TN8410 91-247

Effects of Noble Metal Elements on Properties of Simulated Vitrified Products for High-Level Liquid Waste

—Research Report on Solidification of High-Level Liquid Waste—

Dec.,1991

POWER REACTOR AND NUCLEAR FUEL DEVELOPMENT CORPORATION
TOKAI WORKS

複製又はこの資料の入手については、下記にお問い合わせ下さい。

〒319-11　茨城県那珂郡東海村大字村松４－33
動力炉・核燃料開発事業団
東海事業所（Tokai Works）
技術協力部　技術管理室
（Technology Management Section）

Inquiries about copyright and reproduction should be addressed to: Technology Management Section, Tokai Works, Power Reactor and Nuclear Fuel Development Corporation 4-33, Muramatsu Ooaza, Tokai, Naka-gun, Ibaraki, 319-11, Japan)

Ⓚ

PNC TN8410 91-247
Dec., 1991

EFFECTS OF NOBLE METAL ELEMENTS ON PROPERTIES OF SIMULATED VITRIFIED PRODUCTS FOR HIGH-LEVEL LIQUID WASTE

-Research Report on Solidification of High-Level Liquid Waste-

Hiroshi Igarashi, Kazuhiro Kawamura and Takeshi Takahashi

ABSTRACT

The effects of noble metal elements such as ruthenium, rhodium and palladium on the viscosity and electrical resistivity of simulated nuclear waste glass were studied. The glass enriched with noble metals showed the viscosity of a non-Newtonian fluid. The viscosity of the waste glass with 10 wt% RuO_2 was 3 to 7 times higher than that of glass without noble metals. The RuO_2 was mainly responsible for the increase in viscosity for the glass enriched with noble metals. Electrical resistivity of the glass with 15 wt% RuO_2 was one seventh to two orders of magnitude lower than that of glass without noble metals. The three noble metals contributed to the decrease in resistivity. The quantitative effects of noble metals on these properties were obtained.

High-Level Waste Technology Section, Waste Technology Development Division.

This report is based on the content presented in 'Effects of Noble Metal Elements on Viscosity and Electrical Resistivity of Simulated Vitrified Products for High-Level Liquid Waste',The XV International Symposium on the Scientific Basis for Nuclear Waste Management, Material Research Society,1991 Fall Meeting, Strasbourg, France,November 4-8, 1991.

PNC TN8410 91-247
１９９１年１２月

EFFECTS OF NOBLE METAL ELEMENTS ON PROPERTIES OF SIMULATED VITRIFIED PRODUCTS FOR HIGH-LEVEL LIQUID WASTE

-Research Report on Solidification of High-Level Liquid Waste-

五十嵐　寛，河村　和廣，高橋　武士

要　　　旨

模擬高レベル廃棄物固化ガラスの粘性および電気抵抗に及ぼす白金族元素の影響について調べた。白金族元素は廃棄物中に核分裂生成物成分として含まれるもので，Ru,RhおよびPdからなる。粘性は回転式粘度計で，電気抵抗は二電極式測定装置により測定した。温度は約500 ℃から1200℃まで変化させた。白金族元素が高濃度のガラスの粘性は非ニュートン流体挙動を示した。ルテニウムを10%含有する場合，他の白金族元素の多少にかかわらず，ガラスの粘性は白金族元素を含まないガラスに比べ３～７倍高かった。これは主としてRuO_2によるものであった。RuO_2を15%含有するガラスの電気抵抗は白金族元素を含まないガラスに比べ 1/7から最大２桁低下した。電気抵抗の低下に対しては白金族三元素が寄与していると考えられた。

著者所属：環境技術開発部、環境技術第一開発室（ＨＴＳ）

本報は「'Effects of Noble Metal Elements on Viscosity and Electrical Resistivity of Simulated Vitrified Products for High-Level Liquid Waste' The XV International Symposium on the Scientific for Nuclear Waste Management, Material Research Society 1991 Fall Meeting, Strasbeurg, France,November 4-8, 1991」での発表を中心にまとめたものである。

CONTENTS

1. INTRODUCTION

High-level liquid waste (HLLW) separated in the reprocessing of spent nuclear fuel is immobilized into glass which is a stable form from the viewpoint of storage, handling and final disposal. The HLLW contains noble metal elements such as ruthenium, rhodium and palladium. These noble metals are extremely insoluble in the glass[1] and tend to settle in the glass melter[2,3]. These elements exist in the glass mainly as RuO_2 , $Ru(Rh)O_2$, Pd-Te and Pd-Rh-Te [1,4]. The sediments enriched with noble metals are formed when these elements are precipitated in higher concentration in the melter. The sediments are not only more electrically conductive but also more viscous than the reference glass with the noble metals in standard concentrations. The changes in these properties affect the electric glass melting and the pouring of glass into canisters. The engineering approaches such as melter structural design and operational technique have been developed so that the melter should be compatible with the effects of noble metals on the operation of the melter in Japan[5-7], Germany[8] and U.S.A.[9]. But the effects of noble metals on the properties have not been studied extensively although understanding them is important to establish the vitrification technology.

In this paper, the effects of noble metals on viscosity and electrical resistivity are studied as functions of concentrations of noble metal elements.

2. EXPERIMENTAL

2.1 Glass composition

The simulated waste glasses were studied and varied in concentrations of noble metal elements. The glass composition of reference glass studied in this work is shown in Table I. Noble metal elements are expressed in possible oxide forms, whichever form of oxide or metallic alloy they may be in glass. Detailed formulation of typical simulated waste glass was shown elsewhere[2]. When the concentrations of RuO_2 or three noble metals being RuO_2 , PdO and Rh_2O_3 were varied, all other components were adjusted in concentrations proportionally. Table II shows the noble metal concentrations in the glasses. One series of the glasses with variation only in RuO_2

concentration is referred to as Ru-glass, and the other series with variation in three noble metals is NMs-glass hereinafter.

Table I. Reference composition of simulated waste glass

(wt %)

glass additives		wastes	
components	contents	components	contents
SiO_2	45.0~ 46.6	Na_2O	10.0
B_2O_3	14.2	P_2O_5	0.3
Al_2O_3	3.6~ 5.0	Corrosion products*	~ 3.5
Li_2O	3.0	Fission products	10.0
CaO	3.0	RuO_2	0.74
ZnO	3.0	Rh_2O_3	0.14
		PdO	0.35
		Actinides	~ 2.4

note*; corrosion products: Fe_2O_3 ,NiO and Cr_2O_3

Table II. Compositions of noble metal elements in the glasses

(a) For viscosity measurement (wt %)

assumed oxide	Ru-glass (variation only in RuO_2)				NMs-glass (variation in three noble metals)				
	0.9 Ru	1 Ru	7 Ru	10 Ru	0NMs(P0797) *1	4NMs	5NMs	10NMs	13NMs
RuO_2	0.93	1.00	7.00	10.00	—	2.60	3.25	6.50	8.67
Rh_2O_3	—	—	—	—	—	0.39	0.49	0.98	1.30
PdO	0.37	0.37	0.35	0.34	—	0.96	1.20	2.41	3.21

(b) For resistivity measurement (wt%)

assumed oxides	Ru-glass (variation only in RuO_2)				NMs-glass (variation in three noble metals)		
	0 Ru	5 Ru	10 Ru	15 Ru	reference(P0798)*1	MB *2	MU1 *2
RuO_2	——	5.0	10.0	15.0	0.74	13	12
Rh_2O_3	——	——	——	——	0.14	(2)	(2)
PdO	——	——	——	——	0.35	3	(6)

note*; *1:PNC's glass code

*2:The concentration of Rh_2O_3 and PdO in parentheses were estimated with assumption that they are proportional to RuO_2 concentration obtained from analysis.

2.2 Glass preparation

The glass additives and wastes were melted in platinum crucibles at 1150 ℃ for 2.5 hours. For the Ru-glass for the viscosity measurement, glass fiber additives of 10 μ m in diameter were used; the cylindrically formed fiber absorbed simulated liquid waste with additional $RuCl_3$ at expected concentrations, so that RuO_2 should disperse homogeneously. Insoluble RuO_2 crystals were a few μ m in their sizes and no significant sedimentation of a few μ m of insoluble RuO_2 was observed during about 4 hours of viscosity measurement. Therefore, the Ru-glasses for resistivity measurement were prepared by melting crushed waste glass smaller than 100 μ m and RuO_2 powder of 0.43 μ m as additional ruthenium at expected ratio for the ease of preparation.

When melting glass with excess noble metal oxides preliminarily to prepare the glasses with variations in their concentrations, small fractions of insoluble Rh_2O_3 and PdO particles floated on the surface of the glass melts. Therefore the NMs-glasses were prepared in different ways from Ru-glass preparation to avoid the floatation of the noble metals, which would affect measurement accuracy. The NMs-glasses were made by melting the mixture of the reference glass with the glasses enriched with noble metals, which was taken from the melter. Two glasses enriched with noble metals: MB and MU1 were made in melters which had been continuously operated for a long time. The glass MB had been held around 900℃ for several months and MU1 had been held above 1100℃ for about one month in the melter. NMs-glass for viscosity measurement was made from the mixture of the reference glass with MB glass at various ratios. For resistivity measurement, MB and MU1 glasses were used as NMs-glass.

