strain, and  $\eta_2$  is the value derived from the time constant of the transient creep or creep recovery. To examine the validity of this model, stress relaxation experiment is conducted by using an equipment cited in Fig. 11. The change in the gauge length during the experiment is kept constant automatically within  $0.5 \mu\text{m}$ . In all cases, the observation of the change in stress is carried out at the stage of the steady-state creep region. Figure 12 shows the stress relaxation curves of Pd-Si alloy at  $150^\circ$ ,  $185^\circ$  and  $210^\circ\text{C}$ . The activation energy derived from the temperature dependence of the stress relaxation rate is estimated to be  $15 \text{ kcal/mol}$  which agrees well with the value for the steady-state creep rate. A broken line is

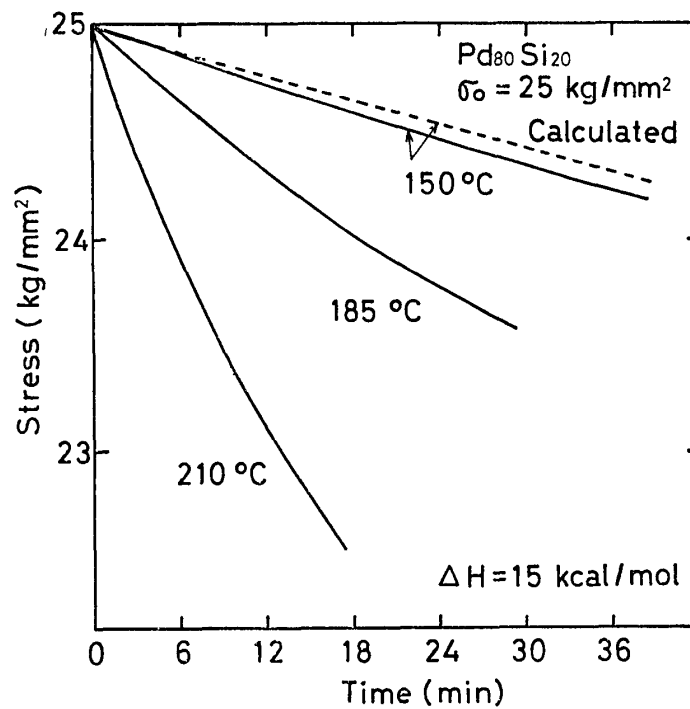


Fig. 12. Stress relaxation curves (solid lines) of Pd-Si alloy at 150°, 185° and 210°C and a curve at 150°C (broken line) calculated from rheological model.

the calculated value from the following differential equation

$$\frac{\eta_2}{K_1 K_2} \cdot \frac{d^2 \sigma}{dt^2} + \left( \frac{1}{K_1} + \frac{1}{K_2} + \frac{\eta_2}{K_2 \eta_1} \right) \frac{d\sigma}{dt} + \frac{1}{\eta_1} \sigma = 0,$$

where  $K_1 = 7.6 \times 10^3 \text{ kg/mm}^2$ ,  $\eta_1 = 1.7 \times 10^7 \text{ kg} \cdot \text{min/mm}^2$ ,  $K_2 = 5.0 \times 10^4 \text{ kg/mm}^2$  and  $\eta_2 = 1.5 \times 10^6 \text{ kg} \cdot \text{min/mm}^2$ . The initial stress  $\sigma_1$  is taken to be 25 kg/mm<sup>2</sup> which is equal to the creep stress and initial stress decrement is given by the experimental value of  $d\sigma/dt$  at  $t=0$ . As is seen from this figure, good agreement is obtained between them, suggesting the creep properties of the amorphous metals can be represented approximately by the model of this kind. To study the essential nature of  $K_2$  and  $\eta_2$ , which are considered to be closely related with the inhomogeneous deformation of the sample during creep, is the important problem left behind. It is thought that the observation of the internal stress will play an important role for the better understanding of the deformation mechanism of amorphous metals.

### Summary

This paper reports the tensile creep properties of amorphous Pd-Si, Fe-P-C and Cu-Zr alloys prepared by splat quenching technique. The results obtained are summarized as follows:

1) All amorphous metals used exhibit transient and steady-state creep in a manner similar to crystalline pure metals. However, they do not exhibit a

pronounced tertiary creep as compared with that of pure metals in crystalline state.

2) The creep strain is composed of recoverable and irrecoverable components which are nearly equal to transient and steady-state creep strain, respectively. This fact shows that the creep strain can be described in terms of viscoelastic elements in rheology.

3) The stress exponents of the steady-state creep rate are nearly equal to unity and the activation energies for creep are the same order to those for the major constituent atoms in liquid state.

4) The activation energy for steady-state creep shows an anomaly at the Curie temperature in a manner similar to that of ferromagnetic crystalline metals.

5) Calculated stress relaxation curve based on the rheological model shows a good agreement with the experimental one, and the activation energy for the stress relaxation of amorphous Pd-Si alloy agrees well with the value for steady-state creep.

#### **Acknowledgement**

The authors wish to thank Mr. S. Tomizawa who prepared the amorphous Cu-Zr alloy.