# In-site Observation of Deformation Behavior of Pt-based Metallic Glass

# Pt基金属ガラスの変形挙動のその場観察

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**Abstract:** $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons prepared by a single-roll melt-spinning method were deformed in tension at a strain rate of $2\times10^{-2}s^{-1}$ in the supercooled liquid region. In-situ observations of the deformation behavior of the metallic glass ribbons were carried out by using an optical microscope. It was found that a homogeneous deformation of more than 200% elongation was taken place by a viscous flow of supercooled liquid of the $Pt_{60}Ni_{15}P_{25}$ metallic glass at 523K, a medium temperature among the supercooled liquid region. In the case of tensile tests after partially crystallized at 543K, it was found that the residual supercooled liquid deformed preferentially without deformation of the crystalline solid, and therefore an inhomogeneous deformation occurred.

## 1. Introduction

It is well known that metallic glasses have various useful properties. In tensile testing, the maximum elongation of the metallic glasses is limited to less than 100% at a strain rate below $10^{-3}s^{-1}$ at a temperature of about 100K below crystallization temperature (Tx). Therefore, it had been difficult to work the metallic glasses plastically for the industrial application.

Recently, metallic glasses with a wide supercooled liquid region of more than 60K have been developed [1)-7)]. Here, the supercooled liquid region means a temperature range between glass transition temperatute (Tg) and Tx. The metallic glasses have high glass forming ability and high stability of the supercooled liquid against crystallization. The high glass forming ability leads to the possibility of preparing the metallic glasses with bulky-shape by an injection molding. The high stability of the supercooled liquid leads

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to the possibility of plastic working of the metallic glasses in the supercooled liquid region. It has been reported that $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ and $La_{55}Al_{25}Ni_{20}$ metallic glasses exhibit superplasticity with preserving an amorphous structure at a temperature in the supercooled liquid region [8)-12)]. This superplasticity is considered to be useful for making industrial products by plastic working of bulk metallic glasses, and for expanding the practical application of the metallic glasses. However, many detailed reports on the deformation behavior of metallic glasses with a wide supercooled liquid region have not been available at the moment.

In the present study, in-situ observations of the deformation behavior of $Pt_{60}Ni_{15}P_{25}$ metallic glass with a wide supercooled liquid region were carried out. The $Pt_{60}Ni_{15}P_{25}$ metallic glass is suitable for the in-situ observation in air, because it is little oxidized in the supercooled liquid region.

## 2. Experimental Procedure

$Pt_{60}Ni_{15}P_{25}$ alloy ingots were prepared by arc-melting of pure metals in an argon atmosphere. The metallic glass ribbon with a cross section of about $0.7 \times 0.02 mm^2$ was produced by a single-roller melt-spinning method in an argon atmosphere. The formation of a single amorphous phase was confirmed by X-ray diffraction and TEM observation. By means of DSC analysis, Tg and Tx were determined to be 487K and 553K, respectively.

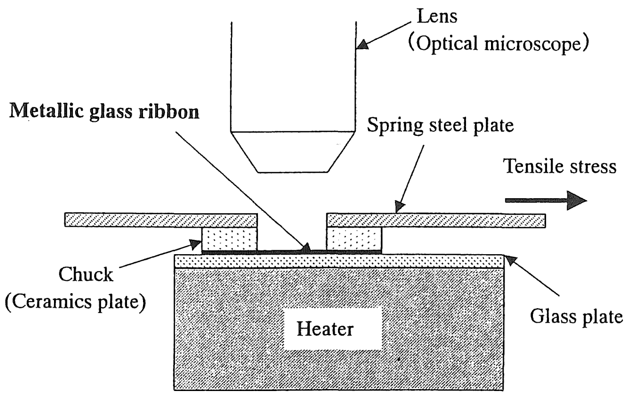


**Fig.1.** Schematic illustration of in-situ observation method of tensile test of a metallic glass ribbon under heating condition.

Figure 1 shows a schematic illustration of in-situ observation method of tensile test of a metallic glass ribbon under heating condition. The tensile test pieces were prepared by bonding a $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbon onto the ceramic holders (chucks) with a ceramic cement. The gauge length was 5 mm. The metallic glass ribbon which touched a glass plate on an electrical heater was heated at a temperature in the range of 493K to 543K for a duration of 4 to 40 min, and deformed in tension at 493K and 523K. A strain rate of the tensile tests was $2 \times 10^{-2} s^{-1}$. The tensile deformation process of the metallic glass ribbon was observed and recorded by using an optical microscope connected to a video recorder. The maximum elongation which the tensile-testing apparatus generated was 250%.