2.3 Measurement

Viscosity was measured by rotational viscometer shown in Fig.1. A platinum rotor of 12 mm diameter was rotated in 90 g of molten glass in the alumina crucible of 27 mm inner diameter. The viscosity was calculated from the measured torque and rotational speed which was varied from 1 to 32 rpm equivalent to 0.0043 to 0.140 s^{-1} shear rate. Temperature of glass was varied from 850 to 1150℃ . In calibration of measurement, the known viscosity of NBS710 at 0.140 s^{-1} shear rate and 1050℃ was used as a

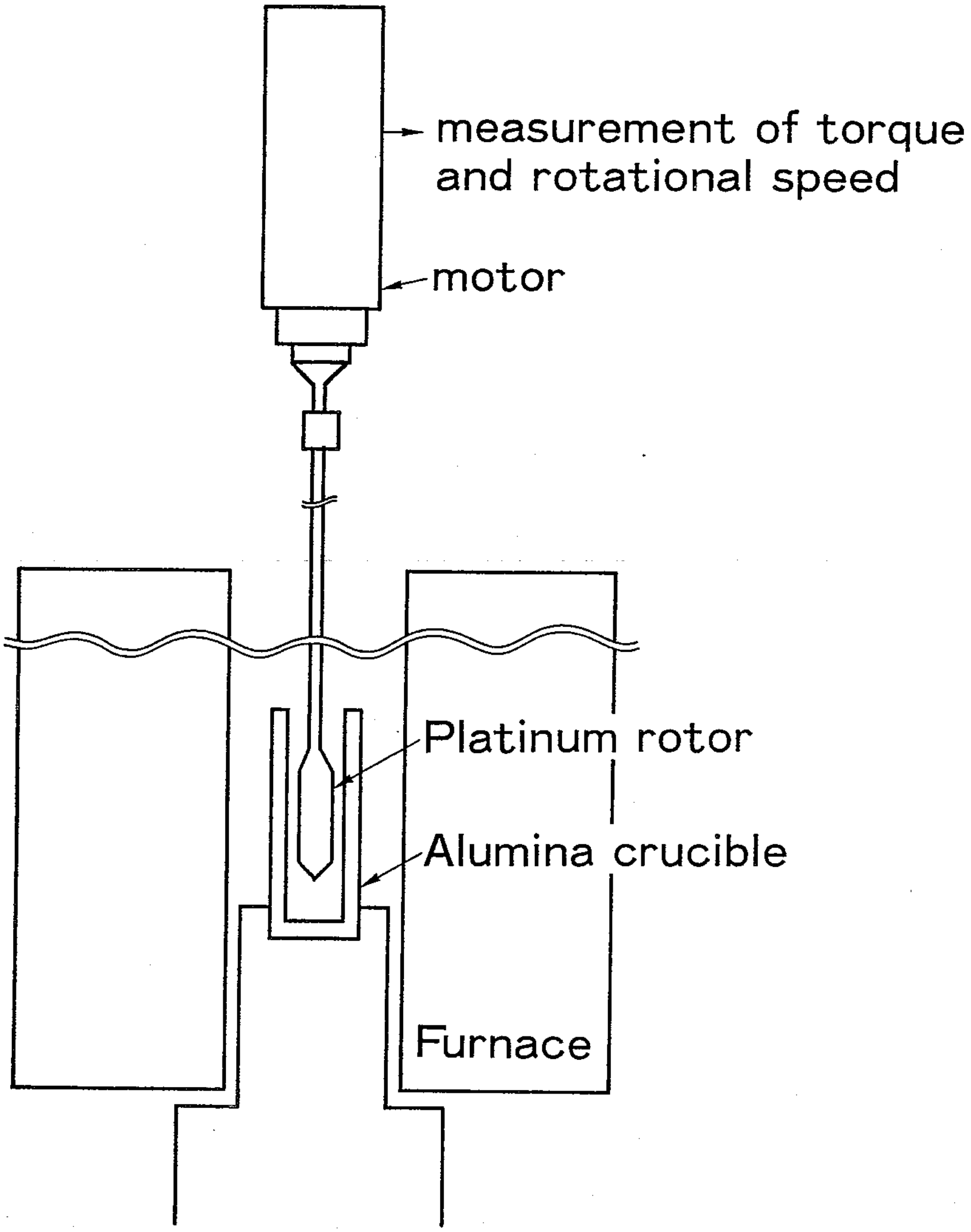


Fig.1 Rotational Viscometer

standard. The viscosity of NBS710 glass is shown in Appendix A.

Electrical resistivity was measured between two platinum electrodes of 6 mm diameter immersed into the molten glass in 50 mℓ alumina crucible as shown in Fig.2. The immersion depth of the electrodes were about 40 mm which was close to the bottom. The upper part of each electrode was covered by an alumina tube; only its lower tip of 6 mm length was exposed to the molten glass to prevent electrical shortage via noble metal oxides potentially floating on the melt surface. The frequency of alternating current used in the experiment was 1 kHz. Temperature of the glass was varied from 525 to 1226℃ . The measurement was calibrated by using NaCl solution of known resistivity.

3. RESULTS AND DISCUSSION

3.1 Noble metal phase in glass

The noble metal elements segregated in the glass were observed by electron probe micro analyzer after viscosity measurement to confirm the state of the noble metal phases.

In the Ru-glasses for viscosity measurement, the RuO_2 particles were dispersed in the size of a few μ m. In the NMs-glass, the sizes of RuO_2 and alloy particles of noble metals were a few tens μ m. Sedimentation was negligible for about 4 hours of the measurement since a significant difference in dispersion density was not observed between top and bottom glass in the crucible after measurement.

For the resistivity measurement, the noble metal phases of the Ru-glass were not observed. But no significant sedimentation was expected during the resistivity measurement because the 0.43 μ m in particle size of RuO_2 added was smaller in resistivity measurement than in viscosity measurement. The noble metal phases of MB were similar to those of NMs-glass for viscosity measurement. In the NMs-glass MU1 for resistivity measurement, RuO_2 crystals were observed in needle shape of several tens to a hundred μ m in length before measurement. The needle shaped crystals had grown at higher temperature for long residence times, and can be paths of electrical conduction.

The noble metal phases in the glass are shown in Appendix B.

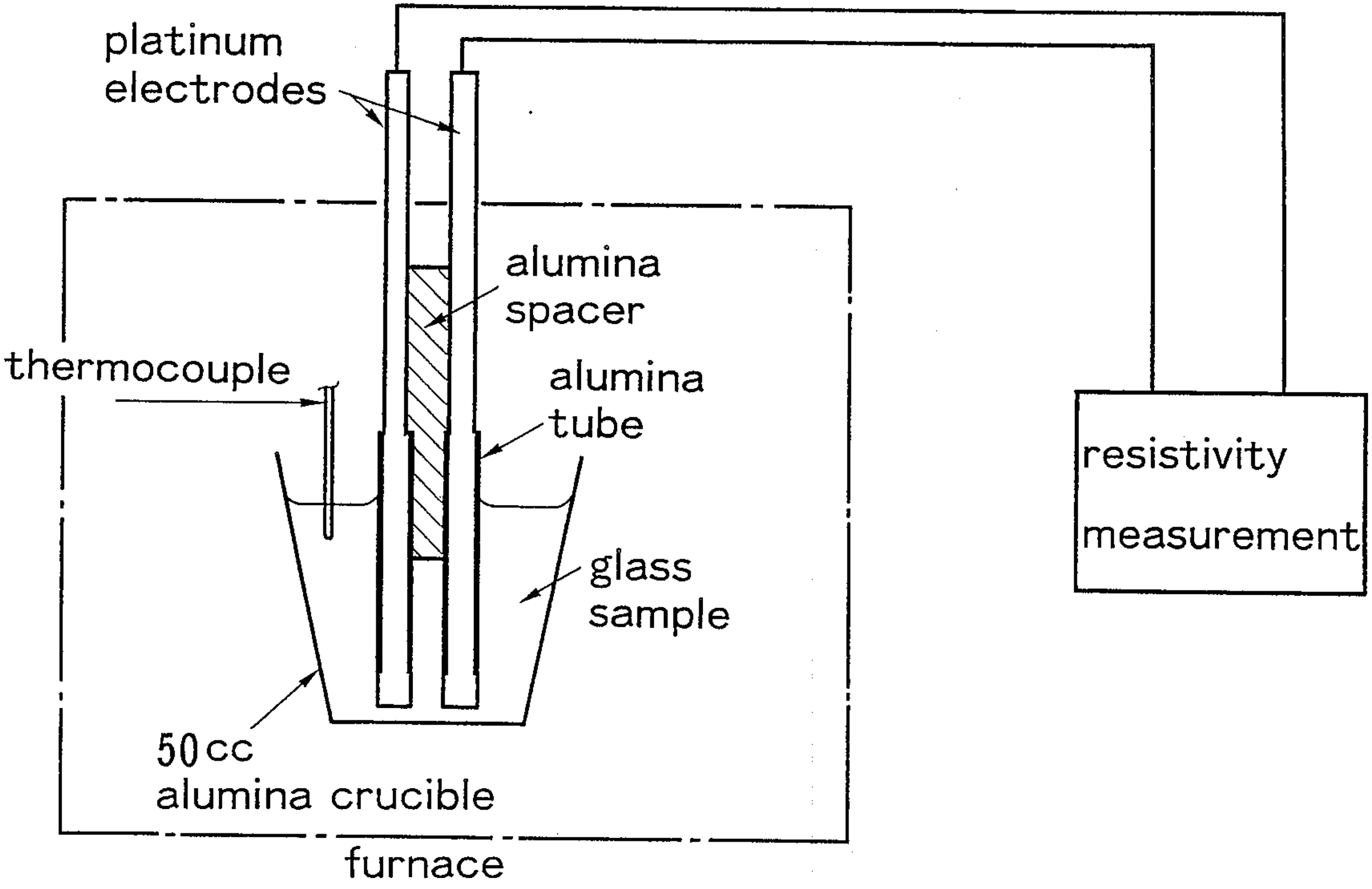


Fig.2 Apparatus for electrical resistivity measuement

3.2 Viscosity

The relation between shear stress and shear rate was linear at high shear rate for the glasses with low noble metals as observed for Newtonian fluids. Figure 3 shows shear stress vs. shear rate for 1 Ru-glass; its shear rate dependence of shear stress was quite small and no yield stress was observed. The shear stress was not available in lower shear rate and at higher temperature because torque was too low to detect in those conditions. A similar relation between shear stress and shear rate was observed also for the 0NMs-glass and soda-lime-silicate glass NBS 710. But the shear rate dependence of shear stress became significant for the glasses enriched with noble metals such as the 7 and 10 Ru-glass and the 10 and 13 NMs-glasses. As an example, Fig.4 shows the shear stress vs. shear rate for 10 Ru-glass. These glasses indicated pseudo-plastic flow of non-Newtonian fluid and their flows were subject to the equation:

$$\tau - \tau_y = m D^n \qquad (1)$$

where τ = shear stress, τ_y = yield stress, D = shear rate and m and n = experimental constants. The m and n depend on the glass composition and temperature. Although the physical meaning of viscosity of the glasses enriched with noble metals is different from that defined for Newtonian fluid, the apparent viscosity obtained from τ /D is referred to as viscosity also for non-Newtonian fluid in this paper.

Figure 5 shows the relation between viscosity and shear rate for the 1 Ru-glass. Its viscosity increased slightly with decrease in shear rate whereas the effect of shear rate was negligible in higher shear rate. The viscosity at 0.0043 s^{-1} was two times higher than that at 0.140 s^{-1}. The shear rate dependence of viscosity became remarkable with the concentrations of noble metals. Figure 6 shows the viscosity vs. shear rate for the 10 Ru-glass. For this glass, the viscosity at 850℃ increased by a factor of 5.5 with decrease in shear rate from 0.140 to 0.0043 s^{-1}, and viscosity at 1150℃ increased by a factor of 20. Tobie et al. reported the similar shear rate dependence of viscosity for German glass with 14.8 RuO_2 and 4.5 Pd in wt % [8]. Plodinec studied rheology of glasses containing spinel crystals and reported the similar dependence [10].

