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Investigation of metastable immiscibility in borate-waste-glasses

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The Technical University of Denmark, December 1981

SVENSK KÄRNBRÄNSLEFÖRSÖRJNING AB / AVDELNING KBS

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INVESTIGATION OF METASTABLE IMMISCIBILITY IN NUCLEAR-WASTE-GLASSES I-III

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A list of other reports published in this series during 1981, is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28) and 1980 (TR 80-26) is available through SKBF/KBS.

INVESTIGATION OF METASTABLE IMMISCIBILITY IN NUCLEAR-WASTE-GLASSES I-III

Abstract

Metastable liquid-liquid separation in glasses can often cause significant changes in physical and chemical properties of the original homogeneous glass. In some technical borosilicate glasses this phenomenon is used to change the chemical durability of the glass. For potential nuclear-waste-glasses the slow cooling through the temperature range 550°C - 700°C may lead to such a liquid-liquid phase separation. In order to investigate the susceptibility of phase separation of nuclear-waste-glasses, two KBS model glasses, ABS-39 and ABS-41, were investigated. Two of the subsequent reports are concerned with this problem. The third report also takes into consideration the effects of MoO_3 on the immiscibility gap. The maximum amount of MoO_3 that can be dissolved in ABS-39 and ABS 41 is also determined.

The Institute of Ceramics
The Technical University of Denmark

February 1981

REPORT

INVESTIGATION OF METASTABLE IMMISCIBILITY IN BORATE-WASTE-GLASSES.

by

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The present work was initiated by Mr. Lars Werme SKBFx) after preceeding discussions with Professor L.L. Hench and Mr. G. Roed on the stability prospects for potential waste-glasses. SKBF has financed the work carried out during january and february 1981.

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x) Svenska Kärnbränsleförsörjning.

INTRODUCTION

Metastable liquid-liquid separation in glasses is often attended by a significicant change in physical and chemical properties of the original homogeneous glass. In some technical borateglasses this phenomenon is specifically utilized to change the chemical durability of the glass, in order to be able to extract selectively the alkali- and borate-rich phase after a separation heat treatment (Ref. 1). Fig. 1 shows the immiscibility area in the ternary Na_2O-$SiO_2B_2O_3$-system, and it is seen that heattreatments in the temperature range 55o°C to 7oo°C, difficult to avoid in real waste-glasses, may lead to liquid-liquid separation depending on glass composition.

In the present work two borate-waste-glasses, ABS-39 and ABS-41, were investigated. Their compositions are listed in Table I. The composition of these glasses projected from the multicomponent composition space, into the ternary ground plane Na_2O-B_2O_3-SiO_2 is marked in Fig. 1 as "ABS-39" and "ABS-41" respectively, and it will be noticed that the projected compositions are located close to or within the immiscibility area. However, the influence of fission products and additional compounds in the glass, on the immiscibility - space is unknown and it has therefore been the aim of this work to provide experimental data to localize the immiscibility boundary in the complex waste-glass-system.

EXPERIMENTAL TECHNIQUE

The technique used to determine the immiscibility boundary has been evaluated in a previous investigation of liquid-liquid separation in binary alkali-silica glasses, (Ref. 3). The method is based on the observation, that phase-separated glass shows a strongly increased reactivity towards HF-vapour compared to a homogeneous single phase glass of same chemical composition. This difference in behaviour enables a unambigious identification by optical microscopy in reflected light of phase separated regions in a heat treated sample having a smooth composition profile varying across an immiscibility boundary.

The composition profile in the sample is established by interdiffusion of two glass melts with compositions on either side of the expected immiscibility boundary. In the present work the two waste-glasses ABS-39 and ABS-41 are considered to be located on the unseparated side of the boundary, and two different diffusion paths have been investigated. In test series I and II a composition profile from the original glasses ABS-39 and ABS-41 in the direction of SiO_2-rich compositions is established in diffusion couples of solid SiO_2/ABS-39 and solid SiO_2/ABS-41.

In test series III, a diffusion path of constant SiO_2/B_2O_3-ratio from ABS-41 composition was intended, using a binary SiO_2-B_2O_3-glass (7o% SiO_2, 3o% B_2O_3) as the diffusion partner.

For test series I and II the diffusion process was carried out by melting coarsely ground bulk-glasses in SiO_2-test tubes, 2 cm long o.5 cm ID and o.1 cm wall thickness and closed in one end. Because thermogravimetric measurements on bulk-glasses had indicated a significant weight-loss from open tubes heated above 135o°C (∿o.2 mg per min.), the SiO_2-tubes were closed in both ends for samples heat treated above this temperature.

Samples in test series III were prepared by melting together the two end-member glasses in the diffusion couple, in small platinum boats of 5 mm length and approximately 2 x 2 mm in cross-section. In all cases the samples were transfered to a preheated metal block with holes fitting the samples, directly after the diffusion heat treatment and kept there at constant temperature in the range of 55o - 65o°C for varying periods of time (Table II). After a specified period the samples were quenched in water, mounted in resin, cut to expose a cross section and finally ground and polished.

Before examination in the optical reflected microscope the polished samples were etched by holding the polished surface a few inches above the surface of 4o% HF-acid for 5 - lo sec. Phase-separated regions in the samples are now easily recognized as an bluish colored zone with a sharp boundary to the non separated glass. A typical sample showing phase separation in the SiO_2-rich part of the composition profile is shown in Fig. 2.

Microprobe

Selected samples showing phase separation regions on the diffusion path were examined in an ARL electron microprobe type EMX-21ooo for determination of the chemical composition on the immiscibility boundary. Prior to the microprobe examination the boundary in the etched sample was carefully marked with indentor-marks and the HF-etch layer then removed and replaced by a thin carbon coating.

In order to eliminate the alkalimigration during measurements the applied voltage was reduced to lo KV and the current 15 mA. For the same reason the samples had to be moved relatively to the beam during the measurements at a speed of loo µm/min. Accumulated counts were automatically readout every lo sec and the total counting-time was more than loo sec. in all measurements. The bulkglass ABS-41 with known composition was used as a standard for the calculation of the oxide contents.

The 95%-confidence limit was calculated individually for all measuring positions and in all cases the calculated error was found to be the statistical counting-error.

RESULTS AND DISCUSSION

Microscopic examination

The qualitative microscopic results from the three test series are listed in Table II.

It is seen that regions, phase separated in nature, were observed in test series II and III, but not in samples of test series I. Typical polished samples from test series II and III are shown in Fig. 2 and Fig. 3.

At the extreme left in Fig. 2, a part of the amorphous SiO_2-tube can be seen. The layer "A" is the inner part of the tube, which has crystallized at the high temperature during the diffusion heat treatment. Zone B consists of the phase separated part of the composition profile, while C represents non separated glass compositions of the diffusion profile. Between zone A and B a thin layer of secundary precipitated SiO_2-crystals is formed in samples with extremely long annealing times. Before etching, both of the zones B and C appears as clear transparent glass without any structure. Samples which is quenched directly after the diffusion heat treatment do not develop zone B by etching in HF-vapour. On the contrary, these samples show a decreased reactivity towards the HF-etchant in the SiO_2-rich part of the composition profile.

The needle like surface-pattern in the B and C region is caused by surface crystallization of the etch-layer and does neither reflect inhomogenities nor any structure in the glass beneath. This phenomenon is characteristic for etch-layers in borate-glasses, possibly because of a more pronounced hygroscopicity of these layers.

The unsuccessful attempts in detecting phase-separated compositions in any sample of test series I may be caused by kinetic difficulties. This point of view is supported by the fact that no socundary precipitation of SiO_2-crystals at the SiO_2-glass boundary is observed in any of the annealed samples in this series.

Microprobe examination

In two samples the content of the oxides SiO_2, Na_2O, B_2O_3, Fe_2O_3 and MoO_3 was measured at different positions in the samples. The locations analysed are indicated by black traces in the photomicrographs in Fig. 2 and Fig. 3.

The calculated contents are listed in Table III and shown graphically in Fig. 4. From the analytical results it is seen that the main components SiO_2, Na_2O and B_2O_3 amounts for approximately 80% of the total composition in the three immiscibility-boundary compositions estimated. As this is also the case for the two bulk-glasses ABS-39 and ABS-41, the 80% SiO_2-Na_2O-B_2O_3-plane in the multicomponent system is therefore used to illustrate the location of the estimated immiscibility boundary relative to the two bulk-glasses in Fig. 5.

The immiscibility boundary determined in the present work is here indicated by the solid line and the measured diffusion path is represented by the dotted line from the ABS-41 composition point crossing the boundary.

CONCLUSION

In the present work it has been demonstrated that the gradient technique previously applied in binary alkali-silica-glasses also is a valuable technique in detecting metastable immiscibility areas in much more complex borate-glasses, even that the etch layers in these particular glasses are more susceptible to surface crystallization. The 6oo°C immiscibility boundary detected here is in extremely good agrement with existing immiscibility data in the simple Na_2O-B_2O_3-SiO_2-system.

REFERENCES

1) I.I. Hammel et al.: U.S. Patent 3.43.341 (Act. 1974).

2) E.M. Levin, C.R. Robbins and H.F. McMurdie: Phase Diagram for Ceramists, Fig. 4526. Edited by M.K. Reser. The American Ceramic Society, Inc., Columbus, Ohio, 1975.

3) G. Roed: "New Method for Detecting Phase Separation in Alkali-Silicates". Amer. Ceram. Soc. Bull. 55 (8), pp 722-725 (1976).

TABLE I. CHEMICAL COMPOSITION OF BULK-GLASSES (wt%).

Bulk-glass	SiO_2	Al_2O_3	Na_2O	B_2O_3	ZnO	Fe_2O_3	Li_2O	UO_2	F.P.[x)]
ABS-39	48.5	3.1	12.9	19.1	-	5.7	-	1.66	9.o
ABS-41	52.o	2.5	9.4	15.9	3.o	3.o	3.o	1.66	9.o

x) F.P. = Mixture of simulated fissions products.

TABLE II. TEST SERIES I, II and III.

Bulk-glass	Diffusion treatment		Annealing		B-zone
	T_D (^oC)	time (h)	T_A (^oC)	time (h)	width (µm)
Test series I					
ABS-39	1500	1/6	575	1/3	nil
ABS-39	1500	1/2	640	1/3	nil
ABS-39	1500	1/6	600	18	nil
ABS-39	1270	1 1/2	600	23	nil
ABS-39	1270	12	600	72	nil
ABS-39	1270	12	650	24	nil
ABS-39	1270	1 1/2	550	68	nil
ABS-39	1500	1/3	quenched		nil
Test series II					
ABS-41	1330	1/4	575	1/3	nil
ABS-41	1270	1 1/2	550	68	nil
ABS-41	1270	1 1/2	600	23	80
ABS-41	1500	1/6	600	18	100-150
ABS-41	1300	2	600	18	140
ABS-41	1300	1	600	3	120
ABS-41	1270	1	quenched		nil
Test series III					
ABS-41/SB-glass$^{x)}$	1250	1/2	600	72	zones

x) SB-glass = 70 wt% SiO_2, 30 wt% B_2O_3.

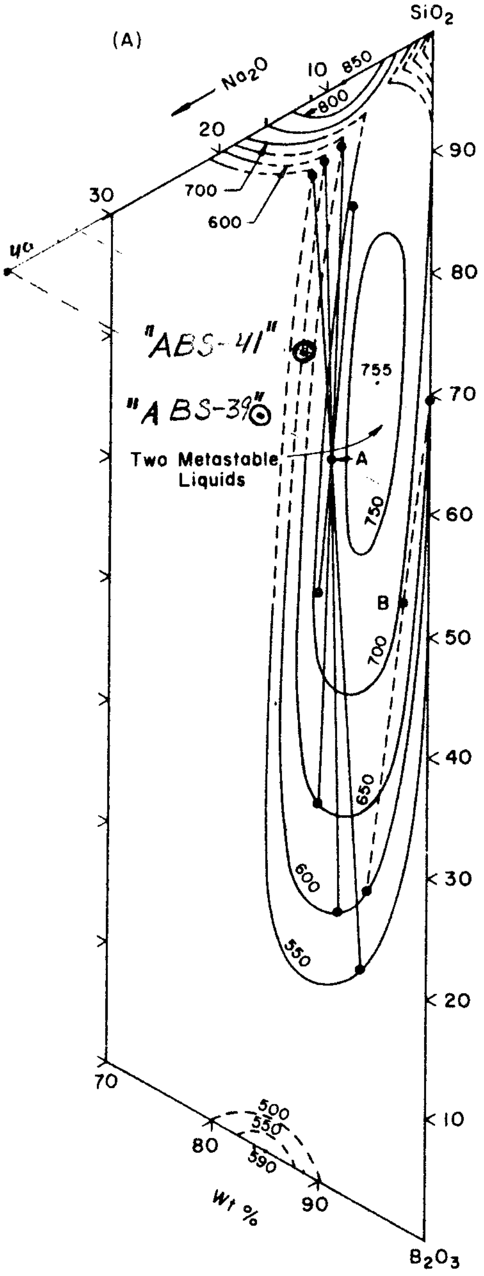
TABLE III. CHEMICAL COMPOSITION IN DIFFUSION PROFILE.

