JOURNAL OF MATERIALS SCIENCE 10 (1975) 777–790

High-temperature metallizing

Part 2 *The effect of experimental variables on the structure of seals to debased aluminas*

M. E. TWENTYMAN, P. POPPER
British Ceramic Research Association, Penkhull, Stoke-on-Trent, UK

Metal–ceramic seals have been prepared with six debased aluminas using molybdenum metallizing paints and with one alumina using tungsten paints. The metallized layers in strong seals (ASTM tensile strength > 55 MN m^{-2}) consisted of a dense metal/glass composite layer which was formed by glass migrating from the alumina into the metallizing layer. Observations on the glass migration agree with the predictions made from the hypothesis suggested in Part 1. The glass migration is favoured by a high metallizing temperature, large grain size of the alumina relative to the particle size of the metallizing, and the use of a reducing atmosphere containing a suitable concentration of water vapour. (The dew point required to form optimum conditions in H_2 is higher than that for 90% N_2 + 10% H_2.) Addition of MnO_2 to the metallizing paint did not appear to aid glass migration nor increase seal strengths. The metallizing layer in weak seals contained comparatively little glass except on one coarse-grained alumina which had been metallized at relatively low temperature (1400° C). This metallizing layer was well filled with glass and tensile failure occurred in the alumina at < 44 MN m^{-2}. Increasing the metallizing temperature to 1500° C increased the strength of the seals to 70 MN m^{-2} without causing any apparent change to the metallizing layer.

1. Introduction

In Part 1 of this work the importance of glass migration in developing strong metal–ceramic seals was discussed and a hypothesis was proposed which describes the migration in terms of a capillary flow mechanism. It was deduced from the hypothesis that strong seals should be produced most easily if the average size of the glass-filled pores in the alumina are greater than the pores present in the unfired metallizing layer. If the average size of the glass-filled pores is equal to the average size of the pores in the metallizing layer, the amount of glass migrating into the metallizing will become more sensitive to the effect of the other variables, such as temperature and furnace atmosphere. When the alumina is of very fine texture, glass migration may be so slight that it may become impossible to produce satisfactory seals. Experiments were, therefore, conducted to cover these three regions.

2. Experimental details

2.1. Metallizing paint preparation

Molybdenum powders were obtained from four commercial suppliers: Lamp Metals, Murex Ltd, Hermann Starck (Berlin) and the Tungsten Manufacturing Co. All four powders were of similar average size (diameter ~ 5 μm); only that supplied by Lamp Metals was used to prepare metallizing paints. As much finer molybdenum powders did not appear to be available commercially, several batches of fine molybdenum powder were produced by the reduction of molybdenum trioxide (MoO_3), using conditions similar to those described by Bender [1]. The batches were then mixed to form a single large batch.

Before mixing the powders into paints, both powders were milled in a stainless steel mill (90 mm diameter × 95 mm) with a charge of 225 g Mo, 300 ml acetone and 500 g carbon steel balls. Scanning electron microscope (SEM) examination of the Lamp Metals molybdenum, after increasing milling times, showed that the milling first broke down agglomerates and then tended to form flakes which gradually increased in diameter up to 10 to 20 μm. The tap density of the powder before milling was ~ 35% of theoretical, and passed through a maximum of