The effect of RuO_2 or three noble metals on viscosity are shown as functions of temperature in Figs 7 and 8. The viscosities of the 10 Ru-glass and the 13 NMs-glass were 3 to 7 times higher than that of the glass without noble metal. Figure 9 shows the effect of RuO_2 concentration on

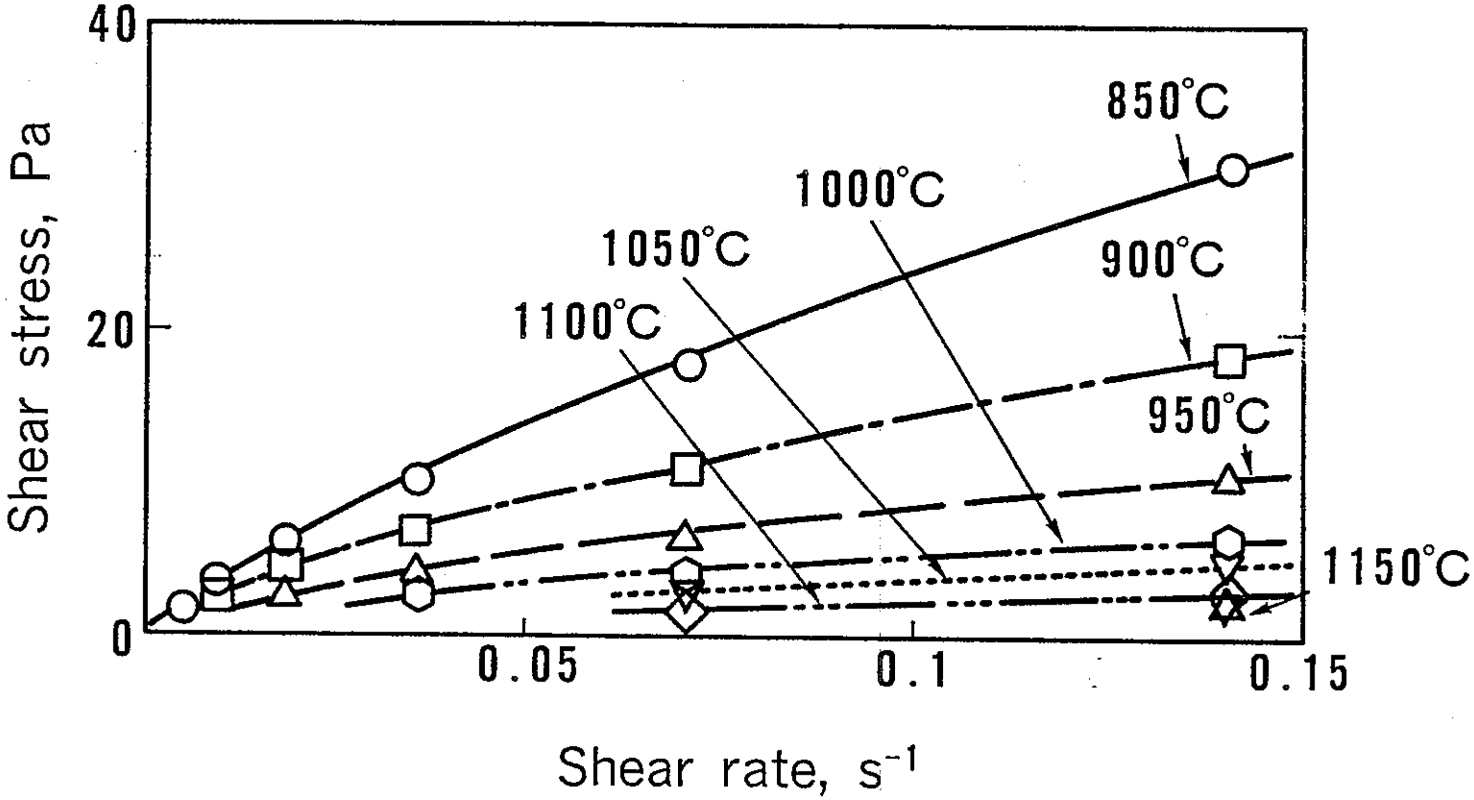


Fig.3 Shear stress vs. shear rate for 1 Ru-glass (wt %: 1.0 RuO_2 , 0.37 PdO)

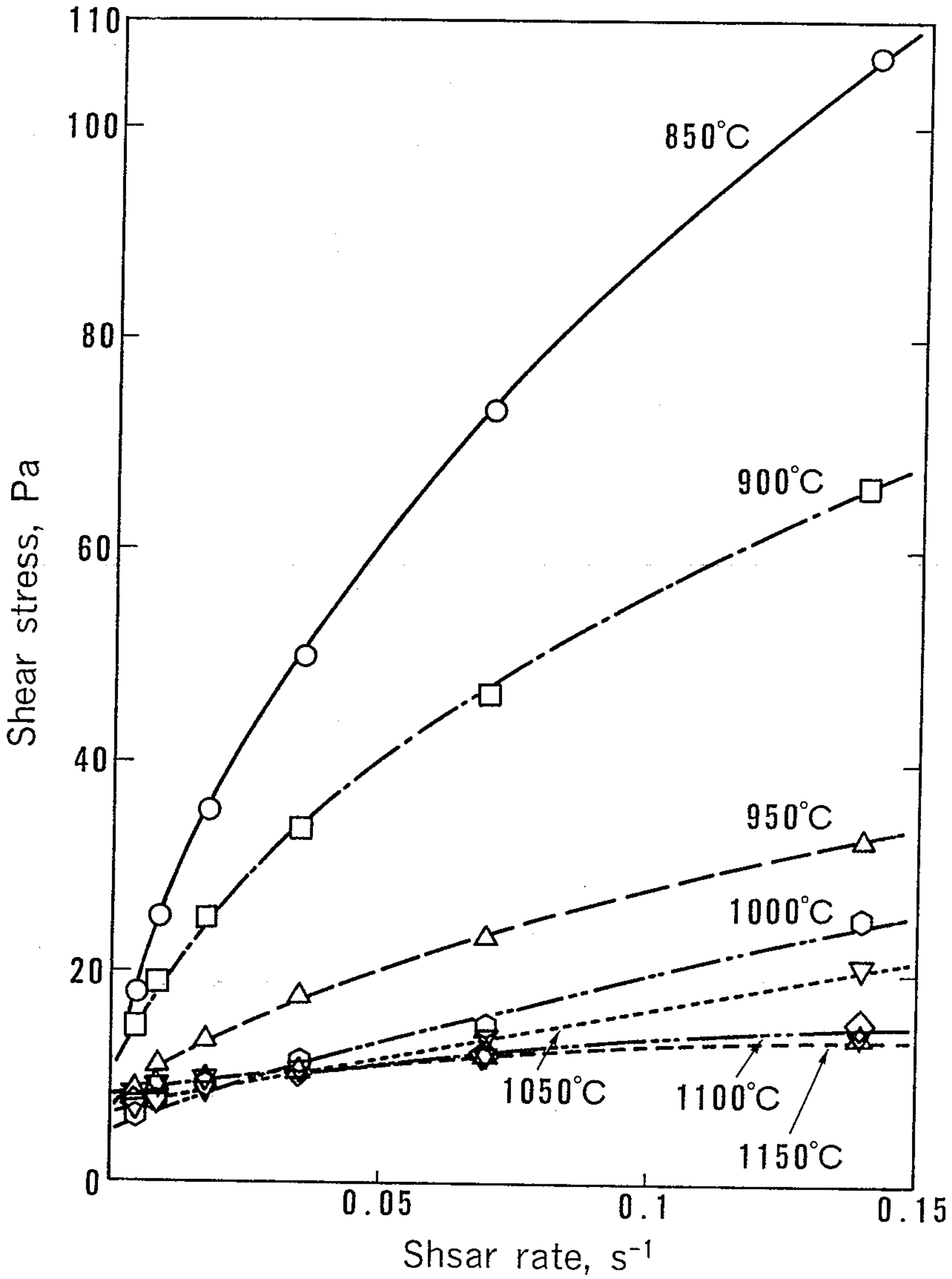


Fig.4 Shear stress vs. shear rate for 10 Ru-glass(wt %: 10.0 RuO_2 , 0.34 PdO)

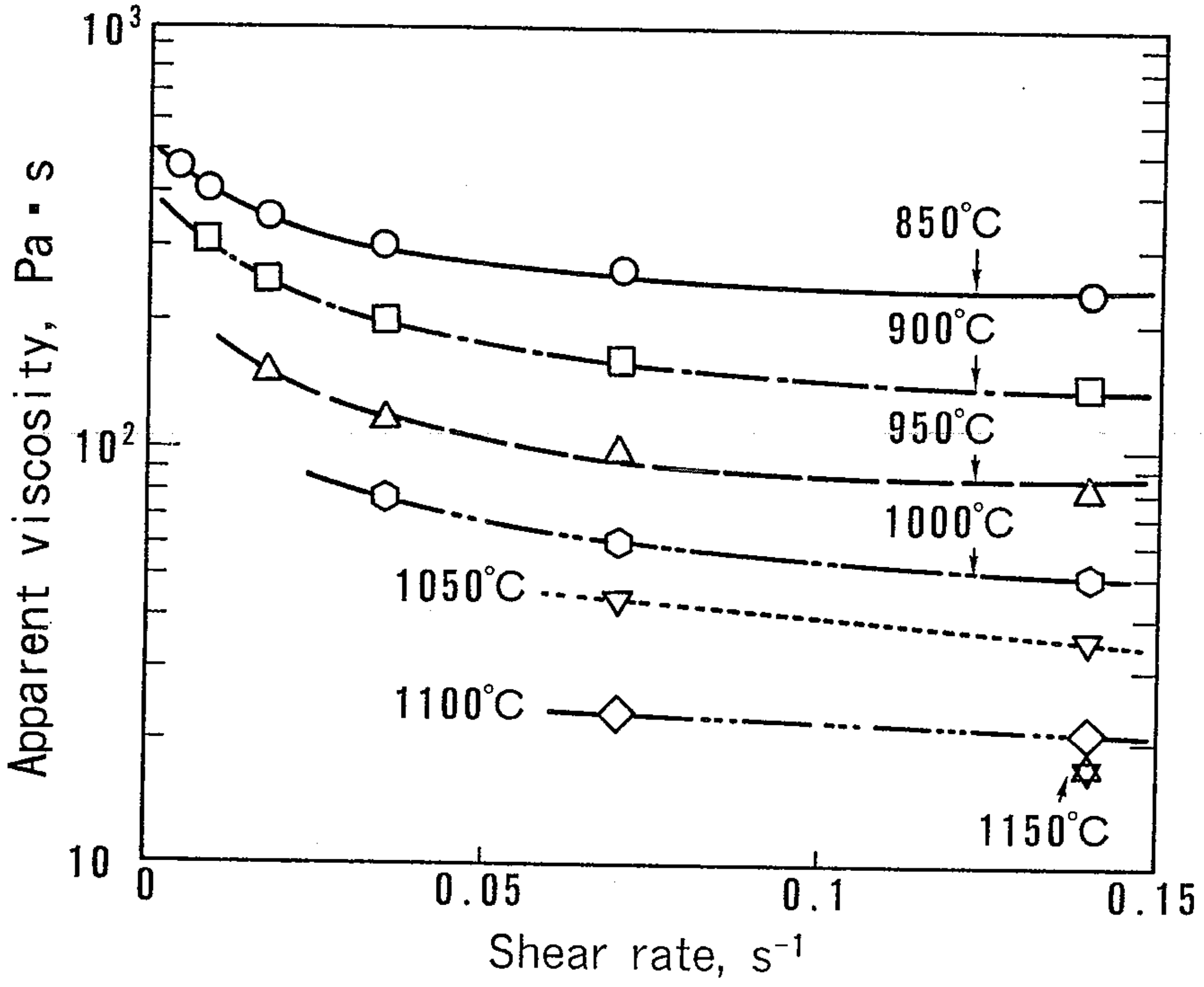


Fig. 5 Apparent viscosity vs. shear rate for 1 Ru-glass (wt%:1.0 RuO_2, 0.37 Pdo)