Distance from SiO_2-tube (µm)	C_{SiO_2} $\pm 0.7^{x)}$ (wt%)	C_{Na_2O} $\pm 0.1^{x)}$ (wt%)	$C_{B_2O_3}$ $\pm 2.0^{x)}$ (wt%)	$C_{Fe_2O_3}$ $\pm 0.1^{x)}$ (wt%)	C_{MoO_3} $\pm 0.1^{x)}$ (wt%)
1500°-sample (test series II)					
65	64.2	7.2	8.9	2.3	1.0
130$^{xx)}$	63.1	7.6	10.7	2.3	1.1
260	57.7	8.0	13.6	2.6	1.3
390	54.7	8.3	14.8	2.8	1.5
520	53.6	8.4	14.2	2.9	1.6
Standard (Bulk-glass ABS-41	52.0	9.4	15.9	3.0	1.63
Sample in test series III					
position 1$^{xx)}$	55.4	7.5	19.0	2.8	1.5
position 2	54.0	7.8	19.3	2.9	1.5
position 3$^{xx)}$	54.8	7.9	16.8	2.9	1.5

x) 95%-confidence limit.

xx) immiscibility boundary composition.

FIGUR 1.



Part of Na_2O-B_2O_3-SiO_2-diagram showing subliquidus immiscibility area (Ref. 2).

FIGUR 2.

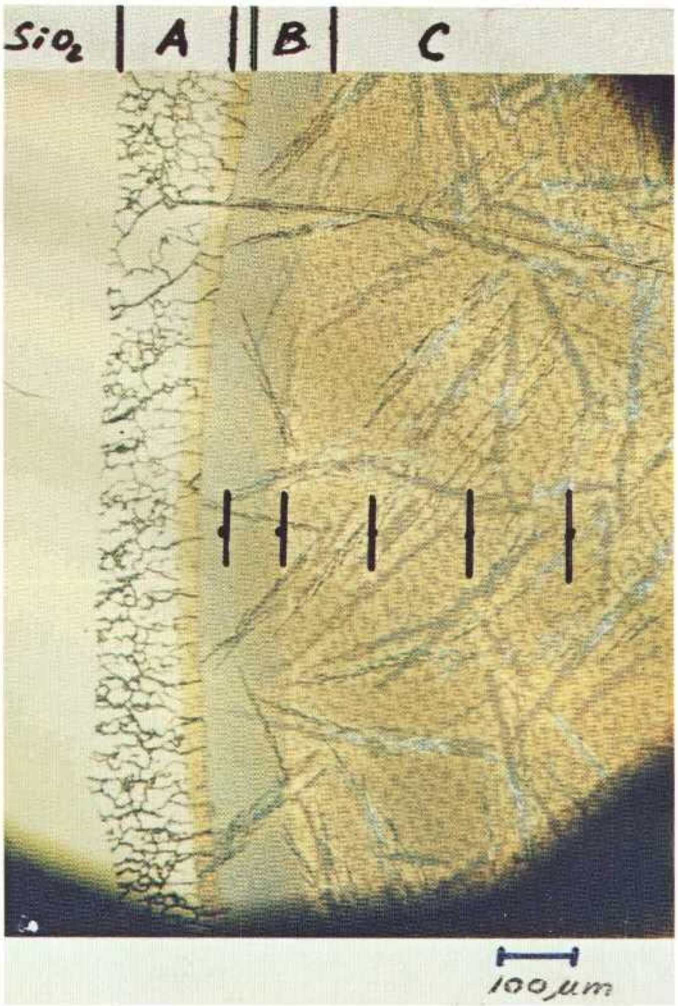


Photo micrograph of polished, HF-vapour etched sample from test series II, phase-separated in blue zone (zone B), (sample heattreated 1o min. at T_D = 15oo°C and 18 hours at T_A = 6oo°C).

FIGUR 3.

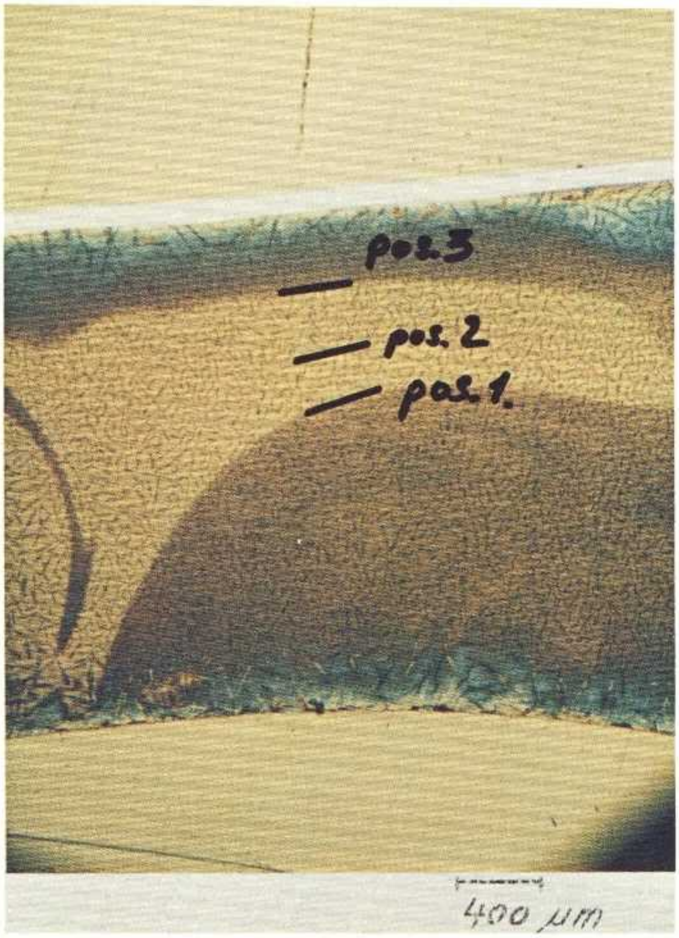
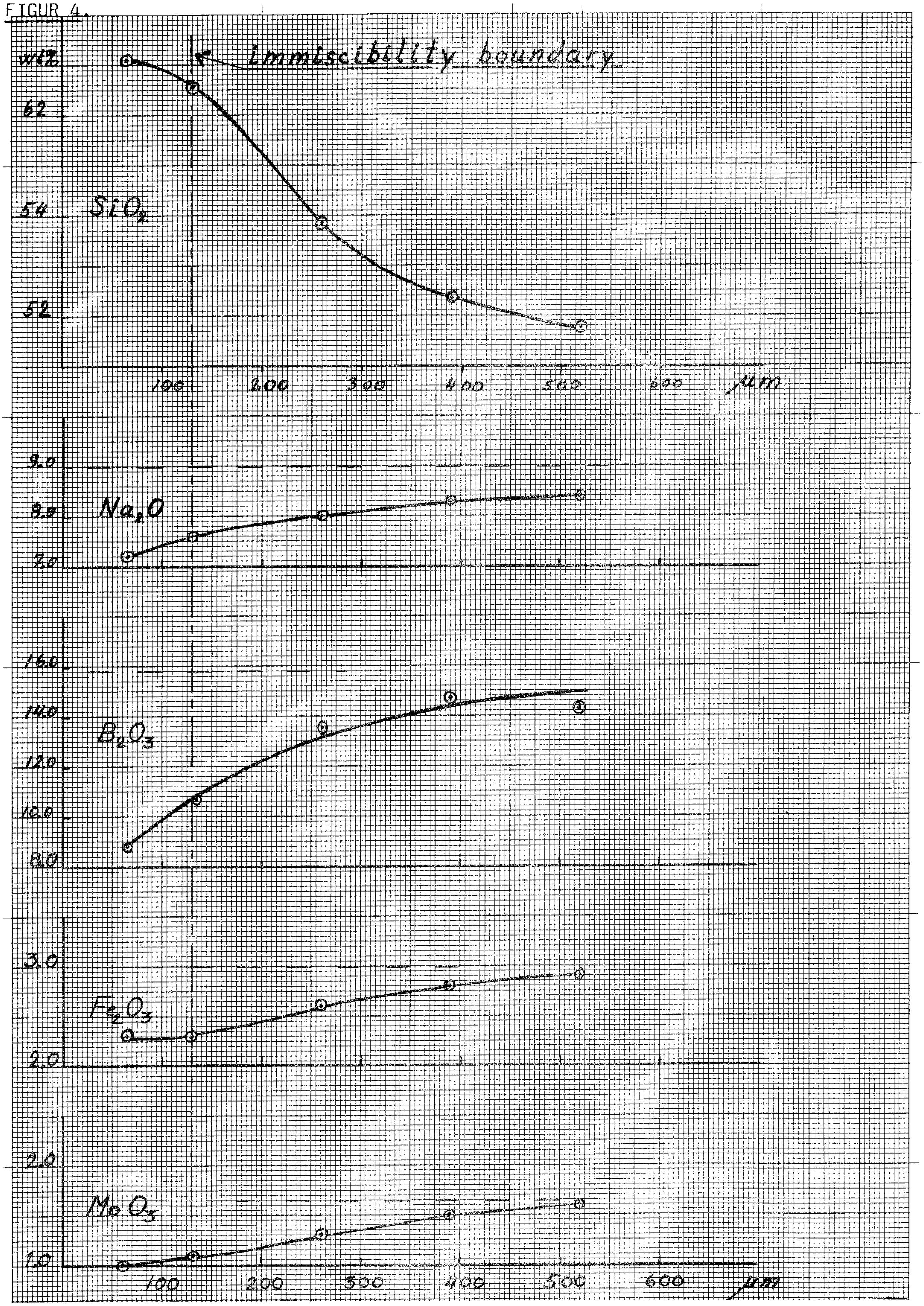


Photo micrograph of polished, HF-vapour etched sample from test series III, phase-separated in blue areas.

FIGUR 4.



Variations in chemical composition along a radius in sample shown in Fig. 2.

INVESTIGATION OF METASTABLE IMMISCIBILITY IN NUCLEAR-WASTE-BORATE-GLASSES

Second Report to SKBF

by

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INSTITUTTET FOR MINERALINDUSTRI
DANMARKS TEKNISKE HØJSKOLE
1981

INTRODUCTION

In the first report on metastable immiscibility in borate-waste-glasses (Roed 1981), the extension of the metastable immiscibility gab from the Na_2O-B_2O_3-SiO_2-system into the more complex system related to the potential nuclear waste-glass ABS-41 (Table 1) was demonstrated.

The results reported by Roed (1981) concern glasses formed in the two diffusion couples ABS-41/SiO_2 and ABS-41/$(B_2O_3)_{3o}(SiO_2)_{7o}$. In both couples the second diffusion-partner contain no fission products. Therefore, in both diffusion paths the concentration of these elements are somewhat lower in the critical glass compositions than in ABS-41.

The aim of the present work was to clarify if an increase of fission products to the level of the ABS-41-glass has any significant influence on the metastable immiscibility-gap at 6oo°C. The glasses studied here are based on diffusion couples between ABS-41 and two glasses A1 and A2 (Table 1) received from Glasteknisk Utveckling AB in Växjö.

EXPERIMENTAL TECHNIQUE

The experimental technique and analytical procedure used are described by Roed (1981). The diffusion experiments were performed in Pt-envelops. The heat treatment of the investigated diffusion couples are given in Table 2.

The resulting glasses were polished, etched by HF-vapour, examined in reflected light and marked. After repolishing the samples were analysed in an ARL-electron microprobe using ABS-39 as a standard (Table 1). In order to interprete the analytical results the carbon film on the surface of the analysed samples was carefully removed with ethanol and the samples etched again in HF-vapour. The tracks of the electron beam is clearly seen on the etched surfaces, as are the position of the metastable immiscibility boundary defined by the change of the surface colour from first order gray-white in the homogeneous glasses to yellow, redbrown, blue and higher order colours in the separeted glasses.

RESULTS AND DISCUSSION

The heat treatment and etching behaviour of the four investigated diffusion couples are reported in Table 2. The quenched samples of both ABS-41/A1 and ABS-41/A2 shows a homogenious etching behaviour, whereas the annealed samples of both diffusion couples show zones of enhanced etching, reflecting compositions within the metastable immiscibility-gap.

The etching behaviour and the position of the microprobe analyses in the critical areas of the annealed samples of ABS-41/A1 and ABS-41/A2 are shown in

Figure 1 and 2 respectively, together with the Na_2O-variation accros part of the diffusion profiles. A total of 2o analyses were made in each sample. Representative analyses of the separated (bulk) and homogenious glasses are given in Table 3.

The spacial positions of the immiscibility boundary in the two samples, as determind in reflected light, are shown in Figure 1 and 2. Due to an artefact of the polaroid film the first order gray-white areas of homogenious glass appear greenish-yellow or, where the surface layer is full of crystalites, brownish (Figure 2) in the colour photographs.

In ABS-41/A1 the polished surface cuts the immiscibility boundary at a shallow angel. Thus, the repolishing of this sample for the microprobe analyses moved the trace of the boundary from about where anal. no 13 was made, to between anal. 18 and 2o (Figure 1). In ABS-41/A2 the polished surface are nearly perpendicular to the immiscibility boundaries.