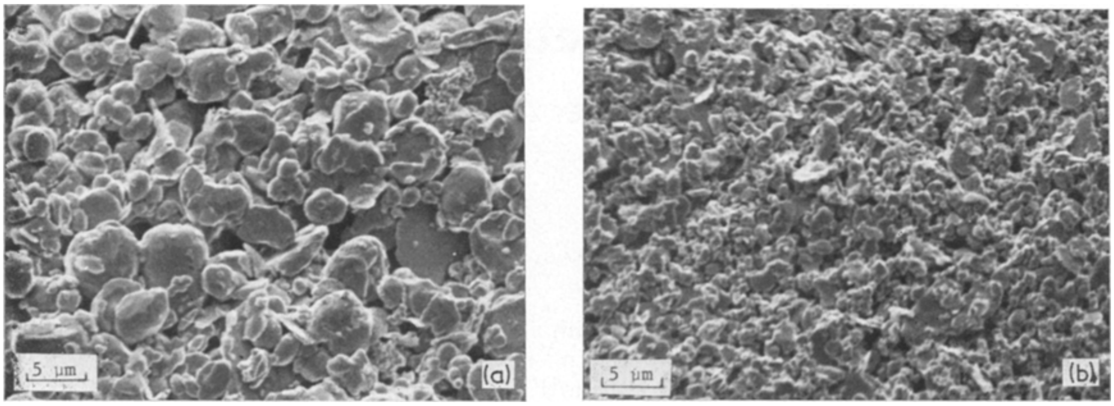

Figure 1 Unfired paints (SEM): (a) coarse molybdenum, (b) fired molybdenum.

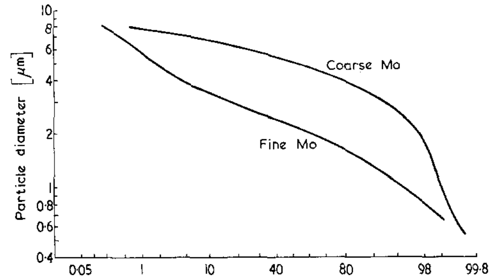

Figure 2 Particle size distribution of two molybdenum paints.

~ 50% after 3 days milling. After 7 days the density decreased to less than 35%. A milling time of 3 days was, therefore, used.

Milling of the molybdenum prepared by reduction of the molybdenum trioxide resulted in even faster formation of flakes, and milling was therefore limited to 24 h. The tap density of the milled powder was 40% of theoretical.

Paints were prepared from both types of molybdenum, either by ball milling the molybdenum powder (50 g) with a 5% solution of ethyl cellulose (N300 Hercules Powder Co.) in 2-ethoxyethanol (30 ml), or by mixing on a triple-roll mill. Fresh batches of paint were prepared every three to four months as the paints tended to stiffen and finally gel. The paints were applied to the alumina ceramic with a fine brush. The weight of paint applied was controlled so that it was 8 to 10 mg cm^{-2}. This gave an average thickness of the metallized layer of 20 to 25 µm. Typical scanning electron photomicrographs of the unfired paints are shown in Fig. 1, and particle size distributions, determined by Coulter counter are shown in Fig. 2.

A few experiments were also done with tungsten powders. Three grades of powder (D, T and K) were obtained from Murex Ltd and milled for 24 h before mixing into paints. Comparison of the unfired tungsten and molybdenum paint films by SEM showed that the average particle size of the grade D tungsten was roughly equal to the Lamp Metals molybdenum, and the grade T tungsten roughly equivalent to the fine molybdenum. The grade K was slightly finer than both the fine molybdenum and the grade T.

2.2. Preparation of the seals

Two types of test samples were used to assess the strength of seals. The first was a simple peel test in which a thin strip of copper (14 mm × 10 mm × 1 mm) was brazed on to a side of an alumina rod (12 mm × 10 mm × 10 mm) and the seal strength was assessed by attempting to peel off the copper strip with a pair of pliers. The second test was the ASTM Tensile Test [2] which gives a quantitative measure of seal strength.

The metallizing on both types of test sample was fired in a horizontal alumina tube (50 mm i.d.) heated with silicon carbide elements. The peel test samples were contained in an alumina boat, which was pushed into the hot zone of the furnace tube with a long alumina thermocouple sheath, left to soak for 30 min, and pushed out of the furnace. A typical temperature-time profile is shown in Fig. 3.