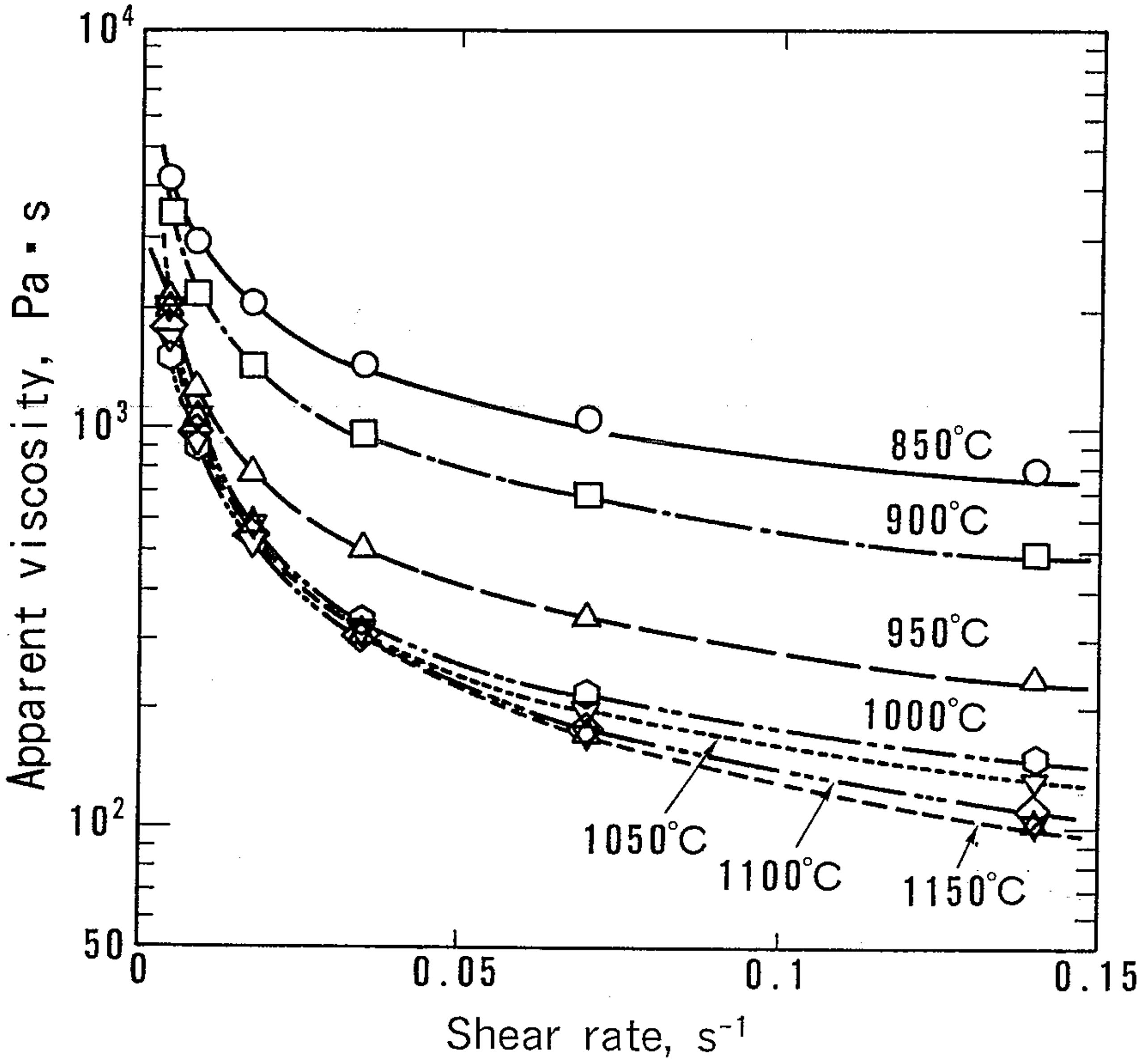


Fig. 6 Apparent viscosity vs. shear rate for 10 Ru-glass (wt%:10.0 RuO_2, 0.34 Pdo)

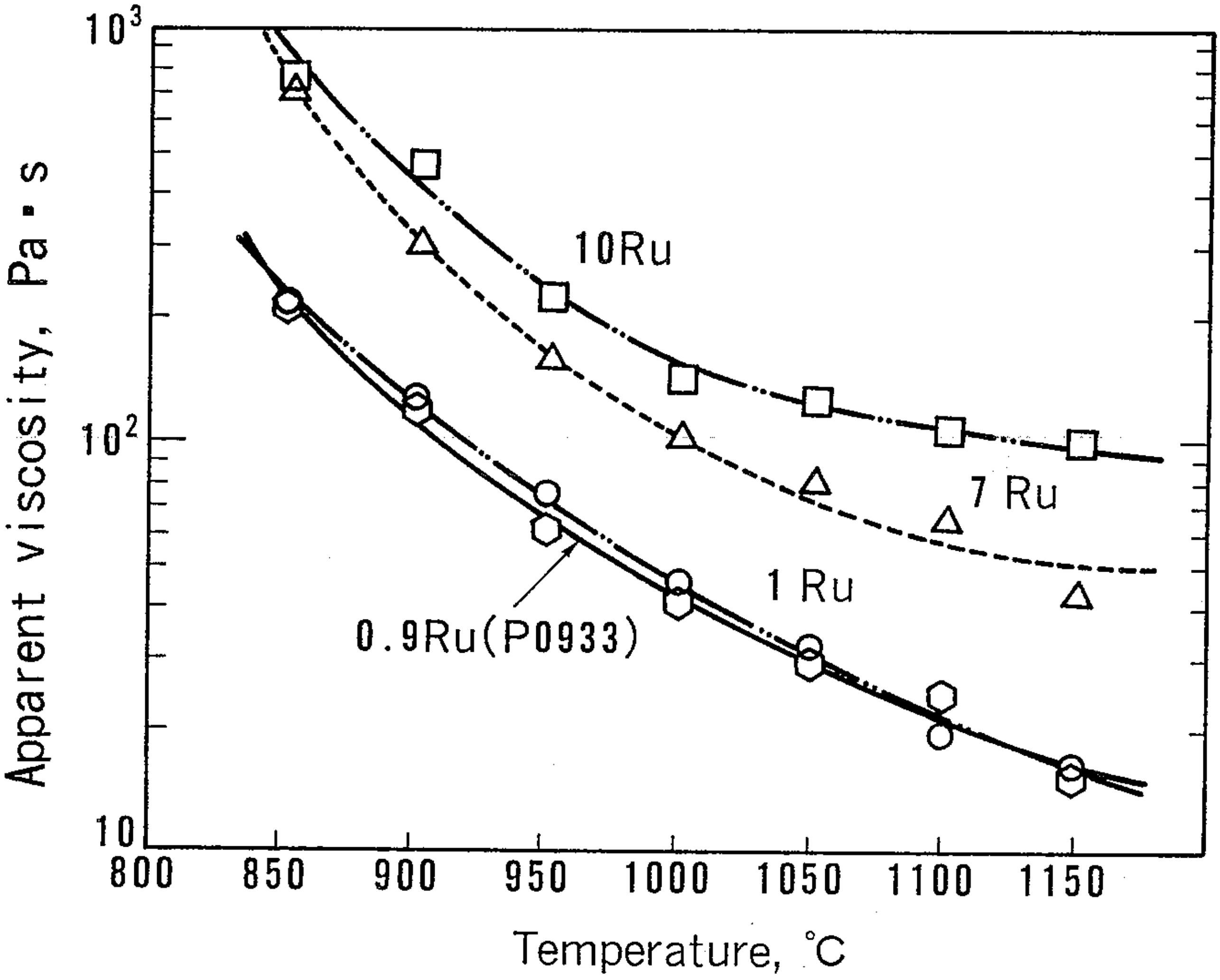
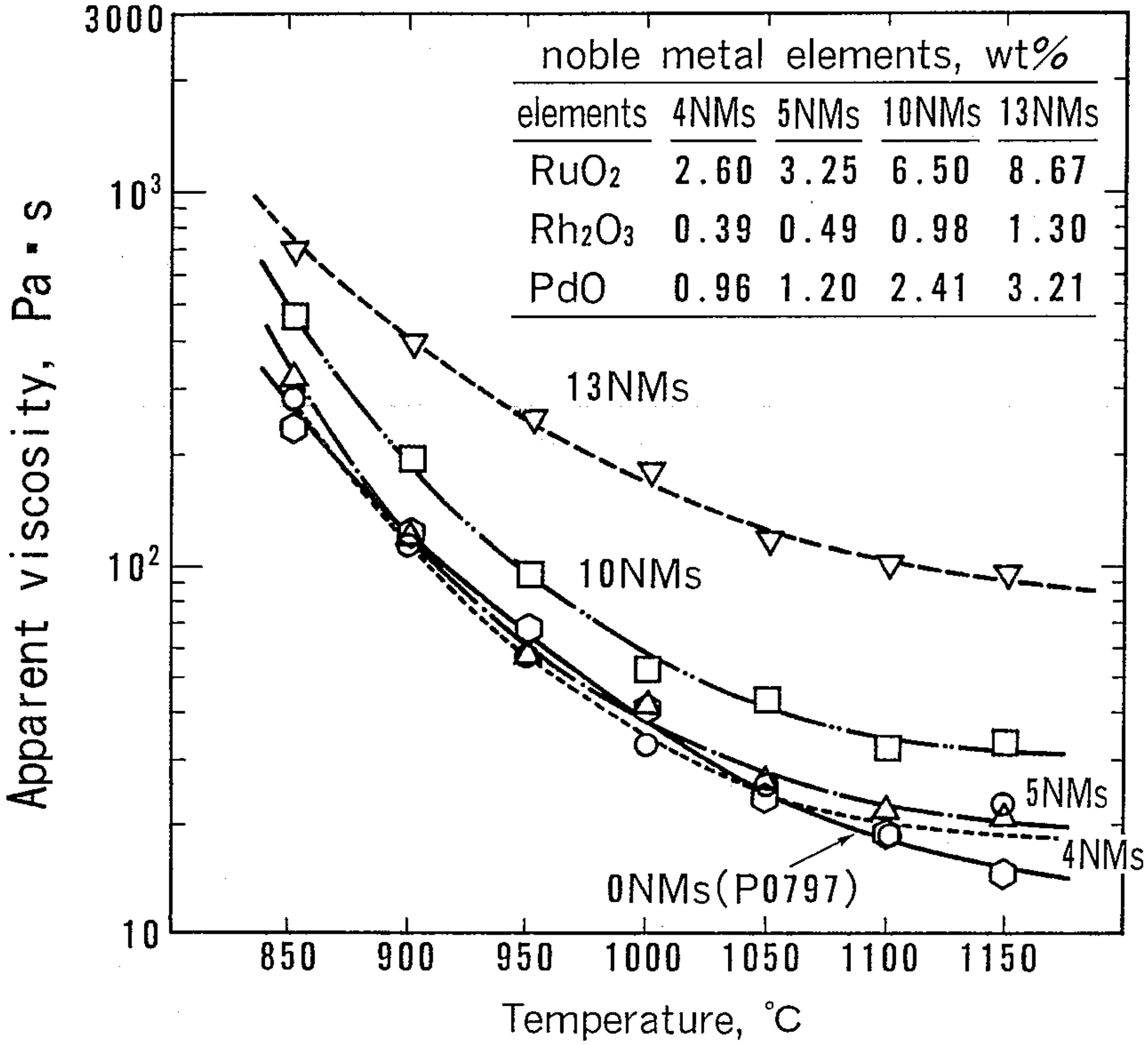