The 6oo°C immiscibility boundary compositions as determined by linear interpolation of the microprobe analyses are given in Table 4 together with the results obtained by Roed (1981). As expected the boundary compositions determined in the present work refers to compositions containing a sum of Na_2O,B_2O_3 and SiO_2 less than 8o%.

The location of the 6oo°C immiscibility-gap in the 8o% Na_2O-B_2O_3-SiO_2-plane related to the multicomponent ABS-41-system is illustrated in Figure 3, as established by the data from Roed (1981) and the present work.

The different data show an excellent internal agreement and indicate that for ABS-41 the 6oo°C immiscibility boundary in the 8o% Na_2O-B_2O_3-SiO_2-plane is located at 7.44±o.15 %Na_2O independent of the B_2O_3/SiO_2-ratio in the interval 52 to 64% SiO_2.

A projection of the ABS-41 data into the pure Na_2O-B_2O_3-SiO_2-system gives a boundary at 9.3% Na_2O (Figure 4) and shows that the addition of the 2o% of other elements which ABS-41 contain disminish the immiscibility-gap relative to the pure system. However, one might argue that the 3% Li_2O, which ABS-41, A1, A2 and presumably the critical glasses in the present work contain, has the same effects as the equivalent amount of Na_2O (6.22%). If so, the projected boundary is located at 16.5% Na_2O in the pure Na_2O-B_2O_3-SiO_2-system (Figure 4). This would indicate a relative widening of the immmiscibility-gap and, that ABS-39 should show spontaneous separation at 6oo°C which appears unlikely. These arguments illustrate the difficulties in applying results obtained for one wasteglass system to another.

CONCLUSION

For ABS-41 the 600 ^{o}C metastable immiscibility boundary has been located in the 80% $Na_2O-B_2O_3-SiO_2$-plane (Figure 3) at 7.44 $\pm$ 0.15 % Na_2O independent of the B_2O_3/SiO_2 ratio in the interval from 52 to 64% SiO_2.

The results should not be applied to other waste-glass-system which differ radically from ABS-41, for instant by containing no Li_2O.

REFERENCES

Roed, G. (1981): Investigation of metastable immiscibility in borate-waste-glasses. Report to SKBF from The Institute of Mineral-industry, D.T.H..

TABLE 1. Chemical composition of bulk glasses in wt%.

	ABS-39	ABS-41	A1	A2
SiO_2	48.5	52.o	62.o	56.o
B_2O_3	19.1	15.9	16.o	22.o
Na_2O	12.9	9.4	2.o	2.o
Sum	8o.5	77.3	8o.o	8o.o
Al_2O_3	3.1	2.5		
Fe_2O_3	5.7	3.o		
ZnO	-	3.o	11.o[+]	11.o[+]
Li_2O	-	3.o		
U_2O	1.66	1.66		
Sum	9o.96	9o.46	91.o	91.o
F.P.[x] MoO_3	1.63	1.63	9.o[+]	9.o[+]
Other F.P.	7.37	7.37		
Sum	99.96	99.46	1oo.o	1oo.o

[x] F.P. Mixture of simulated fission products.

[+] Same relative proportions as in ABS-41.

TABLE 2. Heat treatment of diffusion couples.

Diff. coup.	Diffusion		Annealing		Etching behaviour	
	T°C	t(h)	T°C	(h)	Homogenious	Zones
ABS-41/A1	1145	1	quenched		+	
ABS-41/A2	1145	1	quenched		+	
ABS-41/A1	12oo	1	6oo	19 1/2		+
ABS-41/A2	115o	1/2	6oo	3		+

TABLE 3. Representative microprobe analyses from the annealed diffusion profiles.

Analyse number Sep. Glass bulk	Homog. Glass	SiO_2	B_2O_3	Na_2O	sum	Fe_2O_3	MoO_3	UO_2
ABS-41/A1								
3		60.65	14.62	4.84	80.11	4.07	1.43	1.6
4		59.89	13.78	5.00	78.67	4.09	1.47	1.5
6		59.66	16.37	5.17	81.20	4.06	1.47	1.6
11		58.09	15.18	5.20	78.47	4.05	1.33	1.5
14		56.56	15.18	5.91	77.65	3.78	1.53	1.7
17		55.66	15.39	6.25	77.30	4.07	1.39	1.9
18		53.42	15.67	6.88	75.97	3.31	1.49	2.1
	20	52.56	14.96	7.33	74.85	3.38	1.41	2.1
ABS-41/A2								
1		54.64	16.76	6.39	77.79	3.62	1.31	1.6
2		54.20	16.14	6.59	76.93	3.58	1.21	1.7
4		52.65	18.07	7.28	78.00	3.26	1.40	1.6
	5	52.84	16.37	7.44	76.65	3.33	1.51	1.7
	7	53.70	17.04	7.61	78.35	3.51	1.56	1.8
	9	52.94	16.35	7.61	76.90	3.65	1.58	1.8
	10	53.00	18.55	7.33	78.88	3.43	1.45	1.7
11		55.44	17.86	6.41	79.71	3.76	1.30	1.3
14		55.51	17.45	6.19	79.15	3.79	1.23	1.6
17		52.82	19.51	6.90	79.23	3.37	1.40	1.7
	19	51.69	16.15	7.55	75.39	3.16	1.60	2.0
	20	50.78	17.18	7.45	75.41	3.10	1.50	2.0

TABLE 4. 600°C-immiscibility boundary compositions as determined by Roed (1981) and by interpolation of the microprobe analyses reported in the present work.

	Roed (1981)		Present work				
	ABS-41/SiO_2	ABS-41/$(B_2O_3)_{30}(SiO_2)_{70}$ Average	ABS-41/A1		ABS-41/A2		
			Go	G1	G2	G3	Average G1,G2&G3
SiO_2	63.1	55.1	53.32	52.70	53.20	52.75	52.88
B_2O_3	10.7	17.9	15.59	17.40	18.45	18.85	18.23
Na_2O	7.6	7.7	6.93	7.31	7.25	7.00	7.19
sum	81.4	80.7	75.84	77.41	78.90	78.60	78.30
Fe_2O_3	2.3	2.85	3.32	3.28	3.45	3.30	3.34
MoO_3	1.0	1.5	1.48	1.45	1.45	1.45	1.45
UO_2	-	-	2.1	1.7	1.7	1.9	1.77

Compositions projected into the 80% Na_2O-B_2O_3-SiO_2 plane:

SiO_2	62.01	54.62	56.24				54.03
B_2O_3	10.52	17.75	16.45				18.63
Na_2O	7.47	7.63	7.31				7.34

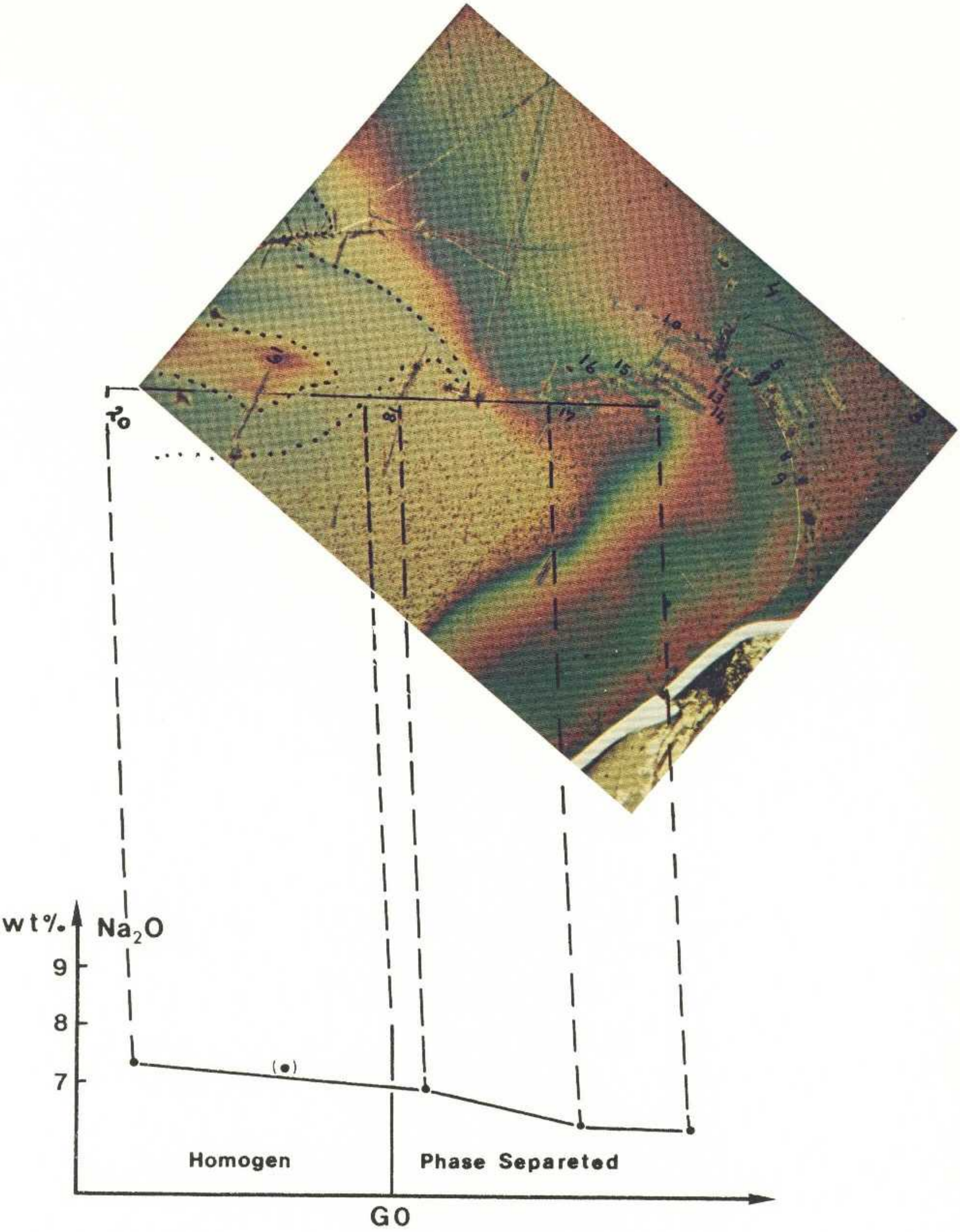


FIGURE 1. Etching behaviour and Na_2O content of critical area of the ABS-41/Al diffusion couple annealed at 6oo^{0}C. Numbers refers to the microprobe analyses (Table 3). The spacial location of the immiscibility boundary (Go) are maked by dates.