To accommodate the more bulky ASTM samples, two cylindrical brass cooling chambers (50 mm i.d. × 250 mm) were fixed on the ends of the alumina tube and a molybdenum boat (200 mm long) containing six samples was used. The boat was connected by a braided molybdenum

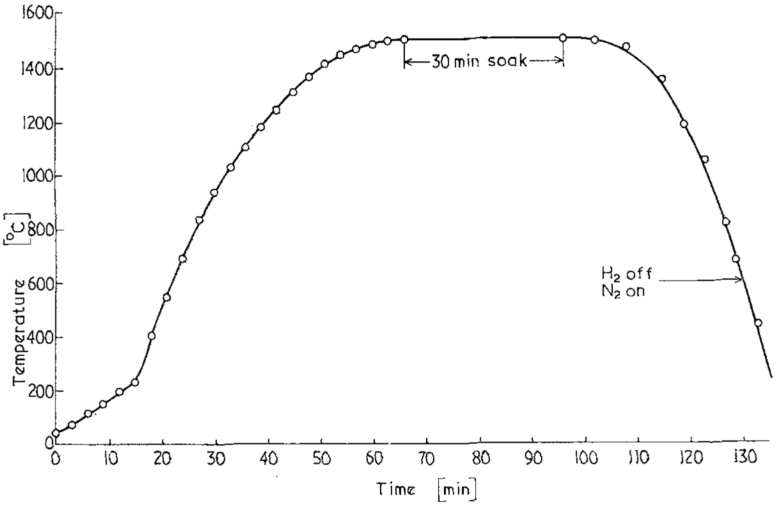

Figure 3 Temperature-time profile during the firing of the metallizing.

wire (six strands, 0.3 mm diameter) to a drive pully and electric motor. A uniform drive rate moved the samples through the furnace (1.2 m) in 3 h. The residence time for each sample in the hot zone is estimated to be 15 to 20 min.

The humidity in the furnace tube was controlled by passing the furnace gases (90% N_2 + 10% H_2, or 100% H_2) over boiling water, and then by condensing excess water vapour in a condenser controlled at the required dew-point temperature, e.g. 40, 20 or 3°C. Condensation of the water vapour was prevented by using water at ~ 50°C to cool the end-caps. This also served to prevent damage to the rubber O-ring seals, which were used to make the furnace tube gas-tight. The furnace temperature was controlled by a Thorn Imp control unit (0 to 1600°C) with a Pt/13% Rh thermocouple touching the outside of the furnace tube. The maximum temperature inside the tube was measured by a similar thermocouple contained in an alumina sheath which passed through the brass end-plate.

After firing, both types of metallized samples were coated with a thin layer of nickel oxide paint (Wesgo Type 532) and refired in dry hydrogen (dew point ~ − 20°C) for 30 min at 950°C. This formed a thin layer of sintered nickel (Fig. 4) which helps the braze to wet the metallizing.*

After coating with nickel, the samples were brazed in dry hydrogen for 5 to 10 min at approximately 800°C, using Ag/Cu eutectic alloy foil (0.080 mm thick).

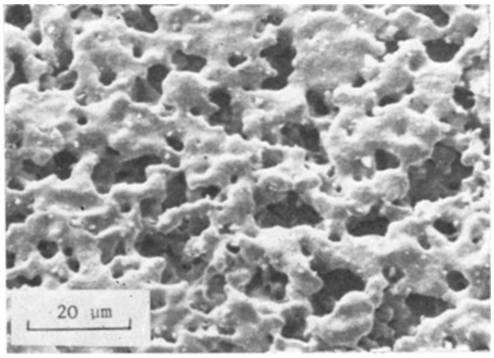

Figure 4 NiO paint reduced in hydrogen at 950°C, (SEM).

3. Effect of furnace atmosphere and metallizing temperature on peel strengths

3.1. Characterization of alumina

The results in this section were all obtained on alumina X. A typical chemical analysis of this alumina has been described by Binns [3]: Al_2O_3, 94.10%; SiO_2, 2.56%; CaO, 2.15%; MgO, 0.09%; Cr_2O_3, 0.15%; Fe_2O_3, 0.11%; Na_2O, 0.29%; K_2O, 0.06%; SnO, 0.30%. A photomicrograph of a polished sample of the alumina used for metallizing is shown in Fig. 5, and the average grain intercept is approximately 8 µm.