Fig. 7 Apparent viscosity vs. temperature for Ru-glass (shear rate:0.140 s^{-1})



noble metal elements, wt%

elements	4NMs	5NMs	10NMs	13NMs
RuO_2	2.60	3.25	6.50	8.67
Rh_2O_3	0.39	0.49	0.98	1.30
PdO	0.96	1.20	2.41	3.21

Fig. 8 Apparent viscosity vs. temperature for NMs-glass (shear rate:0.140 s^{-1})

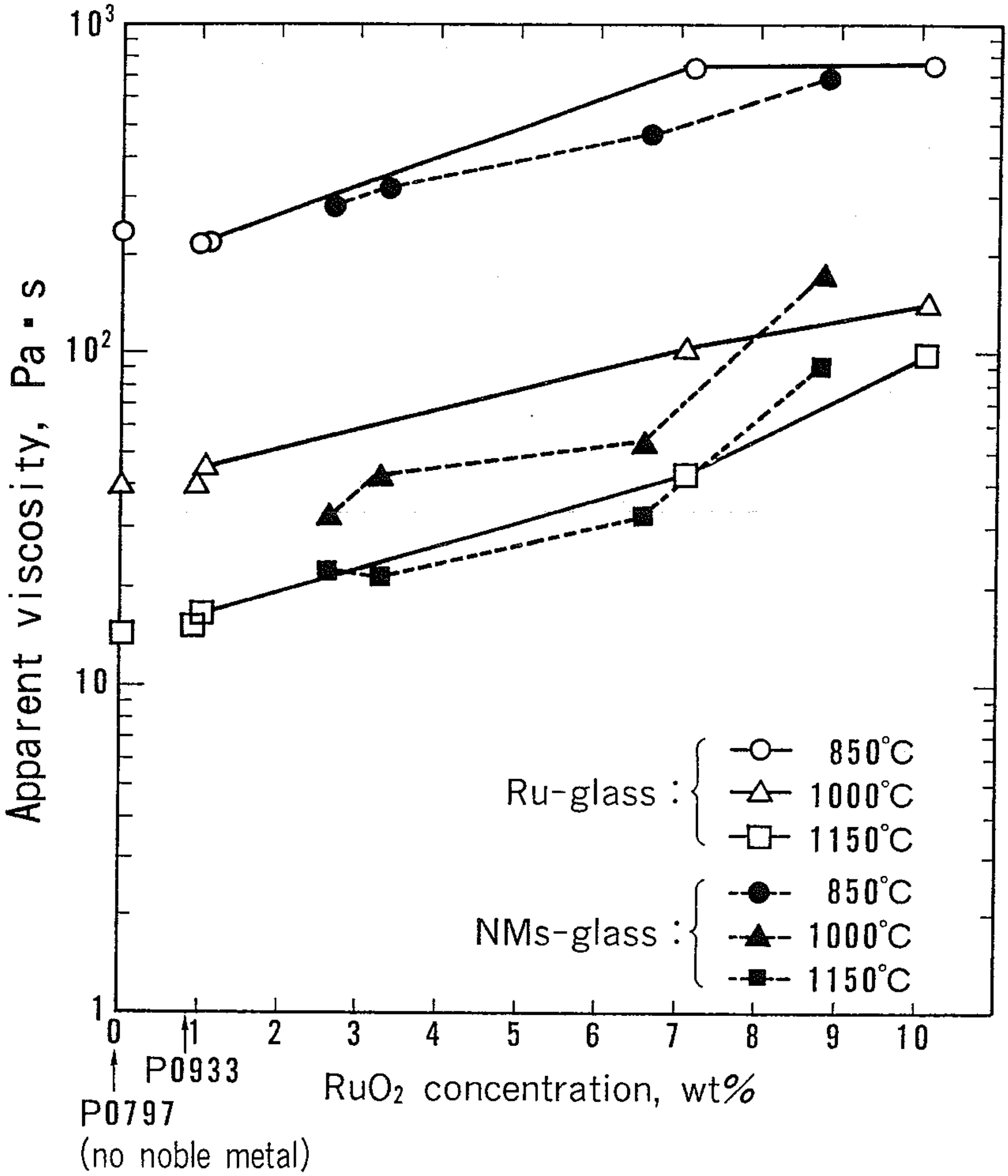


Fig. 9 Apparent viscosity vs. RuO_2 concentration for Ru-glass and NMs-glass (shear rate:0.140 s^{-1})

viscosity for two series of glass : Ru-glass and NMs-glass. The tendency of viscosity as a function of RuO_2 concentration for the NMs-glasses was similar to that for Ru-glass although the total contents of three elements in NMs-glasses are 50 % higher than RuO_2 concentration in Ru-glass. This result indicates that ruthenium is mainly responsible for the increase in viscosity of the glass containing noble metals in higher concentration.

3.3 Electrical resistivity

Resistivities of Ru-glasses are shown in Fig.10. The reference glass with noble metals in standard concentrations was comparable in resistivity with no noble metal glass. In higher concentration of RuO_2, resistivity decreased with RuO_2 concentration; the resistivity of 15 Ru-glass was one seventh lower around 1200℃ and two orders of magnitude lower at 700 ℃ than that of the glass without noble metals. German glass with 14.8 RuO_2 and 4.5 Pd in wt% was also about two orders of magnitude lower in resistivity than the waste glass with standard concentrations of noble metals[8].

The data of the NMs-glasses are also shown in Fig.8 for comparison. The resistivities of the NMs-glasses MB and MU1 were lower than that of glass containing only RuO_2 in equivalent concentration. It is because rhodium and palladium contributes to the decrease in resistivity as well as ruthenium. The other possible reason is the growth of RuO_2 crystals and noble metal alloy particles in NMs-glasses since particle size in NMs-glass was much larger than those in Ru-glasses. Despite NMs-glass MU1 and MB were similar in total concentration of noble metals, the MU1 containing needle shaped RuO_2 crystals was lower in resistivity below 1100 ℃ than the MB containing rectangular shape of RuO_2 crystals. Therefore the shape of RuO_2 crystal could also affect the resistivity.

These results suggest that three noble metal elements contribute to the decrease in the resistivity of the glass, and their size and shape also affect the resistivity.