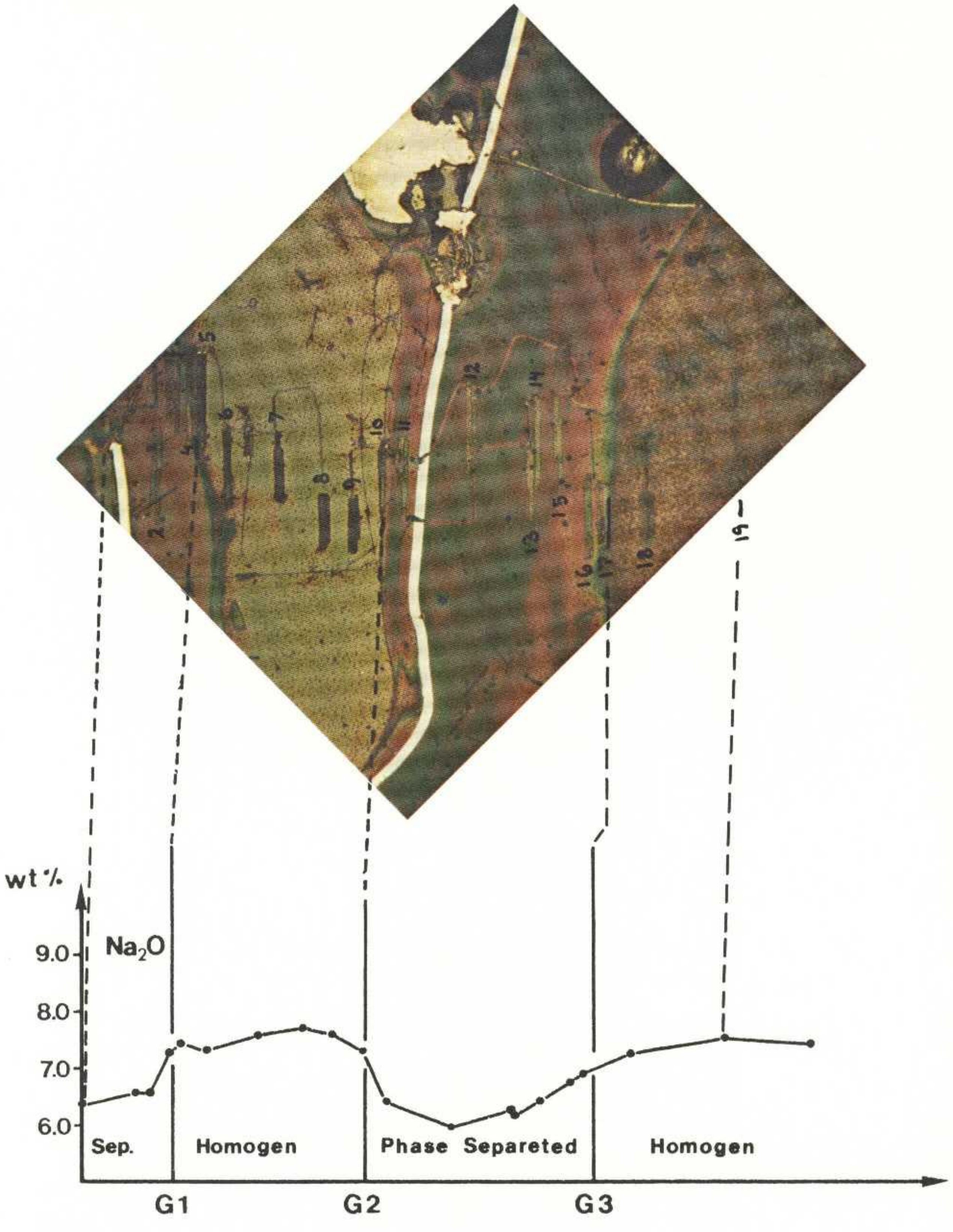
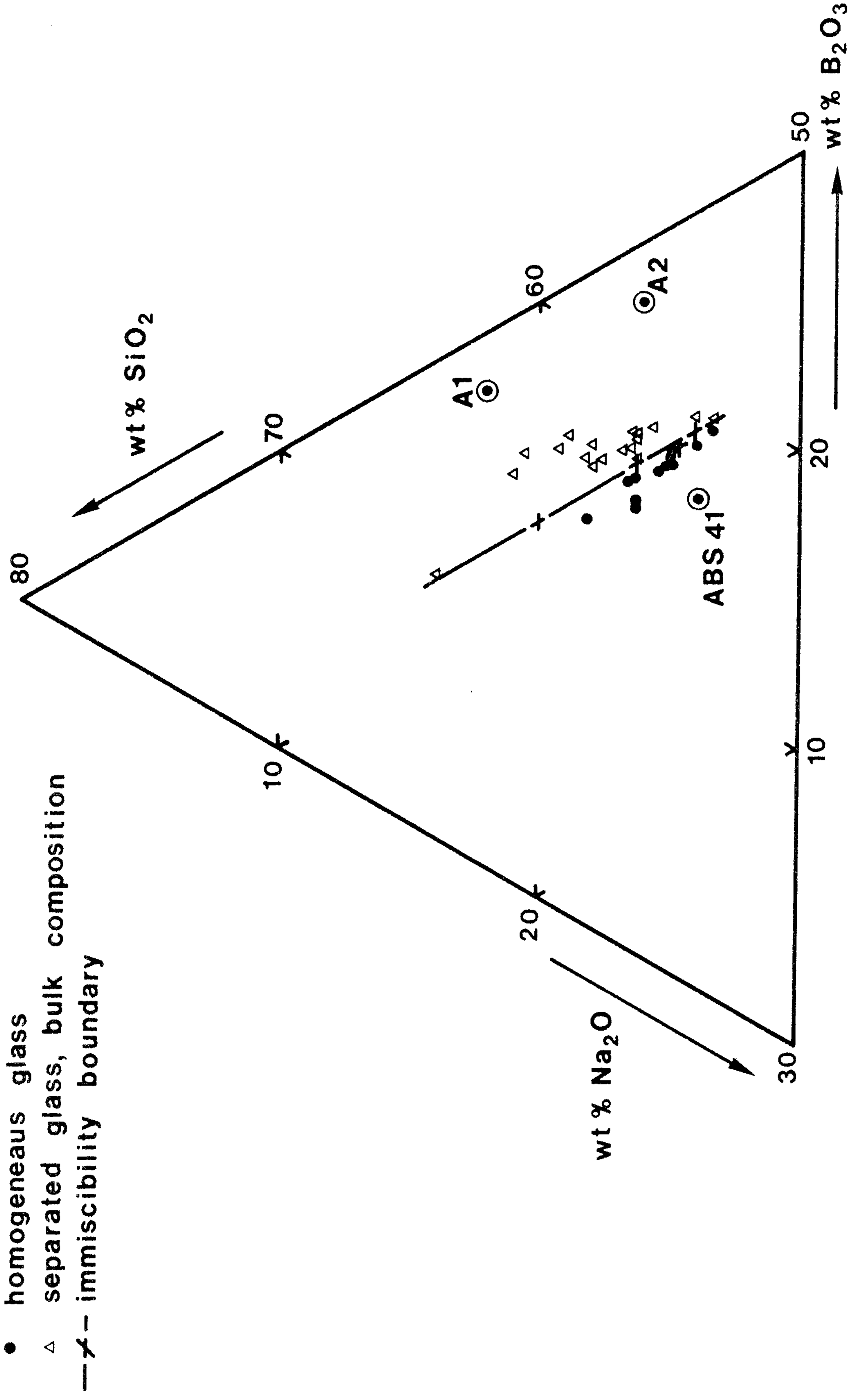


FIGURA 2. Etching behaviour and Na_2O content of critical area of the ABS-41/A2 diffusion couple annealed at 600°C. Numbers refers to the microprobe analyses (Table 3). Location of the immiscibility boundaries are at G1, G2 and G3.

FIGURE 3. Location of the 600^{o}C immiscibility-gap in the 80% Na_2O-B_2O_3-SiO_2-plane related to the multicomponent ABS-41 system as determind by the data from Roed (1981) and the present work.



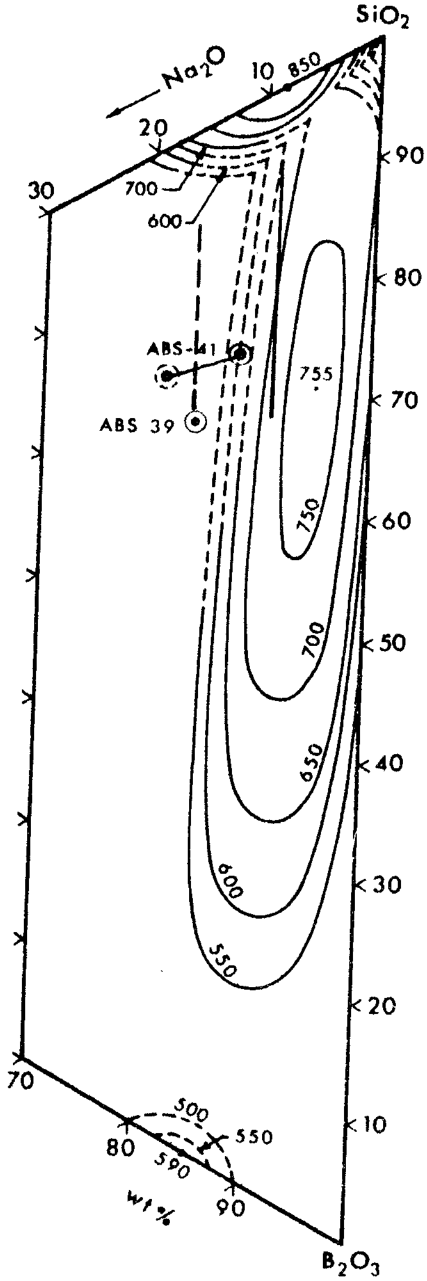


FIGURE 4. A comparison of the subliquidus immiscibility in the system Na_2O-B_2O_3-SiO_2 with the data for the ABS-41 system projected directly (line at 9.30% Na_2O) or after recalculating the assumed LiO_2 content to an equivalent amount of Na_2O (line at 16.5% Na_2O).

INVESTIGATION OF METASTABLE IMMISCIBILITY IN NUCLEAR-WASTE-GLASSES

Third Report to SKBF

by

J. Engell and L. Møller

INTRODUCTION

In the previous work (Roed 1981, Engell & Larsen 1981) the extension of the metastable immiscibility gap from the Na_2O-B_2O_3-SiO_2-system into the more complex system related to the potential nuclear-waste-glass ABS-41 was demonstrated. The data concern glasses containing up to 1.6 wt% MoO_3. The concentration of Mo-oxid in the waste-glass and the oxidation state of the molybdenum are known to have a pronounced effect on the immiscibility gap (Yamane & Nakao 1979, Kawamoto et al 1981 A, Kawamoto et al 1981 B).

The ABS-41 glass contains 3 wt% Li_2O. If it is assumed that Li_2O has the same effect as the equivalent amount (mole) Na_2O the results for the ABS-41 system indicate that ABS-39 might be close to or inside the metastable immiscibility gap.

Thus, the aim of the present work was to locate the metastable immiscibility boundary for the ABS-39 system, and to determine the amount of MoO_3 which can be dissolved in ABS-41 and ABS-39 without causing liquid immiscibility.

METHODS AND MATERIALS

The experimental technique and analytical procedure used are described by Roed (1981) and Engell and Larsen (1981).

For the study of the ABS-39 system, the required glasses were prepared by interdiffusion of ABS-39 (Table 1) with the following glasses:

BS, a binary B_2O_3-SiO_2 glass containing approximately 3o wt% B_2O_3 and 7o wt% SiO_2.

A3, a partly crystallized multicomponent borate glass containing 62 wt% SiO_2, 16 wt% B_2O_3 and 2 wt% Na_2O but otherwise similar to ABS-39.

A3', a homogeneous glass prepared from a 1:2 mixture of ABS-39 and A3.

A4', a homogeneous glass prepared from a 1:3 mixture of ABS-39 and A4, a partly crystallized multicomponent borate glass containing 56 wt% SiO_2, 22 wt% B_2O_3 and 2 wt% Na_2O but otherwise similar to ABS-39.

NBS65-39, a homogeneous glass prepared from ABS-39 by addition of Al_2O_3, Fe_2O_3, UO_2 and simulated fission products in the same relative proportions as in ABS-39. The sum of Na_2O, B_2O_3 and SiO_2 is reduced to 65 wt%.

Mo-ABS-39, prepared by addition of MoO_3 to ABS-39.

For the study of the ABS-41 system, the required glasses were prepared by interdiffusion of ABS-41 (Table 1) with Mo-ABS-41, Mo-A1 and Mo-A2 prepared by adding MoO_3 to ABS-41, A1 and A2 respectively. The compositions of A1 and A2 are given by Engell & Larsen (1981, Table 1).

The glasses ABS-39, ABS-41, A1, A2, A3 and A4 as well as the mixture of simulated fission products used in the preparation of NBS65-39 were prepared by Glasteknisk Utveckling AB, Växjö, Sweden.

RESULTS AND DISCUSSION

The heat treatment and etching behaviour of the investigated diffusion couples are reported in Table II. Representative electron microprobe analyses of the investigated glasses are given in Table III and bulk compositions at the 6oo^{o}C immiscibility boundary as determined in the present study are given in Table IV.

The ABS-39 system

The quenched samples all show a homogeneous etching behaviour. Dark field microscopy revealed no opalescence in the quenched glasses except for the partly crystallized A3 glass. After annealing at 6oo^{o}C the ABS-39/BS sample, the ABS-39/A3 sample diffused for 5 min. and the ABS-39/Mo-ABS-39 sample show zones of enhanced etching.

In the annealed ABS-39/BS sample zones of opalescence were observed beneath the zones of enhanced etching (Fig. 1 & 2). Glasses in the ABS-39/BS diffusion couples span the complete range from homogeneous ABS-39 glass through phase-separated intermediate glasses to a homogeneous sodium poor borosilicate glass containing less than lo wt% of additional components (Fig. 3 & 4).

The A3 composition could not be prepared as a homogeneous glass. Samples quenched in water contain minute brownish crystals. In the ABS-39/A3 diffusion couple the Na-rich front of the zone of enhanced etching coincides with the front of the opalescence below. The A3 glass does not itself show enhanced etching (Fig. 4).

The failure in detecting the immiscibility gap in the ABS-39/A3 diffusion couples diffused for more than 5 min. (Table II) indicate that the diffusion of Na_2O at 1185^{o}C is so rapid that after 15 min. all glasses in the diffusion profile are on the Na_2O-rich side of the immiscibility gap.

The A3' composition made from ABS-39 and A3 in the ratio 1:2 could be prepared as a homogeneous glass. According to the results from the ABS-39/A3 sample the entire ABS-39/A3' diffusion couple should be outside the immiscibility field. As expected, no zones of enhanced etching were observed, but locally thin zones of weak opalescence were seen in the clear glass of the annealed sample (Table II). Microprobe analyses showed no correlation between the Na_2O content of the glasses and opalescence, but that the opalescence was limited to glasses containing less than about 78 wt% of Na_2O, B_2O_3 and SiO_2. We believe this opalescence is caused by partial crystallisation it might indicate the existence of a new intersecting immiscibility gap.

The A4' composition made from ABS-39 and A4 in the ratio 1:3 could be prepared as a homogeneous glass. No zones of enhanced etching were observed in the annealed sample of ABS-39/A4', but zones of weak opalescence were seen (Table II, Fig. 6). The opalescence are here confined to the glasses poorest in Na_2O and having compositions close to the 6oo°C immiscibility boundary inferred from the ABS-39/BS and ABS-39/A3 samples. We believe the glasses showing opalescence are inside the immiscibility gap.