---

*Some seals were also made using an electroplated layer of nickel but this did not appear to have any effect on the seal strength, when compared with seals made with reduced nickel oxide coating. These experiments were, therefore, discontinued and nickel oxide paints were used throughout.

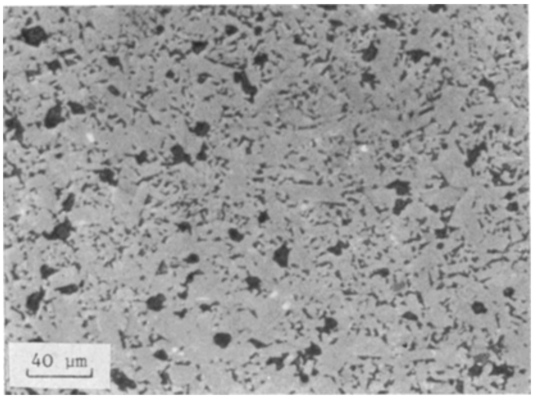

Figure 5 Photomicrograph of alumina X (reflected light).

The average bulk density of the samples was 3.62 mg m^{-3} and the percentage glass content and porosity determined by optical microscopy were 10.6 and 7.2% respectively.*

3.2. Results for metallizing fired in a hydrogen atmosphere

The strength of the seals were assessed qualitatively by gripping the copper strip with a pair of pliers and attempting to peel it from the alumina. Strong seals failed by the copper breaking, while weak seals peeled easily, and usually left a clean alumina surface. Sections of the seal region were examined by optical microscopy either by sectioning the unpeeled seal (strong samples) or by sectioning the copper strip (weak samples). The results are shown in Tables I and II. Some typical seal structures are shown in Fig. 6. In all cases the weak seals showed a metallizing layer which was extensively penetrated by braze, e.g. Fig. 6c, while the strong seals showed metallizing layers which consisted of a glass/metal composite layer which was either free of braze penetration, or contained metallizing which was penetrated by braze only in a few isolated patches. With the coarser paint, in which many of the pores in the metallizing are not much smaller than the glass-filled pores in the alumina, the strong seals were produced only in a narrow range of conditions, i.e. high dew point and high temperature. With the finer grained paint, the metallizing temperature required to produce strong seals was not as high and the dew point was less critical. Another difference between the fine- and the coarse-grained paints is that even in the most favourable conditions for the coarse-grained paint a small amount of braze penetrated the metallizing, thus indicating that it was not completely full of glass.

TABLE I The effect of temperature and furnace humidity on seal structures on alumina X, coarse-grained Mo paint

Metallizing temperature (°C)	Dew point, H_2		
	40°C	20°C	3°C
1500	S*	M*	W*
1450	M	W	W

*Observations based on three to four seal structures obtained in two firings.
S = Strong seals.
M = Marginal, some seals strong, other weak.
W = Weak seals.

TABLE II Effect of temperature and furnace humidity on seal structures on alumina X, fine-grained Mo paint

Metallizing temperature (°C)	Dew point, H_2		
	40°C	20°C	3°C
1500	n.m.	S	S
1450	n.m.	S	W
1410	n.m.	S	W
1375	S	S	n.m.
1330	W	n.m.	n.m.

S = strong seals. W = weak seals.
n.m. = not measured.

TABLE III EPMA measurements of Al_2O_3:SiO_2 ratio at three points in each metallized layer

Metallizing temperature (°C)	Al_2O_3:SiO_2 (wt:wt) (1)	(2)	(3)
1375	0.98	1.02	0.93
1500	0.99	1.01	0.95

To check whether there was any difference in the composition of the glass present in the metallizing fired at 1375°C and that fired at 1500°C, the Al_2O_3:SiO_2 ratio of the glass was measured by EPMA at three points in the metallized layers (see Table III).

No difference between the amount of Al_2O_3 present in the glass in the metallizing fired at 1375°C and that fired at 1500°C is detectable.

---

*Determined by point count analysis.