4. CONCLUSION

The results indicated the quantitative effects of noble metal

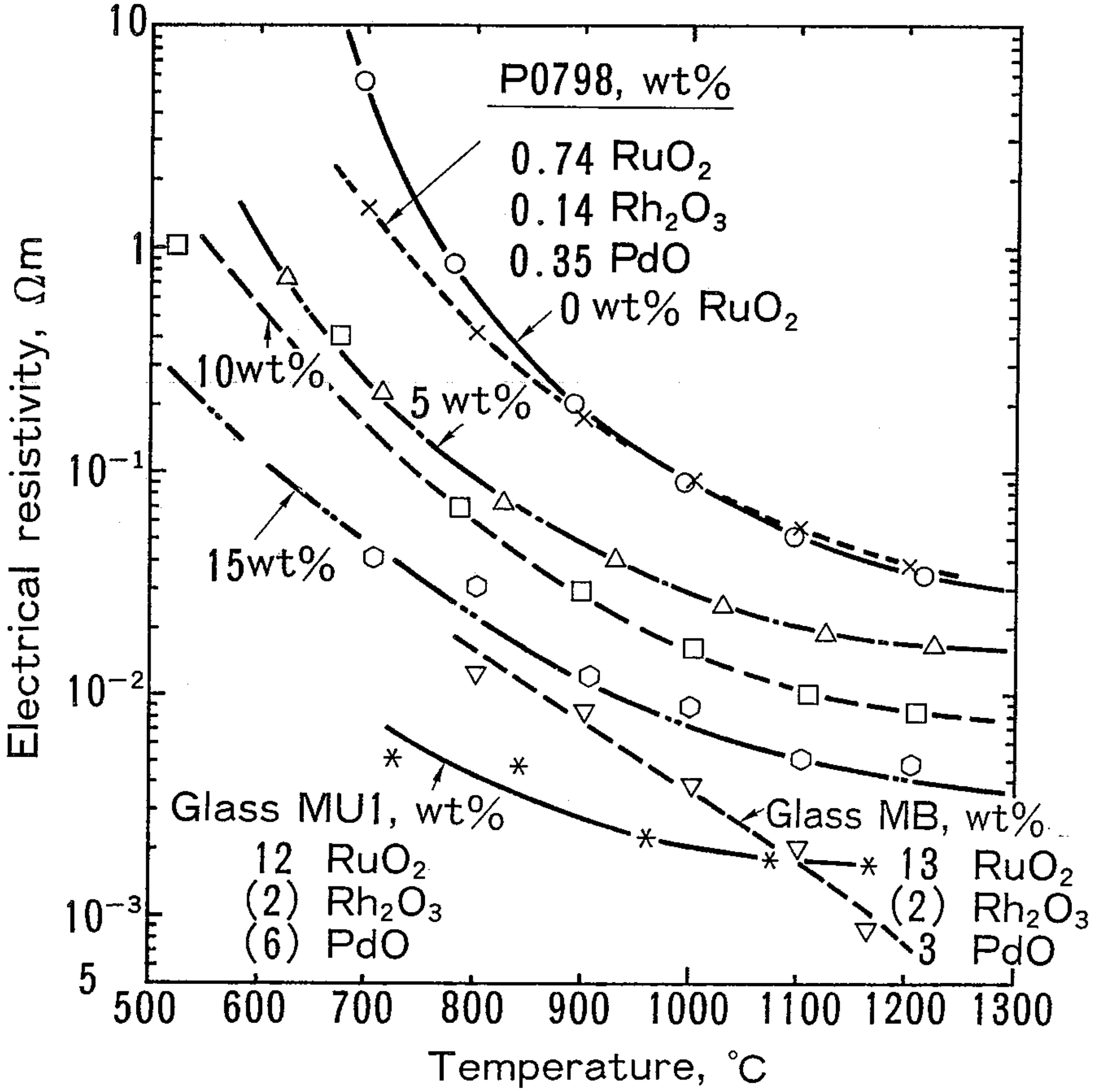


Fig.10 Electrical resistivity of Ru-glass and NMs-glass (concentrations in parentheses for NMs-glass MB and MU1were estimated values)

concentration on viscosity and resistivity which are important in electric glass melter operation.

The glasses enriched with noble metals indicated the pseudo-plastic flow of non-Newtonian fluid which had shear rate dependence of shear stress subject to power law and yield stress. The viscosities of the waste glasses with 10 wt% RuO_2 were 3 to 7 times higher than that of no noble metal glass. The resistivity of the glass with 15 wt% of RuO_2 was one seventh to two orders of magnitude lower than that of no noble metal glass. The RuO_2 was mainly responsible for the increase of viscosity of the glass enriched with noble metals. For the decrease in resistivity, ruthenium, rhodium and palladium were responsible; additionally their size and shape could affect the resistivity.

ACKNOWLEDGEMENT

The authors acknowledge the contribution of Messers. F.Ayuta and I.Nagai of HTS,PNC Tokai-works in viscosity measurement, and the contribution of Mr. H.Takeuchi of Nippon Electric Glass Co. Ltd. and of Mr. M.Honma of HTS in resistivity measurement. We also thank Mr.K.Hatakeyama of HTS for the electron-microprobe analysis of noble metal phase in the glass.

REFERENCES

[1] Malow,G., 'An investigation of crystallization in glasses containing fission products', Ceramics in Nuclear Waste Management, Proceedings of International Symposium held in Cincinnati, Ohio, April 30-May 2, 1979, pp.203-209.

[2] Sasaki,N., Karino,M., Okamoto,H., Kashihara,H. & Yamamoto,M., 'Solidification of the high-level liquid waste from the Tokai vitrification facility' Proc Fuel Reprocessing and Waste Management, Jackson, Aug 26-29, 1984. Vol.1. pp.147-60.

[3] Wiese,H. & Ewest,E., 'Industrial vitrification of high-level liquid wastes in the PAMELA Plant', Proc. Symp. Waste Management, Tucson, Feb 28-Mar 3, 1988, Vol.2. pp.173-179.

[4] Kelm,M., Oser,B., Luckscheiter,B., Bernotat,W. and Pentinghause,H., 'The vitrification of HLLW : Process and product quality studies by means of a lab scale liquid fed ceramic melter', Proc. Joint Int. Conf. Waste Management, Kyoto, Oct 22-28, 1989, Vol.2, pp.171-176.

[5] Sasaki,N., Torata,S., Igarashi,H., Kashihara,H. & Yamamoto,M., 'Advances in vitrification technologies in Japan, Proc. Int. Topical Meet. Waste Management and Decontamination and Decomissioning, Niagara Falls, Sept 14-18, 1986. Am. Nucl. Soc. pp.737-744.

[6] Yoshioka,M. and Takahashi,T., 'Evaluation of glass melter operation using highly simulated waste for TVF', Proceedings of the International topical Meeting on nuclear and hazardsus waste management, Spectrum '90, Knoxville, Tennessee, Sept 30-Oct 4, 1990, pp296-298.

[7] Igarashi,H. and Takahashi,T., 'The draining of noble metals in vitrified nuclear waste by a melter with a sloping floor', Glass Technology,Vol.32 No.2,April,1991,pp46-50

[8] Tobie and Weisenburger,S., 'Advanced Joule-heated nuclear waste glass melters', Proc. Waste Management '90, Tucson, Feb 26-March 1, 1990, Vol.2, pp771-778

[9] Scott,J.L. and Wolfe,B.A., 'Update on the Hanford waste vitrification plant technical developments', Proc. Symp. Waste Management '88, Tucson, Feb 28-March 3. 1988, Vol.2 pp211-214

[10] Plodinec,M.J., 'Rheology of Glasses Containing Crystalline Material', Nuclear Waste Management Ⅱ , Advances in Ceramics Vol.20,Edited by Clark,D.E., et al., The American Ceramic Society, Westerville, Ohio, 1986, pp.117-124.

Appendix A. Viscosity of NBS710 glass

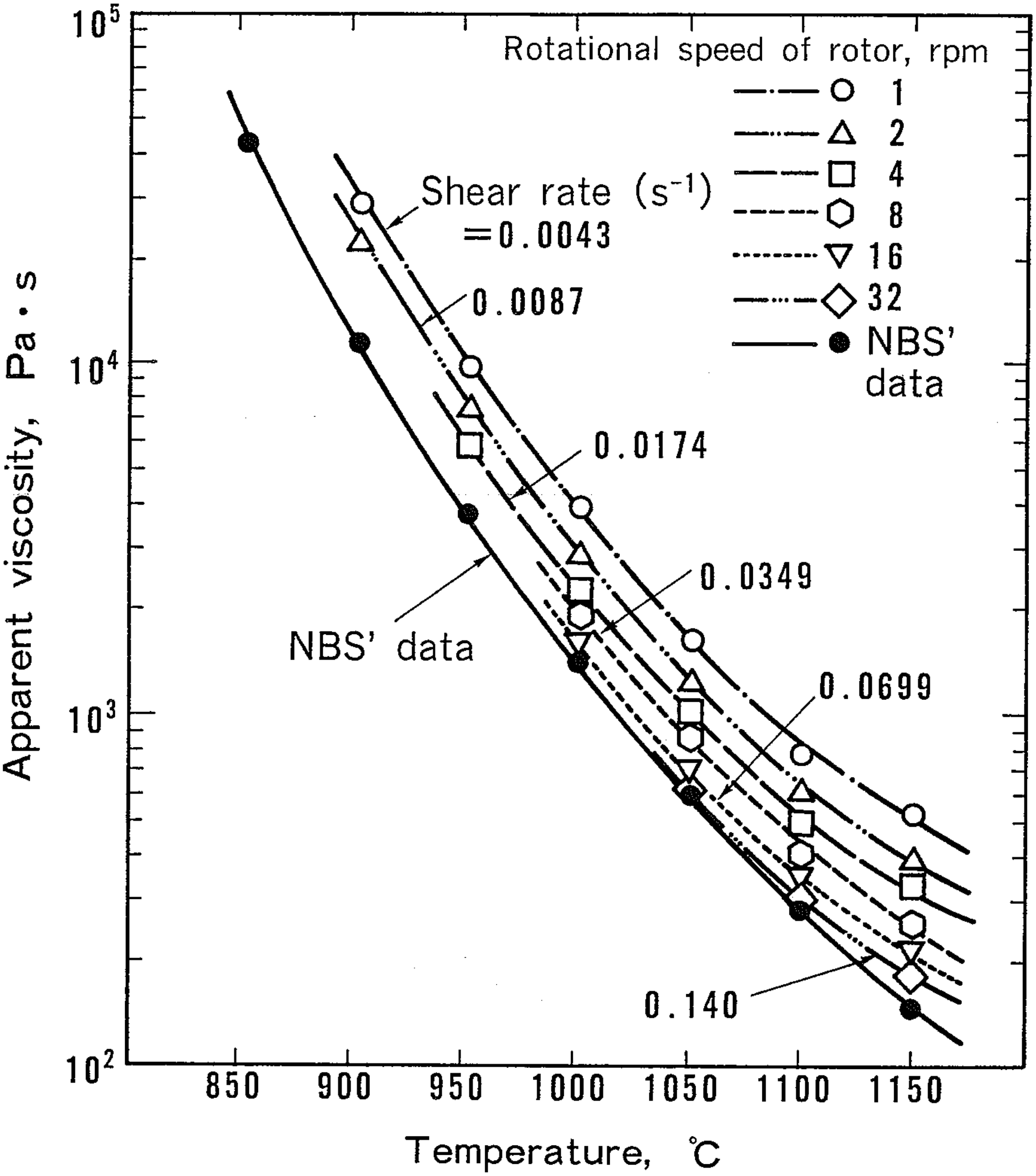
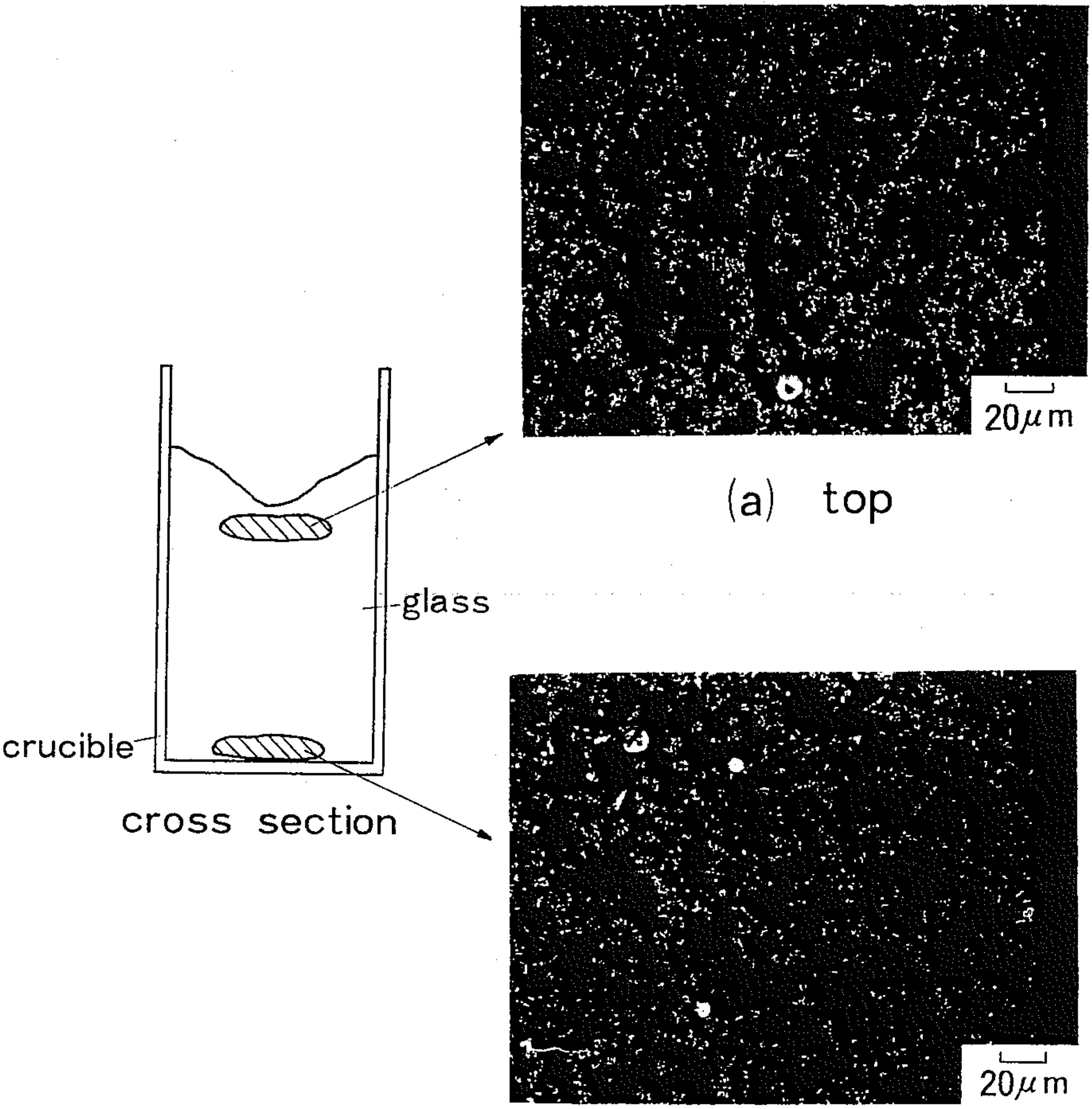