In the ABS-39/NBS65-39 diffusion couple no clear zones of enhanced etching were seen in the annealed sample, but glasses containing less than approximately 7o wt% of Na_2O, B_2O_3 and SiO_2 show weak opalescence (Table III).

In the annealed sample of ABS-39/Mo-ABS-39 a yellow opalescence was observed beneath the zone of enhanced etching (Fig. 7 & 8). The phase separated glasses are partly crystallized. The variation in the MoO_3 content accross the analysed profile is given in Fig. 9. The results show that ABS-39 can disolve up to 4.5 $\pm$ o.5 wt% MoO_3 before it undergoes phase separation at 6oo°C.

For the ABS-39 system, the compositional variation of the investigated glasses containing less than 2 wt% MoO_3 and the determined 6oo°C immiscibility boundary are illustrated in Fig. 15. This figure represent a revised version, based on all the data now available, of Fig. 5B in Engell and Roed (in press) and given here as Fig. 16B. It appears that the immiscibility gap extending into the multicomponent system from the pure Na_2O-B_2O_3-SiO_2-system tends to close as the total concentration of simulated fission products and other additional components increases above about 21 wt%. However, at this level it is intersected by another immiscibility gap which widens as the concentration of Na_2O, B_2O_3 and SiO_2 is reduced further. Interpolation of the data places the 6oo°C immiscibility boundary at about 5.5 wt% Na_2O in the 8o wt% Na_2O-B_2O_3-SiO_2 plane (as compared to 5.2 wt% estimated by Engell & Roed in press). Thus, the data show a significant contraction of the metastable immiscibility field in the ABS-39 system relative to the ABS-41 system (Fig. 16, Roed 1981, Engell & Larsen 1981, Engell & Roed in press).

The failure in detecting the immiscibility gap in the ABS-39/SiO_2 diffusion couples (Roed 1981) is consistent with a contraction of the gab relative to the ABS-41 glasses. The formation of cristobalite crystals on the inner surface of the SiO_2 glass at the diffusion temperature controls the limiting composition of the formed melts/glasses. Apparently a higher diffusion temperature is necessary to ensure the formation of a sufficiently Na_2O poor melt.

The ABS-41 system with added MoO_3

The quenched sample of ABS-41/Mo-ABS-41 shows a homogeneous etching behaviour and dark field microscopy revealed no opalescence. The sample annealed at 6oo°C shows a zone of enhanced etching (Fig. 1o). The glass beneath this zone shows yellow opalescence and is partly crystallized. The variation in the MoO_3 content across the analysed profile is given in Fig. 11. The results show that ABS-41 can dissolve up to 3.7 ± o.3 wt% MoO_3 before it undergoes phase separation at 6oo°C.

The quenched samples of ABS-41/Mo-A1 and ABS-41/Mo-A2 show enhanced etching in the Mo-A1 and Mo-A2 end of the diffusion profiles, and in one of the quenched ABS-41/Mo-A1 samples opalescence is seen (Table 2). This indicates that enough MoO_3 has been added to stabilize the immiscibility gap for the Na_2O-poor glasses. The annealed samples show coinciding zones of enhanced etching and yellow opalescence. The etching behaviour and the position of the microprobe analyses are shown in Fig. 12 and 13 for the critical areas of respectively ABS-41/Mo-A1 and ABS-41/Mo-A2.

The analysed glasses contain from 3.9 to 1.8 wt% MoO_3. The immiscibility boundary as determined from the glasses containing 2-3 wt% MoO_3 is shown in Fig. 14. The boundary appears to be a continuation of the boundary previously determined for glasses containing about 1.5 wt% MoO_3 (Fig. 16A, Roed 1981, Engell & Larsen 1981, Engell & Roed in press). This is somewhat surprising as an expansion of the immiscibility gap with increasing MoO_3 content was expected. However, the data indicate that for ABS-41 the immiscibility gap extending into the multicomponent system from the pure Na_2O-B_2O_3-SiO_2 system tends to close when the concentration of Na_2O, B_2O_3 and SiO_2 decreases belowe about 75 wt% even if the MoO_3 content is increased to about 2.5 wt%.

CONCLUSION

The results presented above show that the composition of ABS-39 is in the one phase glass field, outside the metastable immiscibility field extending from the simple Na_2O-B_2O_3-SiO_2 system into the multicomponent system, down to temperatures below 6oo°C.

In the 8o wt% Na_2O-B_2O_3-SiO_2 plane the 6oo°C immiscibility boundary is 5.5 wt% Na_2O for the ABS-39 system compared to 7.4 ± o.2 wt% Na_2O for the ABS-41 system (Roed 1981, Engell & Larsen 1981, Engell & Roed in press).

For both systems the position of the 600°C immiscibility isotherm appears to be independent of the B_2O_3/SiO_2 ratio. Both waste-glasses contain identical amounts of UO_2 and simulated fission products. The difference between the 600°C immiscibility isotherm for the two systems (Fig. 5) must then be ascribed to the difference in the content of Al_2O_3, Fe_2O_3, ZnO and Li_2O between the two glasses (Table I). The partial subsitution of Al_2O_3 and Fe_2O_3 in ABS-39 with ZnO and Li_2O as in ABS-41 causes an expansion of the metastable immiscibility field.

The maximal amount of MoO_3 which can be dissolved in ABS-39 and ABS-41 without causing phase-separation is 4.5 ± 0.5 wt% and 3.7 ± 0.3 wt% respectively.

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TABLE I
Batch compositions of nuclear-waste-glasses in wt% as given by Glasteknisk Utveckling AB, Växjö, Sweden (personal communication).

	ABS-39	ABS-41	Simulated fission products (F.P.)			
SiO_2	48.5	52.o	MoO_3	1.63	SrO	o.26
B_2O_3	19.1	15.9	ZrO_2	1.28	BaO	o.46
Na_2O	12.9	9.4	Nd_2O_3	1.21	Cs_2O	o.88
Sum	8o.5	77.3	Ce_2O_3	o.75	Ag_2O	o.o11
			La_2O_3	o.71	CdO	o.o26
Al_2O_3	3.1	2.5	Pr_2O_3	o.35	Sb_2O_3	o.oo36
Fe_2O_3	5.7	3.o	Y_2O_3	o.15	Sum	9.oo
ZnO	-	3.o	MnO_2	o.77		
Li_2O	-	3.o	CoO	o.12		
UO_2	1.66	1.66	NiO	o.37		
F.P.	9.	9.	SnO	o.o17		
Sum	99.96	99.46				

TABLE II
Heat treatment and etching behavior of investigated diffusion couples.

Diffusion couples	Diffusion T°C	t(h)	Annealing T°C	t(h)	Etching behavior Homogeneous	Zones	Opalescence in zones
ABS-39/BS	117o	o.5	quenched		+		
do	117o	o.5	6oo	19.5		+	+
ABS-39/A3	1177	1	quenched		+		+[1]
do	1177	1	6oo	17.3	+		+[1]
do	1185	o.25	quenched		+		+[1]
do	1185	o.25	6oo	19	+		+[1]
do	1185	5 min.	quenched		+		+[1]
do	1185	5 min.	6oo	12		+	+[1]
ABS-39/A3'	11oo	o.25	quenched		+		
do	1185	o.25	6oo	17.5	+		+
ABS-39/A4'	12oo	o.25	quenched		+		
do	12oo	o.25	6oo	o.67	+		+
ABS-39/NBS65-39	1195	o.25	quenched		+		
do	1195	o.25	6oo	4.2	+		+
ABS-39/Mo-ABS-39	116o	o.25	quenched		+		
do	116o	o.25	6oo	o.5		+	+
ABS-41/Mo-A1	1o75	o.25	quenched			+[2]	
do	1o75	o.25	6oo	19		+	+
do	12o5	5 min.	quenched			+[2]	+[2]
do	12o5	5 min.	6oo	3		+	+
ABS-41/Mo-A2	1o75	o.25	quenched			+[2]	
do	1o75	o.25	6oo	19		+	+
ABS-41/Mo-ABS-41	1195	o.25	quenched		+		
do	1195	o.25	6oo	3		+	+

1) Opalescence observed in the partly crystallized A3.

2) Enhanced etching (and opalescence) observed in Mo-A1 and Mo-A2, indicating that enough MoO_3 has been added to stabilize the liquid immiscibility.

TABLE III
Representative microprobe analyses from the annealed diffusion couples.

Analyse Number		SiO_2	B_2O_3	Na_2O	Sum	Fe_2O_3	MoO_3	UO_2
Sep. Glass bulk	Homog. glass							
ABS-39/BS:								
1'th profile								
	3	51.4	21.3	8.1	8o.8	5.6	1.5	1.4
boundary:	4	55.6	21.o	7.1	83.7	3.6	o.6	o.4
5		65.1	23.9	4.2	93.2	o.3	o.2	nil
2'th profile								
1		63.1	2o.1	6.4	89.6	1.8	o.4	o.3
	3	55.8	2o.7	8.2	84.7	3.8	o.8	o.9
	4	57.4	21.o	8.1	86.5	2.6	o.8	o.5
5		61.1	21.7	7.4	9o.2	1.3	o.4	nil
ABS-39/A3:								
	2	59.7	14.1	5.4	79.2	6.2	1.6	1.5
boundary:	3	61.4	13.4	3.9	78.7	5.9	1.5	1.5
4		61.3	14.1	3.2	78.6	6.2	1.5	1.5
ABS-39/A3':								
1'th profile								
2^+		54.8	17.1	5.3	77.2	5.5	1.4	-
4^+		54.9	17.o	6.3	78.2	5.7	1.7	-
	5	55.4	17.9	6.7	8o.o	5.6	1.3	-
	6	55.2	17.7	7.1	8o.o	5.9	1.6	-
2'th profile								
	1	57.8	15.2	5.9	78.9	6.2	1.7	1.6
7^+		48.1	19.5	8.3	75.9	7.6	1.8	1.7
ABS-39/A4':								
1^+		56.3	18.8	4.6	79.7	6.4	1.5	1.7
4^+		56.9	19.3	4.9	81.1	6.3	1.7	1.6
7^+		56.6	17.6	5.7	79.9	6.o	1.4	1.4
	1o	52.8	18.5	7.6	78.9	6.2	1.8	1.1
ABS-39/NBS65-39:								
1^+		41.2	17.8	8.2	67.2	12.2	3.o	2.1
2^+		41.1	19.o	8.o	68.1	12.6	3.3	2.3
	7	48.5	19.3	8.9	76.7	8.8	1.9	1.7
ABS-39/Mo-ABS-39:								
1		48.4	16.8	11.1	76.3	5.7	5.5	1.4
4		48.6	2o.2	11.4	8o.2	5.5	5.2	1.2
	5	49.4	19.2	11.5	8o.1	5.8	3.2	1.1
	7	49.o	19.3	12.2	8o.5	5.6	1.6	1.4
ABS-41/Mo-A1:								
1		58.4	13.9	4.7	77.o	4.o	2.8	1.3
3		56.7	13.5	5.7	75.9	3.9	2.1	1.6
	4	52.2	14.5	6.6	73.3	3.1	1.8	1.9
	5	52.9	15.5	6.8	75.2	3.6	2.1	2.1
	6	54.o	15.5	6.6	76.1	3.o	2.5	1.9

TABLE III
continued

Analyse Number Sep. Glass bulk	 Homog. glass	SiO_2	B_2O_3	Na_2O	Sum	Fe_2O_3	MoO_3	UO_2
ABS-41/Mo-A2:								
2		53.4	17.5	4.5	75.4	3.6	3.1	1.6
	3	53.9	16.3	4.9	75.1	3.4	2.1	1.9
	5	52.9	16.6	5.5	75.0	3.7	2.9	1.7
ABS-41/Mo-ABS-41:								
1		51.0	15.5	9.3	75.8	2.7	5.7	1.9
4		52.3	15.5	9.4	77.2	3.0	4.1	1.8
	5	52.5	14.3	9.4	76.2	3.0	2.8	1.7
	6	52.7	14.4	9.4	76.5	2.9	3.0	1.9
	8	52.2	15.0	9.5	76.7	3.0	2.2	1.9

\+ Based on the observation of opalescence, these glasses show no enhanced etching.

TABLE IV
Bulk glass compositions at the 600°C immiscibility boundary.

Diffusion couple	SiO_2	B_2O_3	Na_2O	Sum	Fe_2O_3	MoO_3	UO_2
ABS-39/BS	55.6	21.0	7.1	83.7	3.6	0.6	0.4
do.	58.9	21.3	7.5	87.7	2.9	0.7	0.4
do.	59.3	21.4	7.8	88.5	2.0	0.6	0.3
ABS-39/A3	61.4	13.4	3.9	78.7	5.9	1.5	1.5
ABS-39/Mo-ABS-39	49.0	19.5	11.4	79.9	5.7	4.5	1.2
ABS-41/Mo-ABS-41	52.3	15.4	9.4	77.1	3.0	3.7	1.8

Fig. 1. Opalescence in the ABS-39/BS diffusion couple annealed at 600^{0}C for 19.5 h as observed by dark field microscopy.