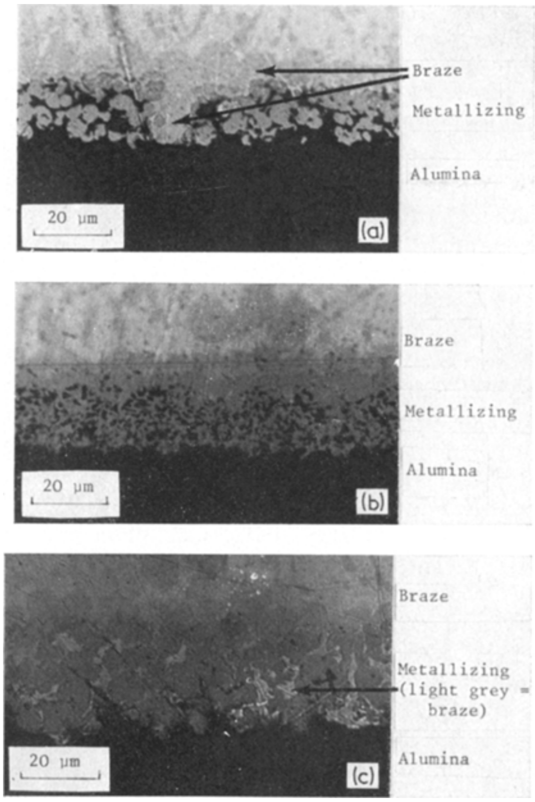

Figure 6 Sections of seals: (a) strong seal using coarse molybdenum fired on alumina X at 1500° C in hydrogen, dew point 40° C; (b) strong seal using fine molybdenum fired on alumina X at 1375° C in hydrogen, dew point 20° C; (c) weak seal using coarse molybdenum fired on alumina X at 1500° C in hydrogen, dew point 3° C.

A noticeable feature of the alumina samples metallized at 1375 or 1400° C was that their surfaces became greyish and blotchy similar to the effect previously described by Reed [4].

A few peel tests were also carried out on the paints prepared from the three grades of tungsten powder. The paints were fired at 1400° C and dew point 20° C and then nickel coated and brazed in the same way as for the molybdenum metallizing. The coarse, grade D tungsten formed weak seals. The metallizing contained little glass and was extensively penetrated by braze. The very fine, grade K tungsten also formed weak seals and consisted of very densely sintered globules or patches of tungsten interspersed with patches of braze (Fig. 7). The grade T tungsten formed strong seals which consisted of a tungsten/glass composite structure with slight penetration of braze.

A very dramatic effect of the furnace humidity on glass migration was obtained by firing the coarse-grained molybdenum paint on a sample of alumina at 1500° C, dew point 40° C, and then changing the gas to dry hydrogen for a

TABLE IV Effect of temperature and furnace humidity on seal structures on alumina X, coarse-grained Mo paint

Metallizing temperature (° C)	Dew point, 90% N_2 + 10% H_2		
	40° C	20° C	3° C
1550	P/M	S/M	S/M
1500	P/M	S/M	S/M
1450	P/M	P/M	P/M

S = strong seals; samples failed by tearing copper.
P = seals failed by peeling of copper strip.
M = texture consists of good regions of glass + Mo but slight braze penetration in some regions.

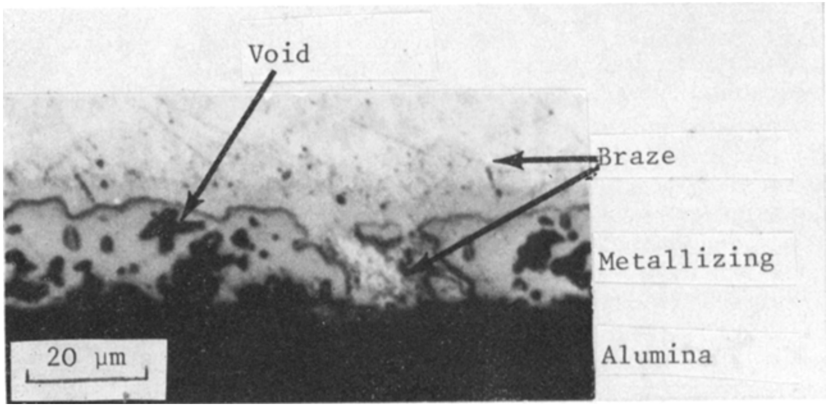

Figure 7 Section of a seal using grade K tungsten fired on alumina X at 1400° C in hydrogen, dew point 20° C.