Fig. A1 Apparent viscosity of NBS 710 by rotational viscometer (calibrated at 1050℃ and 0.140S $^{-1}$: 32rpm)

Appendix B. Noble metal phase in glass

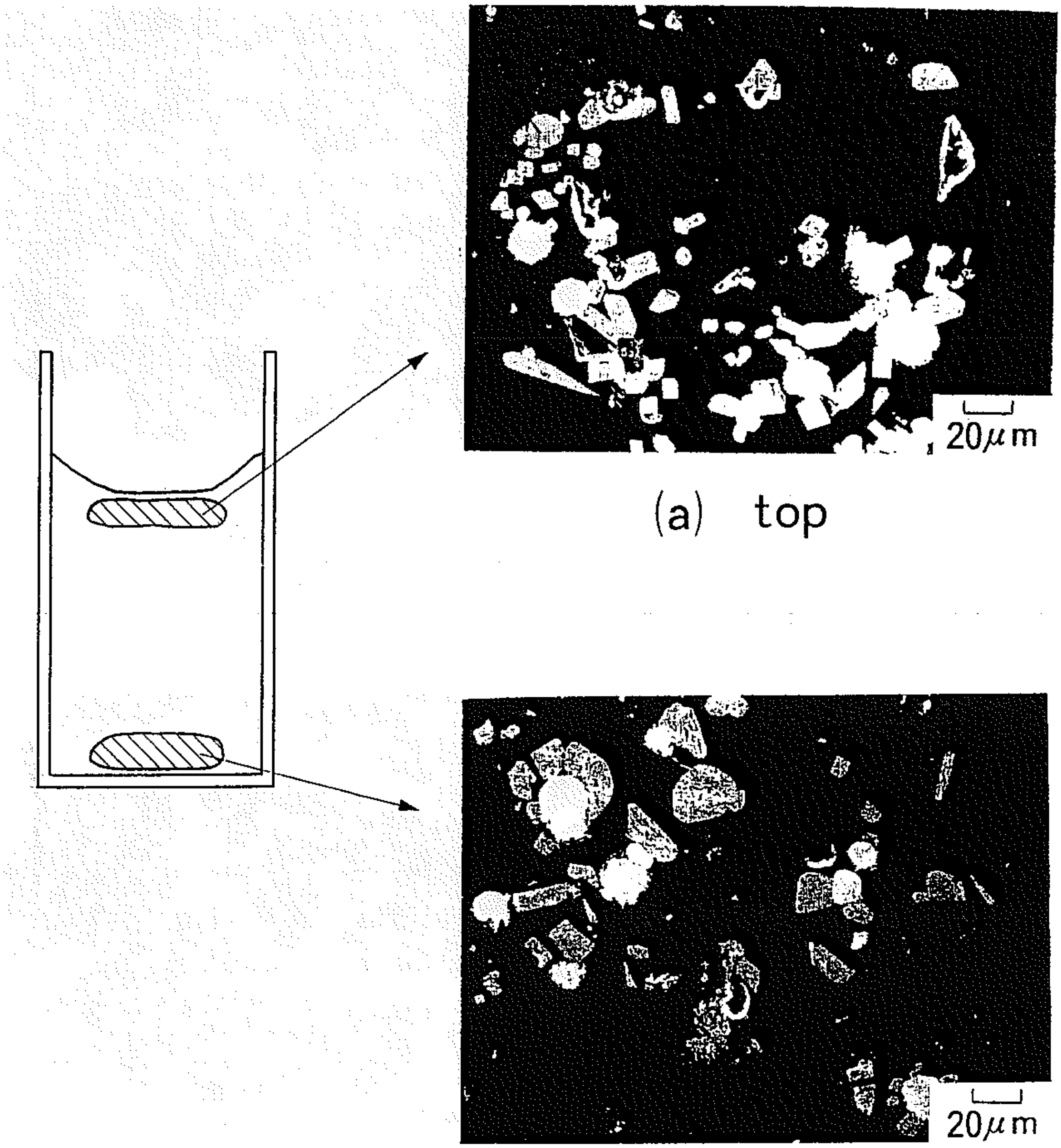
Noble metal phases in the glasses for the measurements of viscosity and resistiveity are shown here. Noble metal phase in the NMs glass for resistivity mesurement is similar to that in the NMs glass for viscosity mesurement because the noble metal rich glass is common for both.



(a) top

(b) bottom

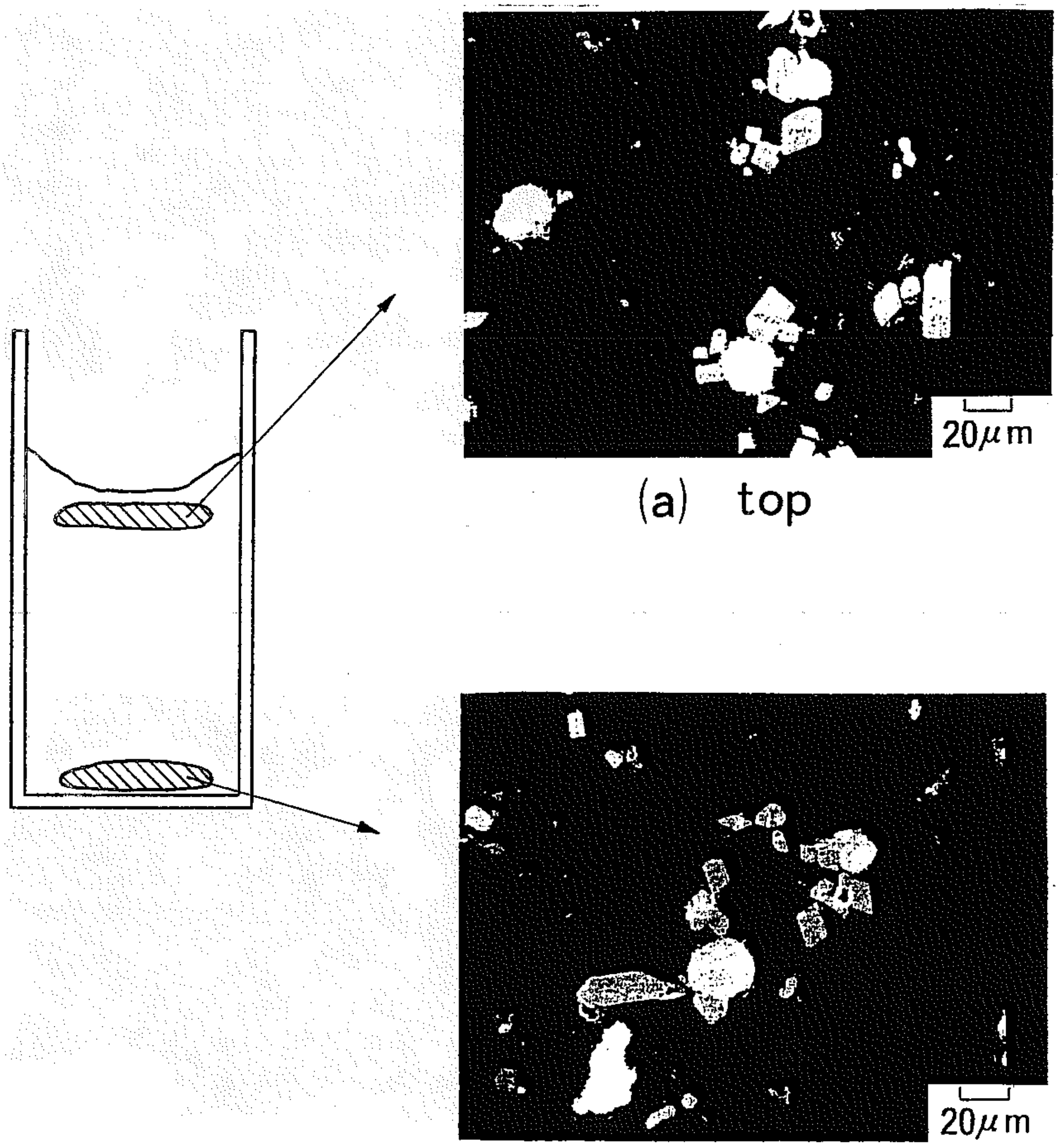
Fig.B1 Noble metal phase in 10Ru glass after viscosity measurement
(wt%:10 RuO_2, 0.34 PdO)