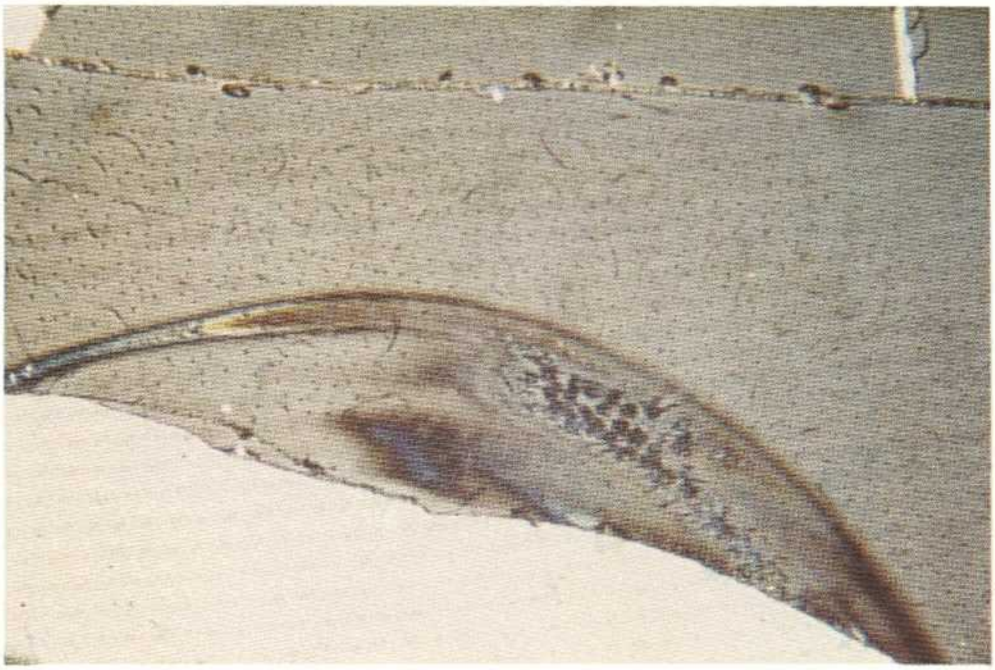

Fig. 2. Etching behaviour of the same area of ABS-39/BS shown as Fig. 1 as observed in reflected light.

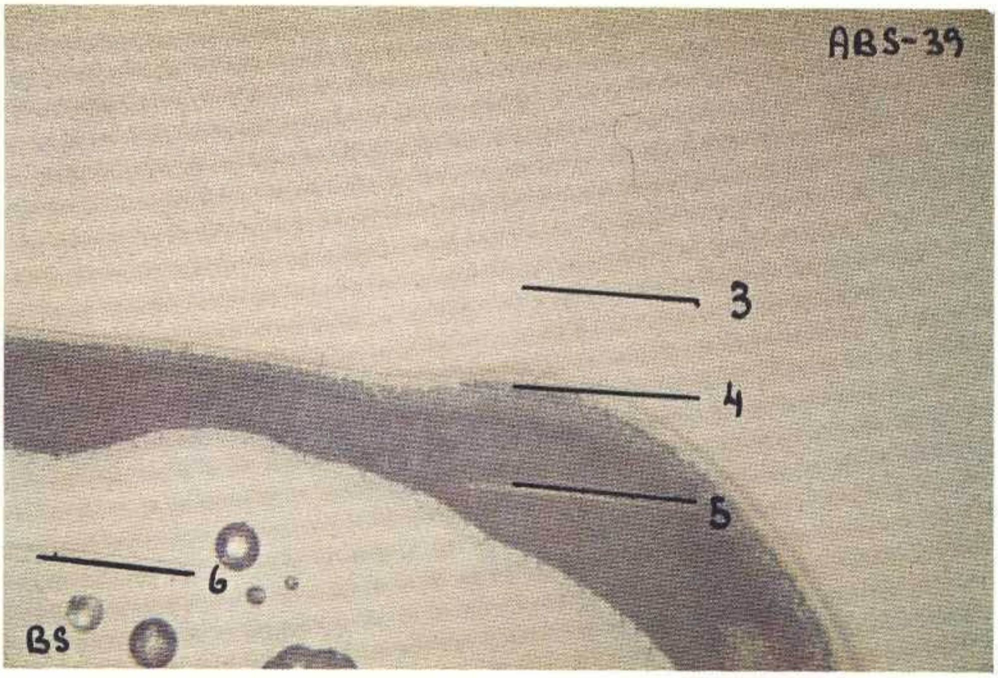

Fig. 3. Etching behaviour and position of critical microprobe analyses in profile 1 in the ABS-39/BS diffusion couple annealed at 600°C for 19.5 h.

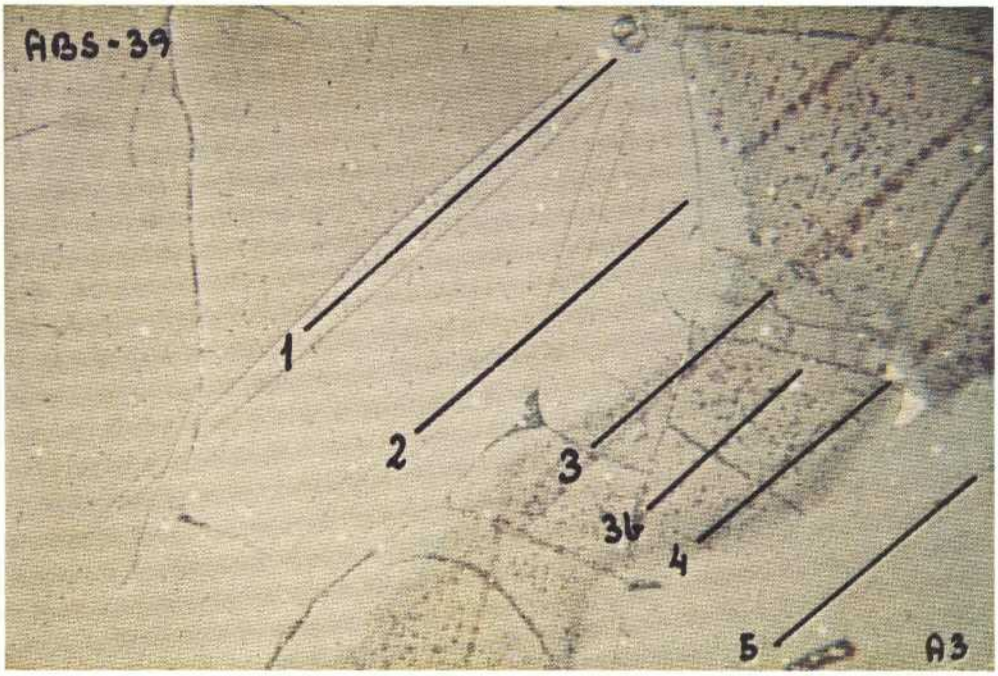

Fig. 5. Etching behaviour and position of microprobe analyses in the ABS-39/A3 couple diffused for 5 min. at 1185°C and annealed at 600°C for 19 h.

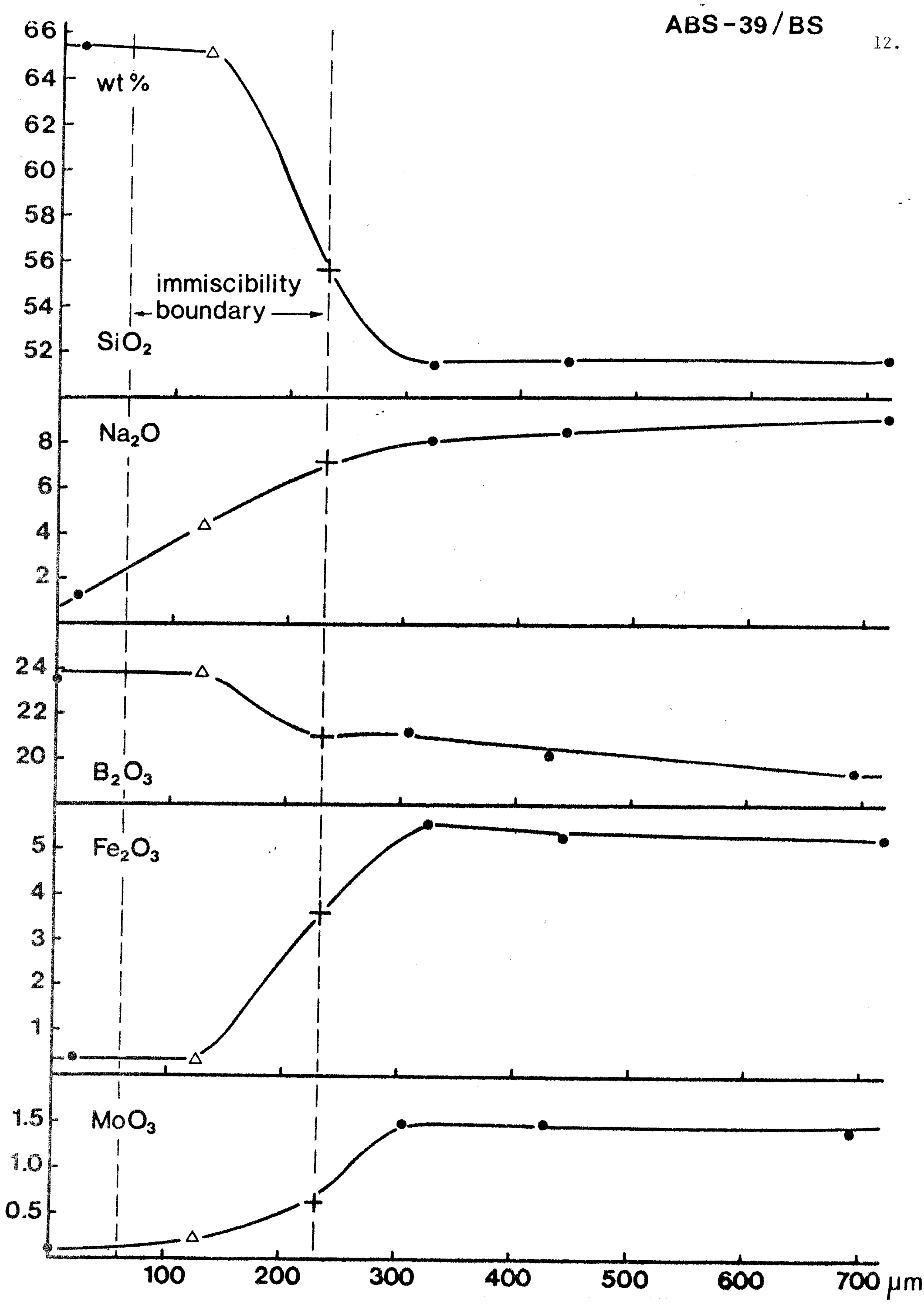

Fig. 4. Compositional variation across profile 1 in the ABS-39/BS diffusion couple.

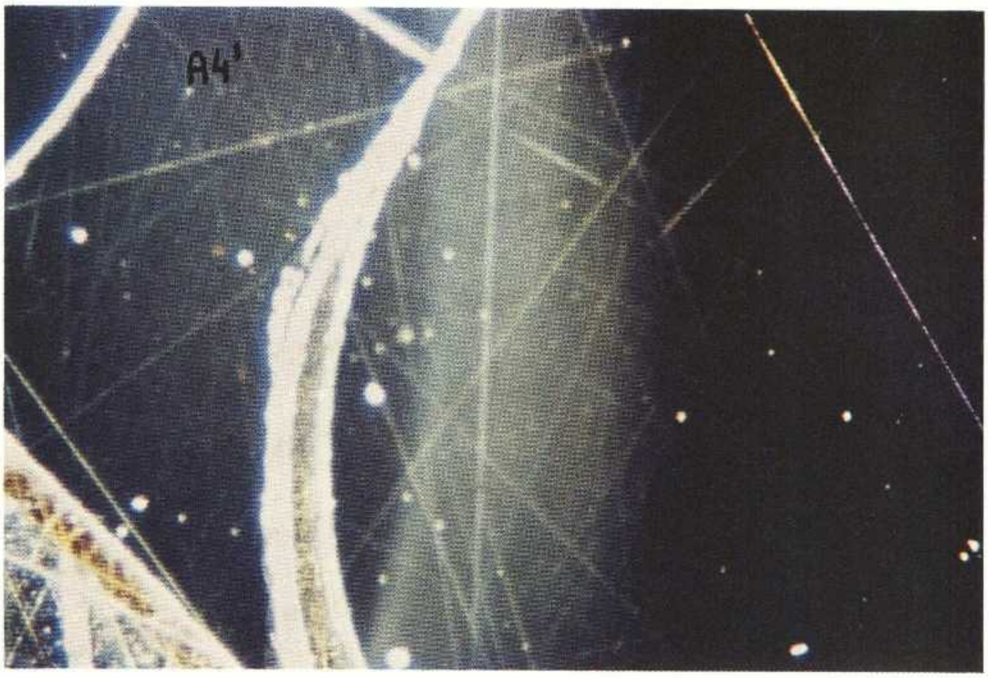

Fig. 6. Weak opalescence observed in the ABS-39/A4' couple after annealing at 600°C for 0.67 h.