After the tensile tests, the surface morphology of the ribbons was observed by SEM, and the structure of them was studied by X-ray diffraction and TEM observation.

## 3. Results and Discussion

Figure 2 shows total elongation of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons deformed in tension under various heating conditions. The metallic glass ribbon was deformed to failure with 34% elongation at 493K just above Tg. At a higher temperature of 523K, it was deformed up to the maximum elongation of 250%, which the present tensile-testing apparatus could generate. Total elongation of the ribbons decreased with increasing heating time at 543K.

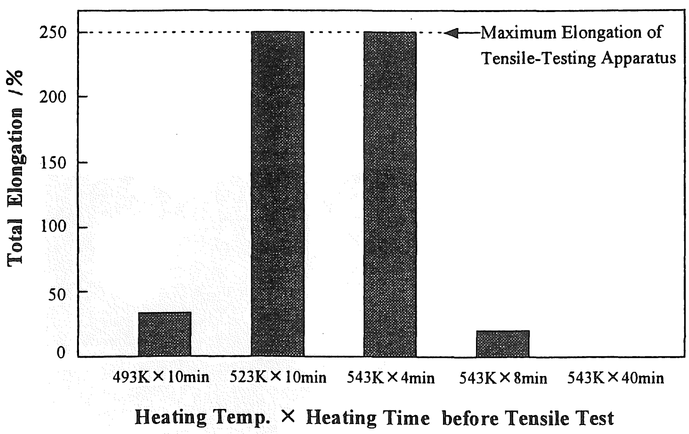


**Fig.2.** Total elongation of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons deformed in tension after heating of various temperatures and various times. The tensile-testing temperatures of the ribbons after heat treatments at 493K and higher than 523K are 493K and 523K, respectively.

The results on in-situ observation of the deformation behavior of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons under various heating conditions are shown in Fig.3. X-ray diffraction patterns of the metallic glass ribbons after tensile tests are shown in Fig.4.

The metallic glass ribbon was deformed plastically to failure with a necking at 493K just above Tg (Fig.3(a)). At a higher temperature of 523K, the metallic glass ribbon exhibited a homogeneous plastic-deformation up to large elongation more than 200% (Fig.3(b)), and an amorphous structure of the ribbon was preserved after the tensile test (Fig.4(a)). Based on these results, it is considered that this large plastic deformation up to more than 200% elongation at 523K is caused by a viscous flow of the supercooled liquid of $Pt_{60}Ni_{15}P_{25}$ metallic glass, and that the failure with a necking at 493K is due to a higher viscosity of the supercooled liquid just above Tg.

Crystallization of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbon occurred in the case of tensile test at 523K after heating at 543K for 4min (Fig.4(b)). In this case, the ribbon exhibited an inhomogeneous deformation up to more than 200% elongation (Fig.3(c)). The deformation area of the ribbon after tensile test was studied by TEM observation. The result, shown in Fig.5, indicates that most of the deformation area consists of single amorphous phase. Based on these results, it