(a) top

(b) bottom

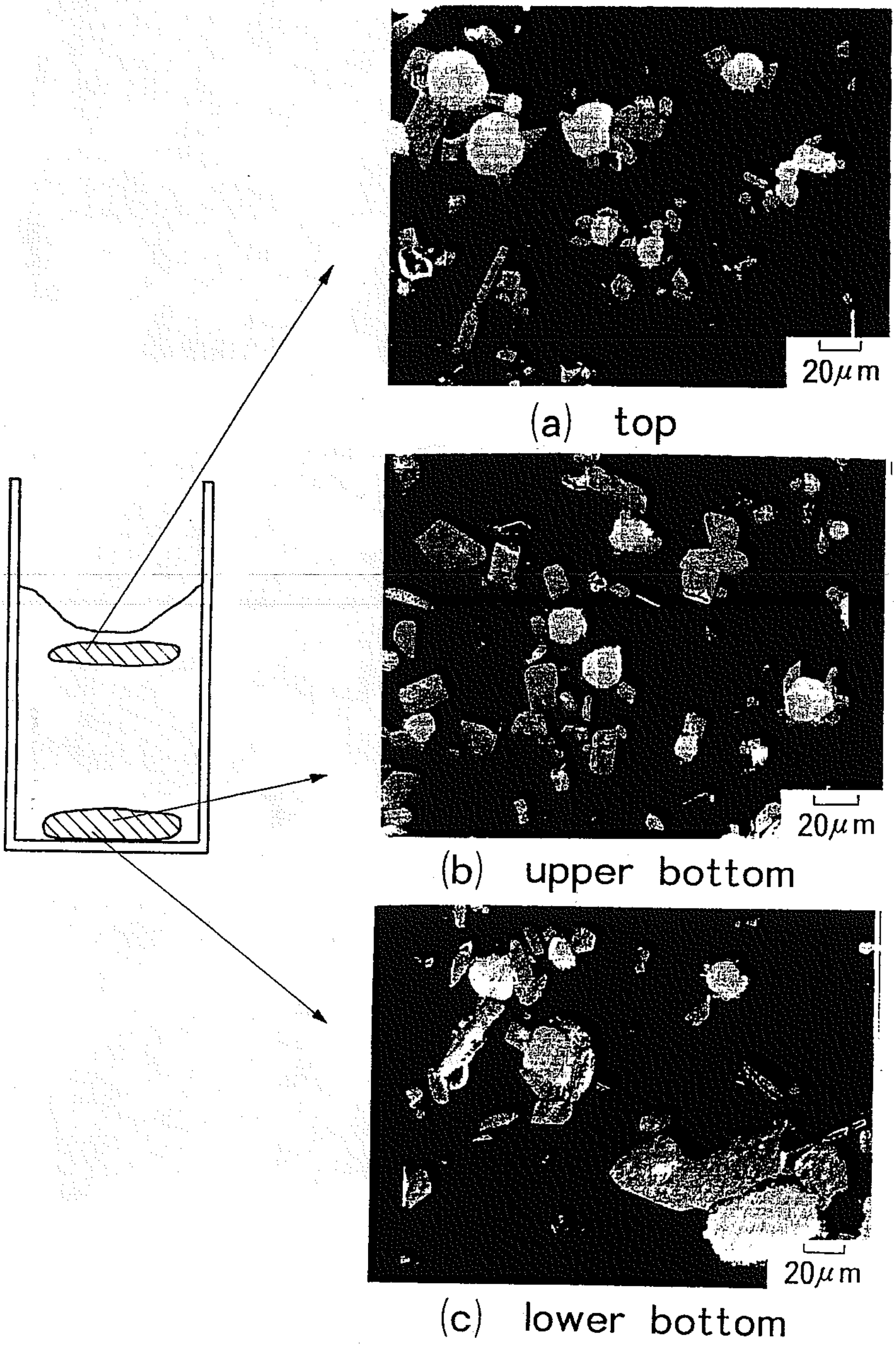
Fig. B2 Noble metal phase in 4 NMs glass after viscosity measurement
(wt%:2.60 RuO_2, 0.39 Rh_2O_3, 0.96 PdO)



(a) top

(b) bottom

Fig. B3 Noble metal phase in 5 NMs glass after viscosity measurement
(wt%:3.25 RuO_2, 0.49 Rh_2O_3, 1.20 PdO)

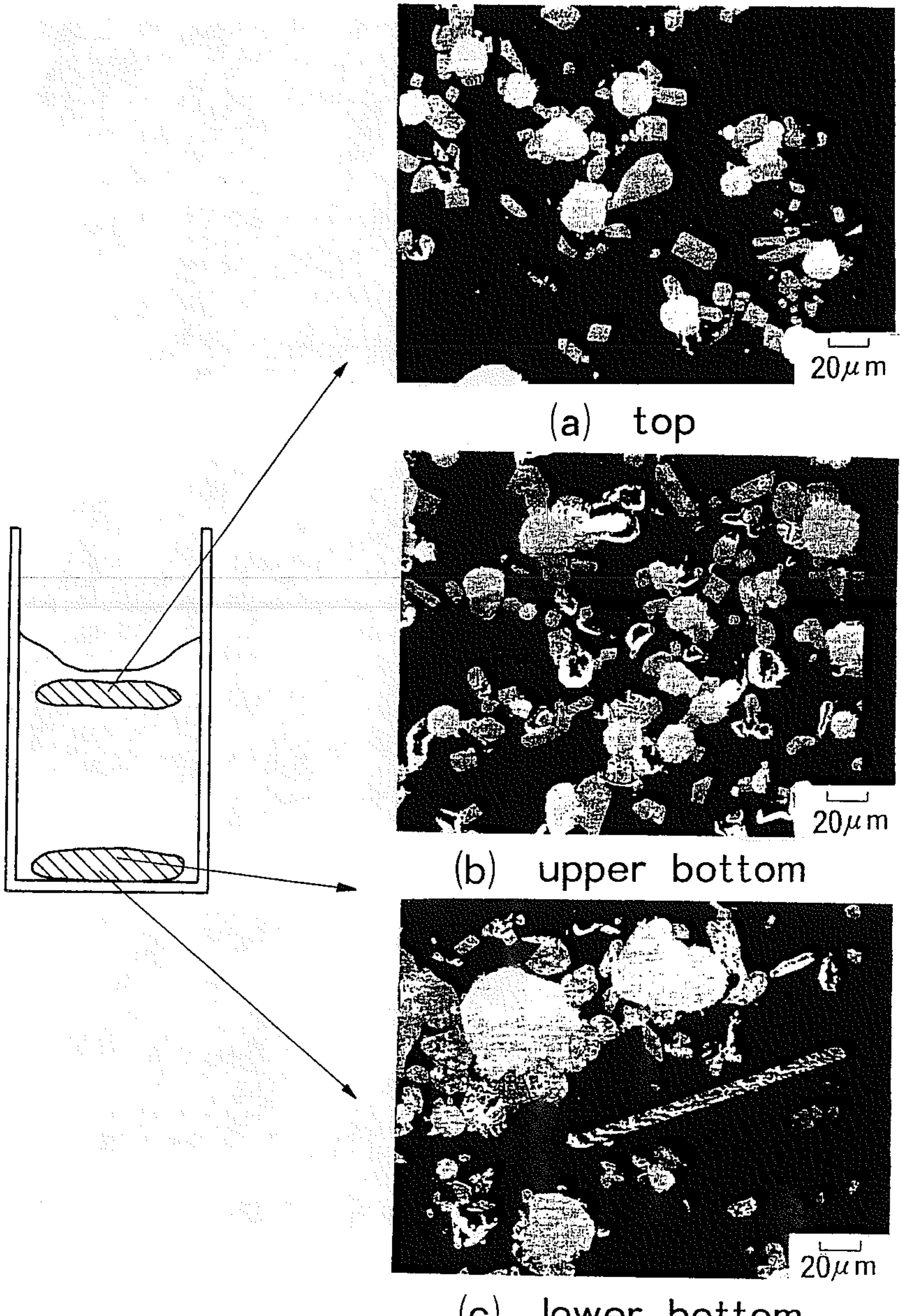


(a) top

(b) upper bottom

(c) lower bottom

Fig. B4 Noble metal phase in 10 NMs glass after viscosity measurement (wt%:6.50 RuO_2, 0.98 Rh_2O_3, 2.41 PdO)



(a) top

(b) upper bottom

(c) lower bottom

Fig. B5 Noble metal phase in 13 NMs glass after viscosity measurement
(wt%:8.67 RuO_2, 1.30 Rh_2O_3, 3.21 PdO)

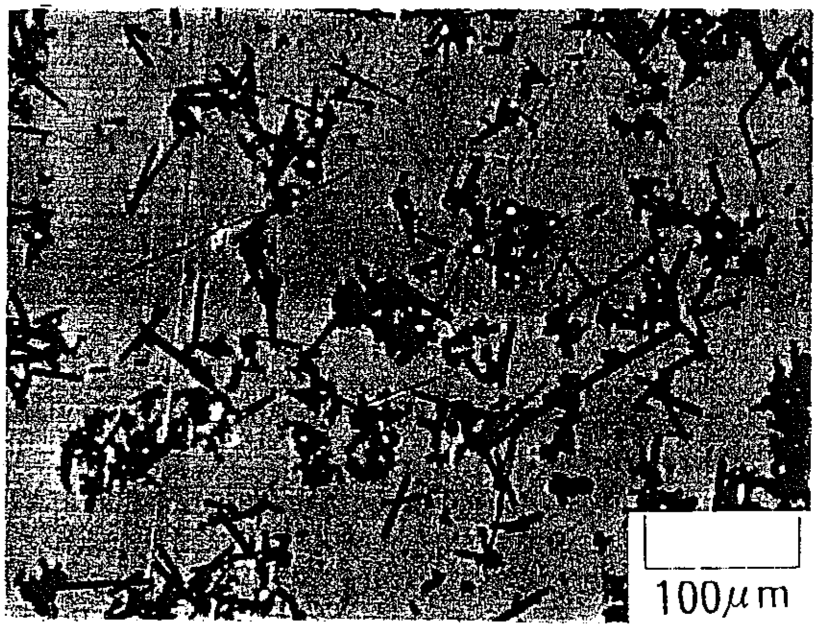


Fig. B6 Noble metal phase in MU1-glass glass used for resistivity measurement
(Optical micrograph : transmitted and reflected light)