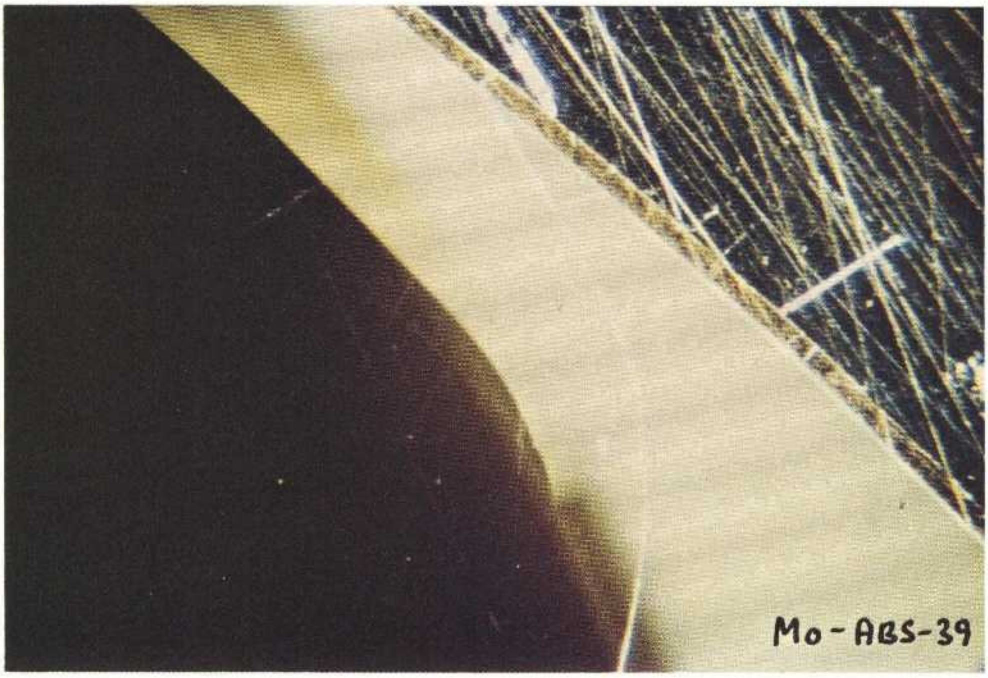

Fig. 7. Opalescence in the phase separated area of ABS-39/Mo-ABS-39 annealed at 600°C for 0.5 h.

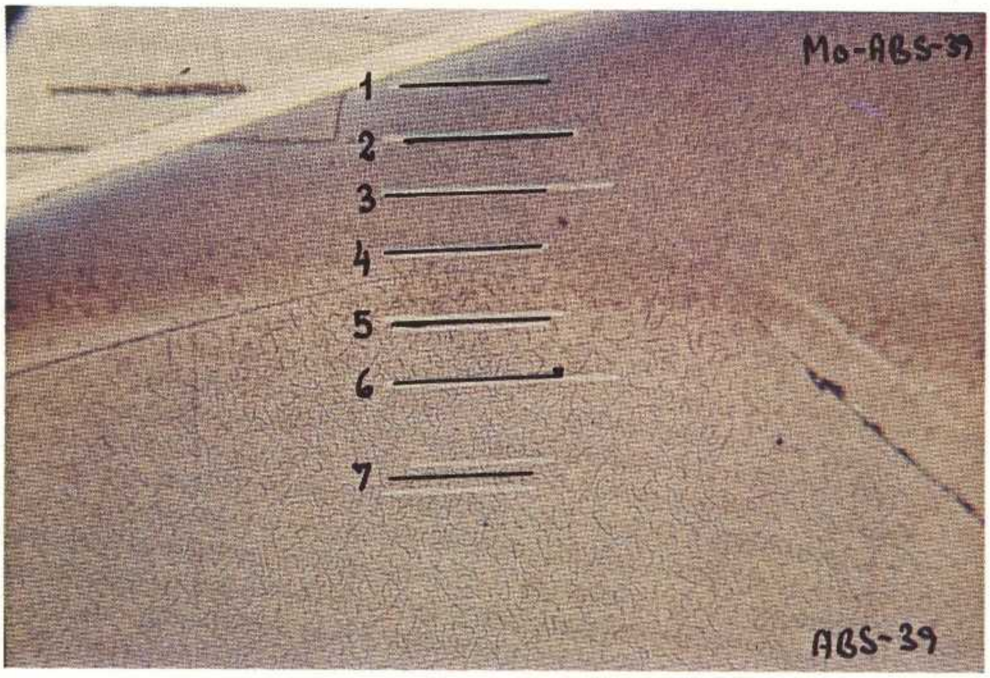

Fig. 8. Etching behaviour and position of microprobe analyses in the same area of ABS-39/Mo-ABS-39 shown in Fig. 7.

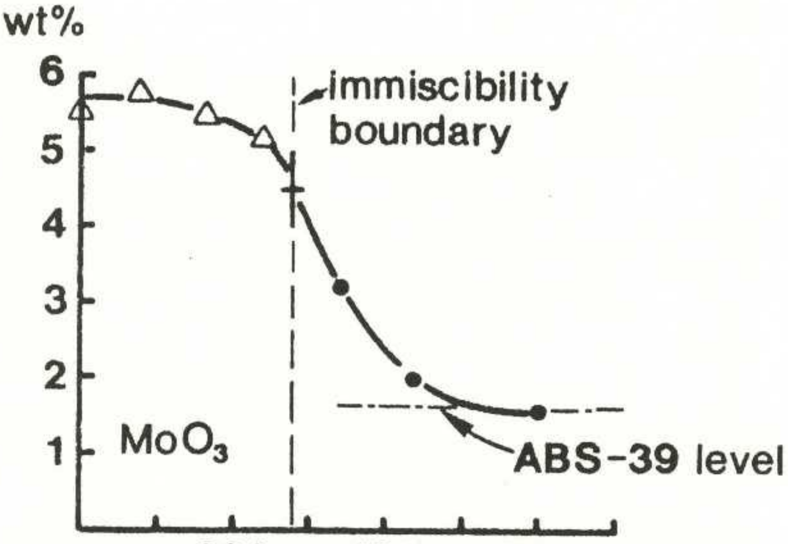

Fig. 9. Variation in the MoO_3 content across the analysed profile in ABS-39/Mo-ABS-39 shown in Fig. 7 & 8.

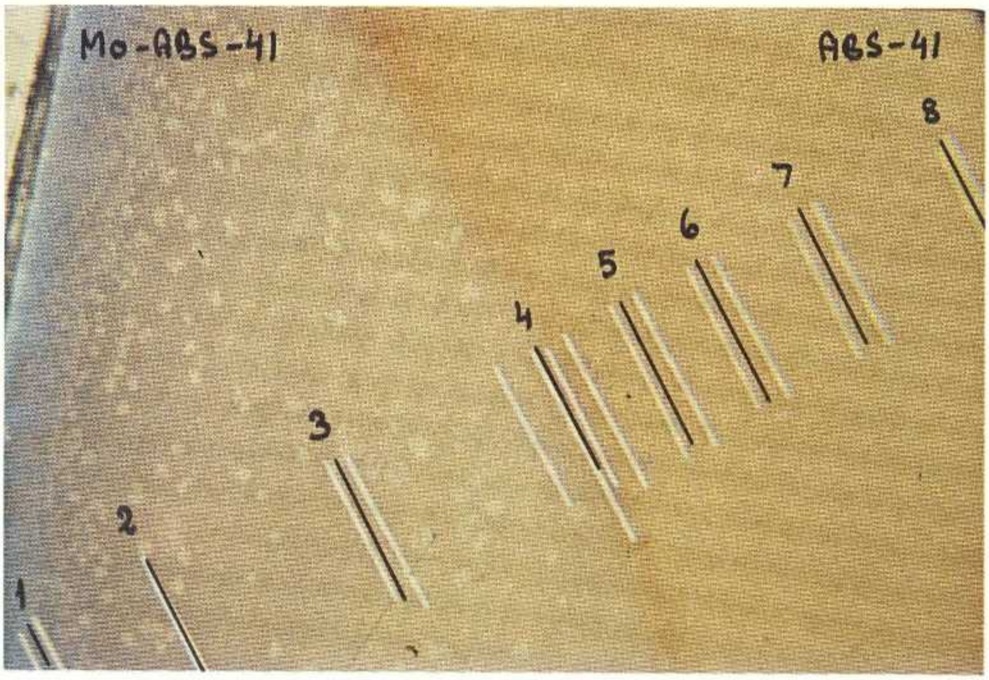

Fig. 1o. Etching behaviour and position of microprobe analyses in the ABS-41/Mo-ABS-41 couple annealed at 600°C for 3 h.

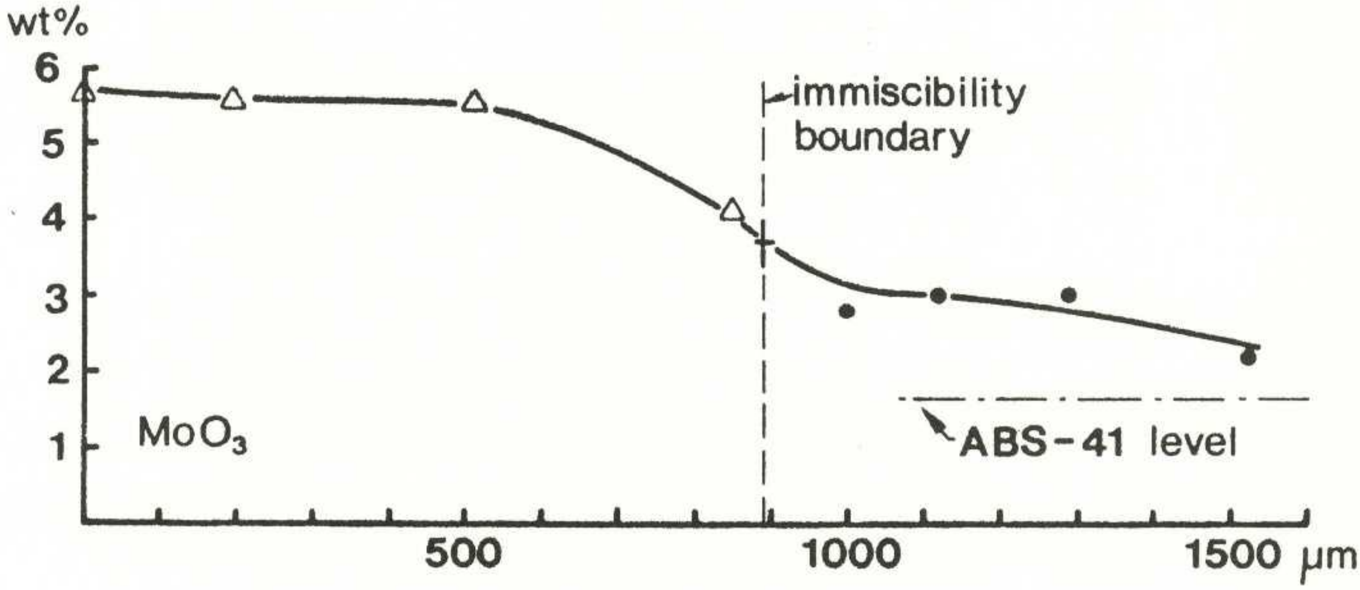

Fig. 11. Variation in the MoO_3 content across the analysed profile in ABS-41/Mo-ABS-41 shown in Fig. 1o.

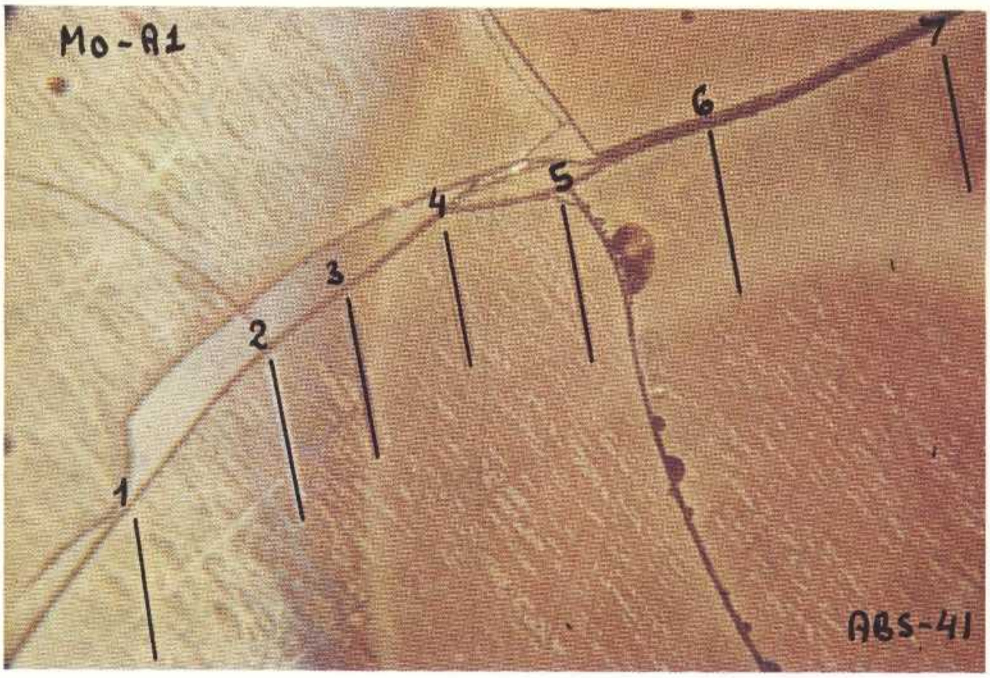

Fig. 12. Etching behaviour and position of microprobe analyses in the ABS-41/Mo-A1 couple annealed at 6oo°C for 19 h.