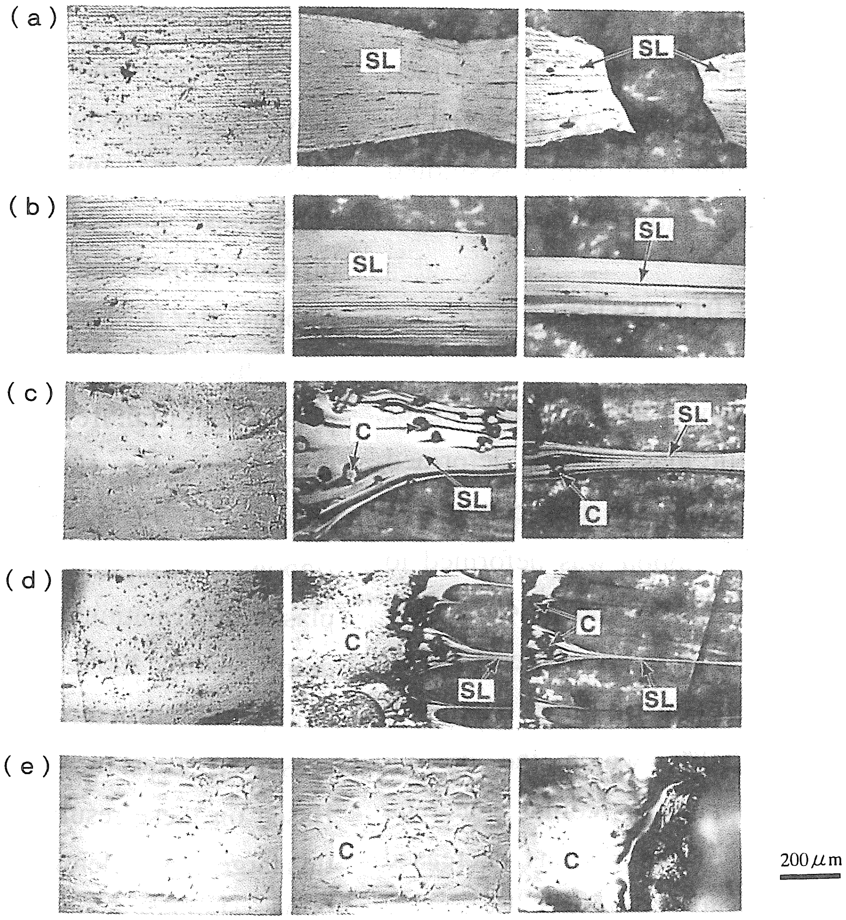


**Fig.3.** Optical micrographs of in-situ observation of the tensile deformation behavior of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons after heat treatments of (a) 493K×10min, (b) 523K×10min, (c) 543K×4min, (d) 543K×8min, (e) 543K×40min. The tensile-testing temperatures of the ribbons after heat treatments at 493K ((a)) and higher than 523K ((b),(c),(d),(e)) are 493K and 523K, respectively. "C" and "SL" denote crystalline phase and supercooled liquid, respectively.

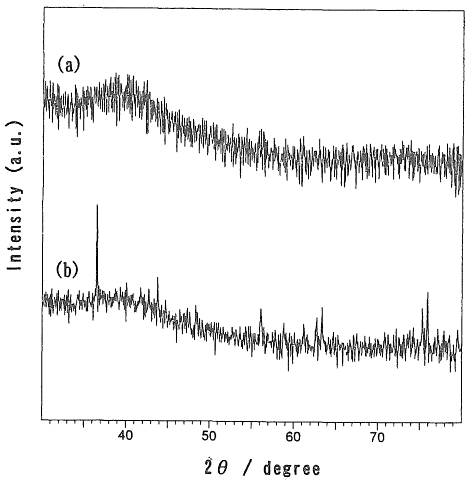


**Fig.4.** X-ray diffraction patterns of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons deformed in tension at 523K after heat treatments of (a) 523K×10min and (b) 543K×4min.

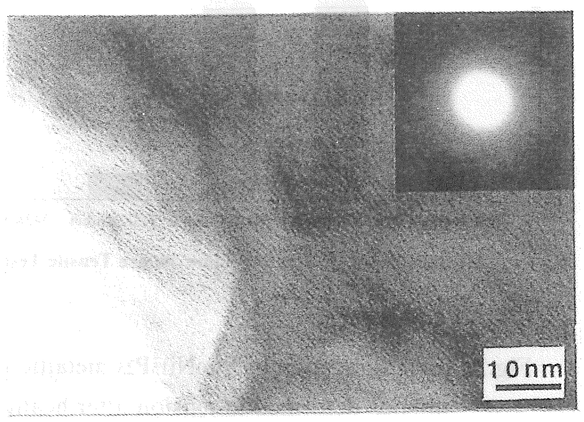


**Fig.5.** TEM micrograph of the deformation area of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbon deformed in tension at 523K after heat treatments of 543K×4min.

is considered that supercooled liquid of the metallic glass was only deformed plastically without deformation of crystallized area (crystalline particles), and that the large plastic-deformation up to more than 200% elongation was caused by viscous flow of the supercooled liquid with a low viscosity. In the case of tensile test at 523K after heating at 543K for 8min, crystallization of the metallic glass ribbon proceeded and the volume of residual supercooled liquid decreased. This small volume of residual supercooled liquid was deformed with viscous flow and fractured at a small total elongation of 20% (Fig.3(d)). In the case of tensile test at 523K after heating at 543K for 40min, crystallization of the metallic glass ribbon proceeded entirely. The ribbon therefore was fractured with little plastic deformation (Fig.3(e)).