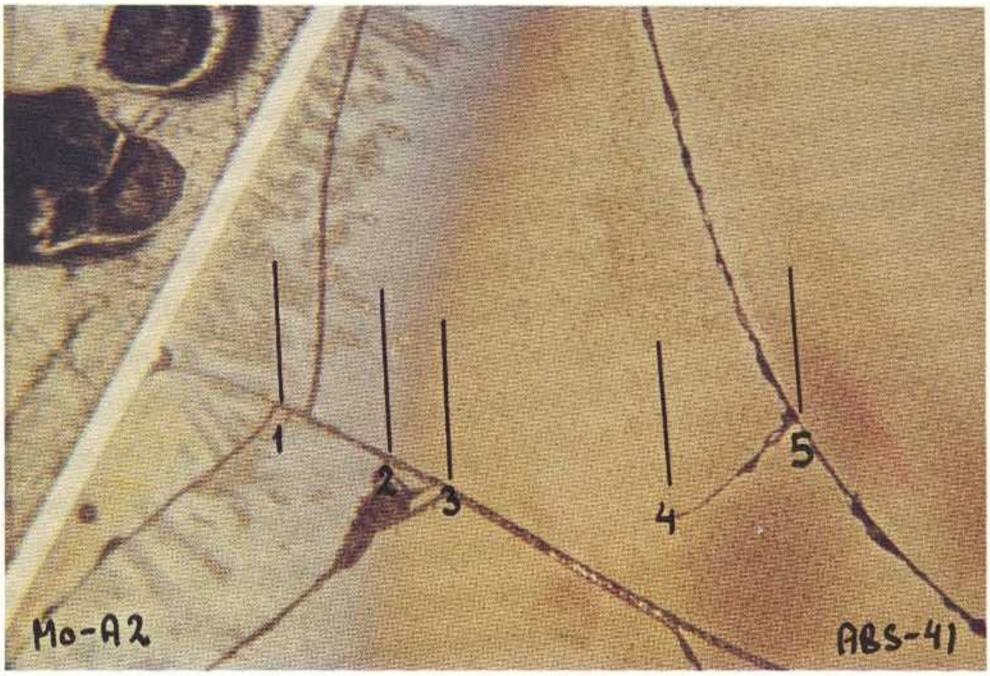

Fig. 13. Etching behaviour and position of microprobe analyses in the ABS-41/Mo-A2 couple annealed at 6oo°C for 19 h.

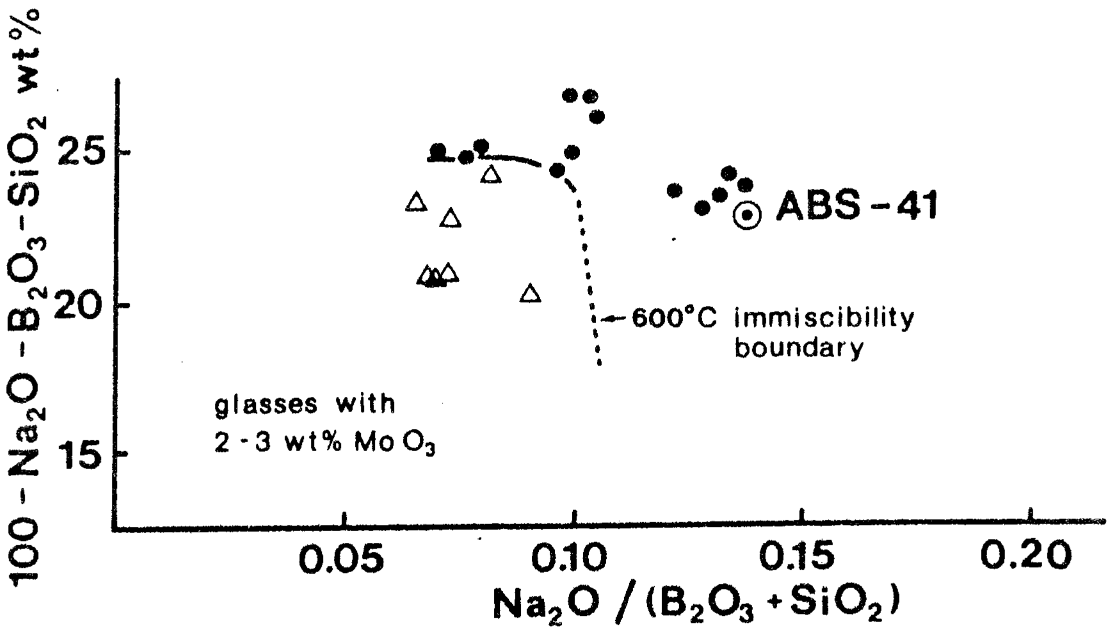

Fig. 14. Variation of the 600°C immiscibility isotherm for glasses in the ABS-41 system containing 2-3 wt% MoO_3 as a function of the content of simulated fission products and other additional components. For explanation of symbols, see Fig. 15.

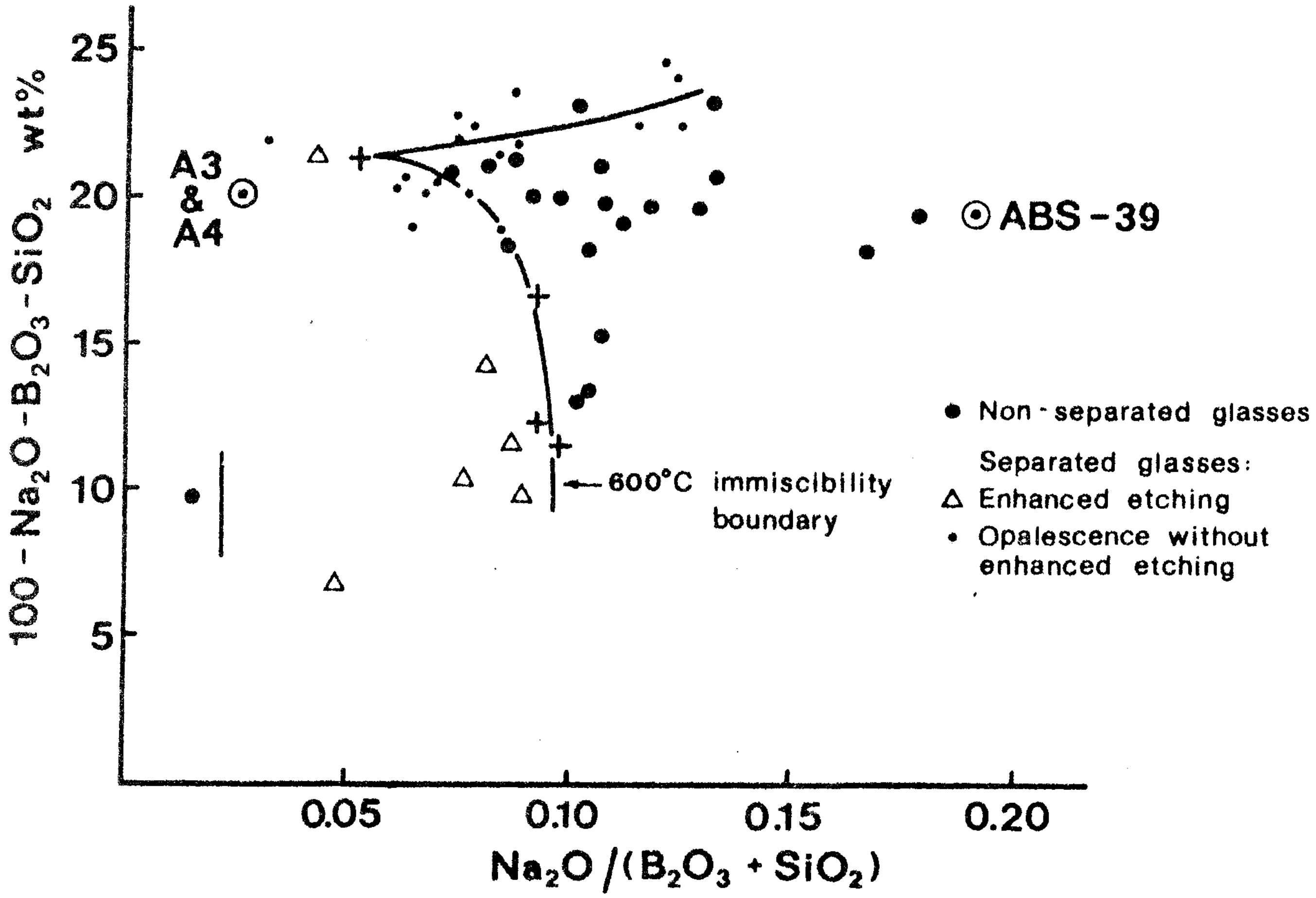

Fig. 15. Variation of the 600°C immiscibility isotherm for glasses in the ABS-39 system as a function of the content of simulated fission products and other additional components. Revised version of Fig. 16B.

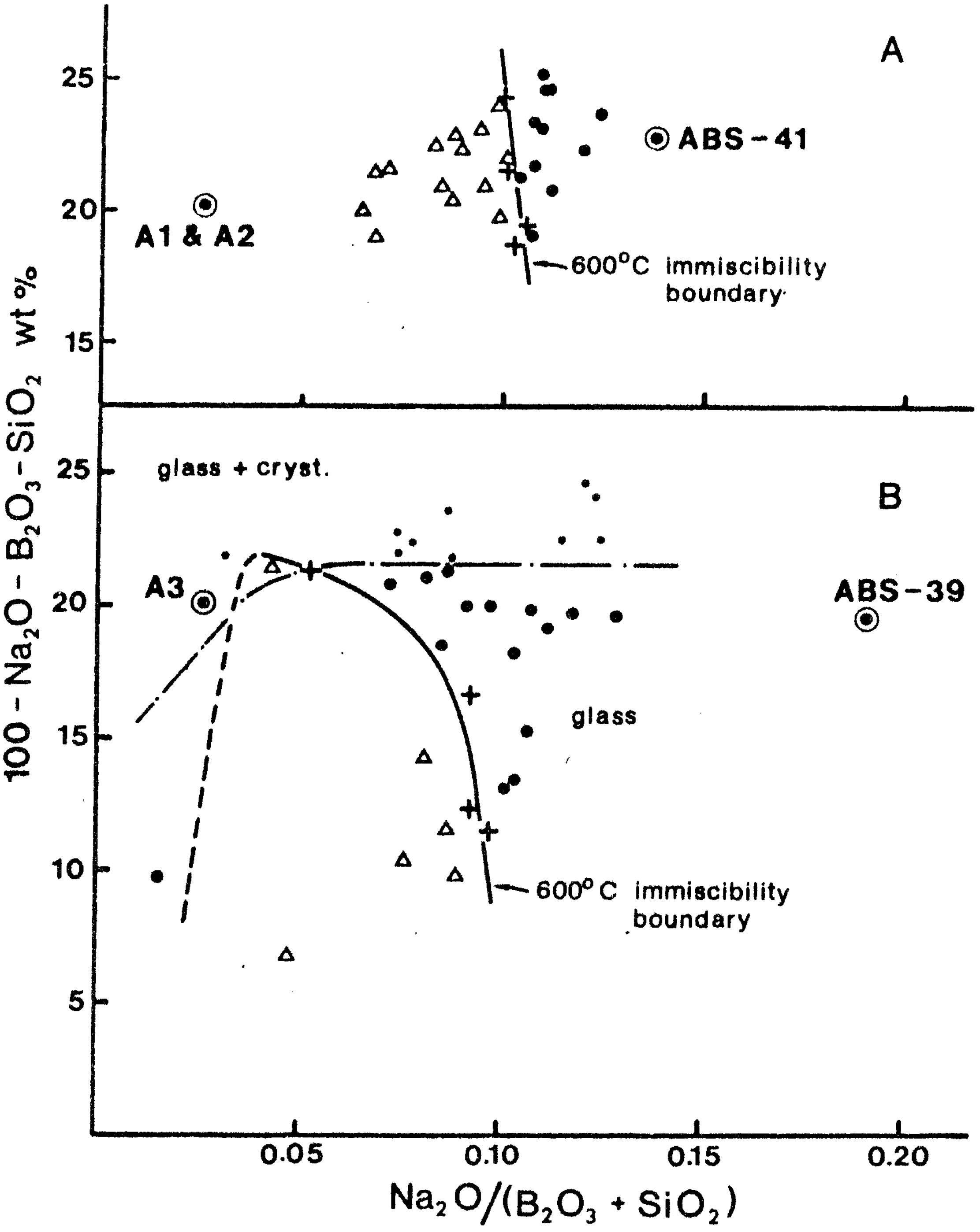

Fig. 16. Variation of the 600°C immiscibility isotherm for glasses in the ABS-41 (A) and ABS-39 (B) system as a function of the content of simulated fission products and other additional components as given by Engell and Roed (in press). For explanation of symbols, see Fig. 15.

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