SEM micrographs of the surface of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons after tensile tests are shown in Fig.6. The ribbon which exhibited a large plastic deformation more than 200% elongation with preserving amorphous structure had a flat and smooth surface similar to that before tensile test (Fig.6(a)). Stripe patterns were observed in the surface of amorphous phase of the ribbon which exhibited an inhomogeneous deformation after heating at 543K for 4min (Fig.6(b)). It is considered that these patterns indicate the viscous flow of supercooled liquid. Another trace which indicated the viscous flow of supercooled liquid was observed in the interface between a crystalline particle and an amorphous phase (region A in Fig.6(b)).

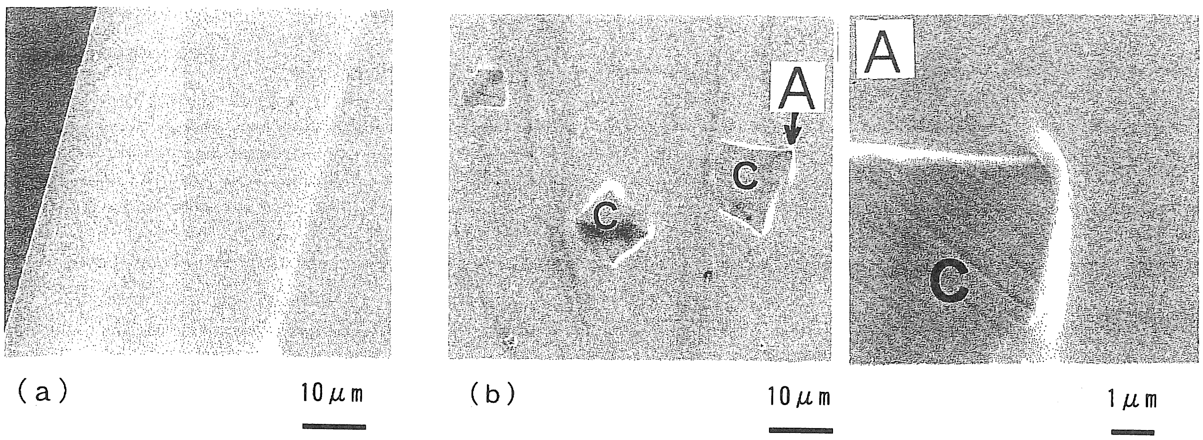


**Fig.6.** SEM micrographs of the surface of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons deformed in tension at 523K after heat treatments of (a) 523K ×10min and (b) 543K×4min. "C" denotes crystalline phase.

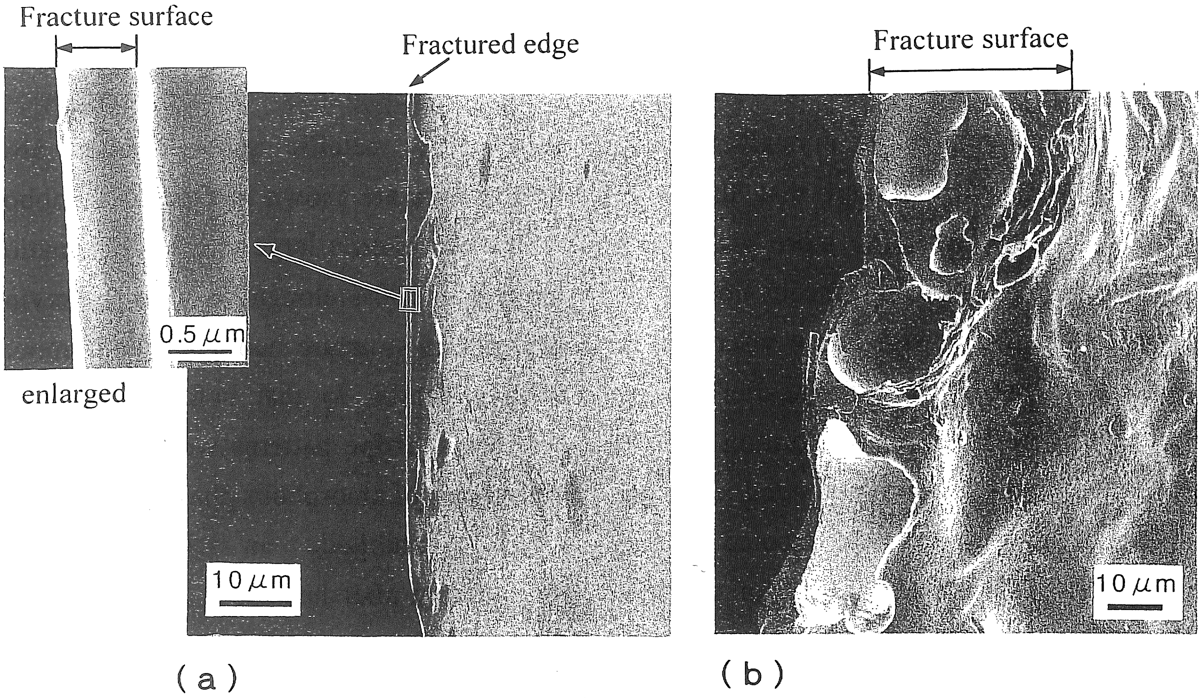


**Fig.7.** SEM micrographs of the fracture surface of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons deformed to failure at (a) 493K after heat treatments of 493K×10min and (b) 523K after heat treatments of 543K×40min.

Figure 7 shows SEM micrographs of the fractured regions of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons after tensile tests. The ribbon deformed plastically to failure with a necking at 493K just above Tg exhibited a ductile fracture which was caused by the viscous flow of supercooled liquid (Fig.7(a)). In contrast, the ribbon of which crystallization proceeded entirely after heating at 543K for 40min revealed a brittle fracture (Fig.7(b)). It seems that this fracture was mainly taken place in grain boundaries.

Based on the abovementioned experimental results, deformation behavior of Pt60Ni15P25 metallic glass ribbon in the neighborhood of supercooled liquid region can be considered as follows.

At a temperature just above Tg, that is, a low temperature among supercooled liquid region, supercooled liquid of the metallic glass is deformed with viscous flow to less than 100% elongation, and fractured with a necking because of a high viscosity of the supercooled liquid. At an intermediate temperature in supercooled liquid region, the viscosity of the supercooled liquid becomes lower than that at a temperature just above Tg. Therefore, the supercooled liquid exhibits a homogeneous deformation with viscous flow to more than 200% elongation at a high strain rate above $1\times10^{-2}s^{-1}$. It is considered that this large plastic deformation behavior corresponds to a high-strain-rate superplasticity.

At a temperature just below Tx, crystallization of the supercooled liquid starts and proceeds with increasing heating time. In the mixed structure of supercooled liquid and crystalline solid, the residual supercooled liquid is only deformed with viscous flow. Therefore, an inhomogeneous deformation occurs and total elongation decreases with the progress of crystallization. When most of supercooled liquid changes to crystalline solid, the material exhibits little plastic deformation and fractures with brittleness.

## 4. Conclusions

In-situ observations of the deformation behavior of $Pt_{60}Ni_{15}P_{25}$ metallic glass ribbons at various heating conditions in the neighborhood of supercooled liquid region were carried out. The following results were obtained.

(1) The metallic glass ribbon exhibits a large plastic-deformation, which seems to correspond to a high-strain-rate superplasticity, at a medium temperature in the supercooled liquid region. This large plastic-deformation is caused by a viscous flow of the supercooled liquid with a low viscosity.

(2) In the case of the occurrence of crystallization, residual supercooled liquid deforms preferentially without the deformation of crystalline solid. An inhomogeneous deformation therefore takes place.

## References


1) A.Inoue, T.Zhang and T.Masumoto: Mater. Trans.,JIM, 30 (1989), 965-972.
2) A.Inoue, T.Zhang and T.Masumoto: Mater. Trans.,JIM, 31 (1990), 177-183.
3) T.Zhang, A.Inoue and T.Masumoto: Mater. Trans.,JIM, 32 (1991), 1005-1010.
4) A.Peker and W.L.Johnson: Appl. Phys. Lett., 63 (1993), 2342-2344.
5) A.Inoue and T.Zhang: Mater.Trans.,JIM, 37 (1996), 185-187.
6) A.Inoue, N.Nishiyama and T.Matsuda: Mater. Trans.,JIM, 37 (1996), 181-184.
7) A.Inoue: Acta Mater., 48 (2000), 277-304.
8) H.Okumura, A.Inoue and T.Masumoto: Mater. Trans.,JIM, 32 (1991), 593-598.
9) T.Masumoto: Mater. Sci. and Engng., A179/A180 (1994), 8-16.
10) Y.Kawamura, T.Shibata, A.Inoue and T.Masumoto: Scripta Mater., 37 (1997), 431-436.
11) M.Takagi, H.Iwata, T.Imura, Y.Soga, Y. Kawamura and A.Inoue: Mater.Trans.,JIM, 40 (1999), 804-808.
12) Y.Kawamura, T.Nakamura, A.Inoue and T. Masumoto:Mater.Trans.,JIM,40(1999),794-803.


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