Figure 8 Surface of metallizing fired on alumina X first in wet hydrogen and then in dry hydrogen (SEM).

TABLE V Effect of temperature and furnace humidity on seal structures on alumina X, fine-grained Mo paint

Metallizing temperature (°C)	Dew point, $90\%\ N_3 + 10\%\ H_3$		
	40°C	20°C	3°C
1550	S/G	S/G	S/G
1500	S/G	S/G	S/G
1450	S/M	S/G	S/G
1400	P/M	S/G	S/G

S = strong seal; copper strip broke.
P = seals failed by peeling of copper strip.
G = good texture of glass and molybdenum with no braze penetration.
M = texture consists of good regions of glass + Mo but slight braze penetration.

further $\frac{1}{2}$ h soak. Examination of the samples after cooling showed that globules of glass had been forced out of the metallizing, presumably by an increase in the glass/Mo contact angle to > 90°. The glass was partially devitrified as shown in Fig. 8.

3.3. Results for metallizing fired in a nitrogen/hydrogen atmosphere

The samples were prepared and tested in the same way as those fired in a hydrogen atmosphere. The results are shown in Tables IV and V. The maximum firing temperature was extended to 1550°C. A striking feature of these results is that the optimum humidities are different from those in 100% H_2. Thus, a dew point of 3°C gives stronger seals than a dew point of 40°C. The overall comparison of the performances of the fine and coarse-grained paints shows the same trend as in 100% H_2, in that the fine-grained paint produces strong seals over greater ranges of temperature and humidity than the coarse-grained paint. Using the coarse-grained paint the quality of the metallizing fired at 1550°C appeared little different from samples fired at 1500°C, as both sets of samples tended to have a few patches of braze in the metallizing. Strong samples of the fine-grained metallizing were not penetrated by braze, except for samples fired at 1450°C, dew point 40°C.

The effect of the high dew point, 40°C in, generally producing poor-quality metallizing, was rather surprising. It indicated that the molybdenum/glass contact angle might pass through a minimum at a lower dew point and then begin to rise again. Contact angles in the 90% N_2 + 10% H_2 atmosphere were, therefore, measured using the same glass (Al_2O_3, 39.5%; SiO_2, 30.6%; CaO, 30.0%) as described in Part 1. The results for dew points of 3 and 20°C showed similar trends to those observed in 100% H_2, (Part 1, Fig. 15). However, at 40°C dew point in 90% N_2 + 10% H_2 the contact angles could not be measured as there was extensive volatilization of molybdenum, and an irregular shaped globule of glass was formed. Using nominally dry 90% N_2 + 10% H_2 the contact angles dropped rather more sharply with increasing temperature than the corresponding values in 100% H_2.

4. Comparison of the tensile strengths of ASTM test samples using a coarse- and fine-grained metallizing paint

4.1. Characterization of the aluminas

Five aluminas were used in these experiments and were obtained from four alumina manufacturers. Samples were examined by optical microscopy, dye testing, density measurement, chemical analysis and X-ray diffraction. Results are listed in Tables VI and VII.

Noticeable features of the aluminas are that alumina A has a very low density and Fig. 9a, shows that it contains an unusually high proportion of pores. Alumina B appeared variable as indicated by a relatively wide range of densities and by the microscopic examination of two samples (Fig. 9b and c). The glass content measured in one of these samples (16%) appears abnormally high and the texture of this sample, shown in Fig. 9b, is more like a 90% Al_2O_3. Fig. 9c shows another sample in which there is less glass present and the grain size is smaller.

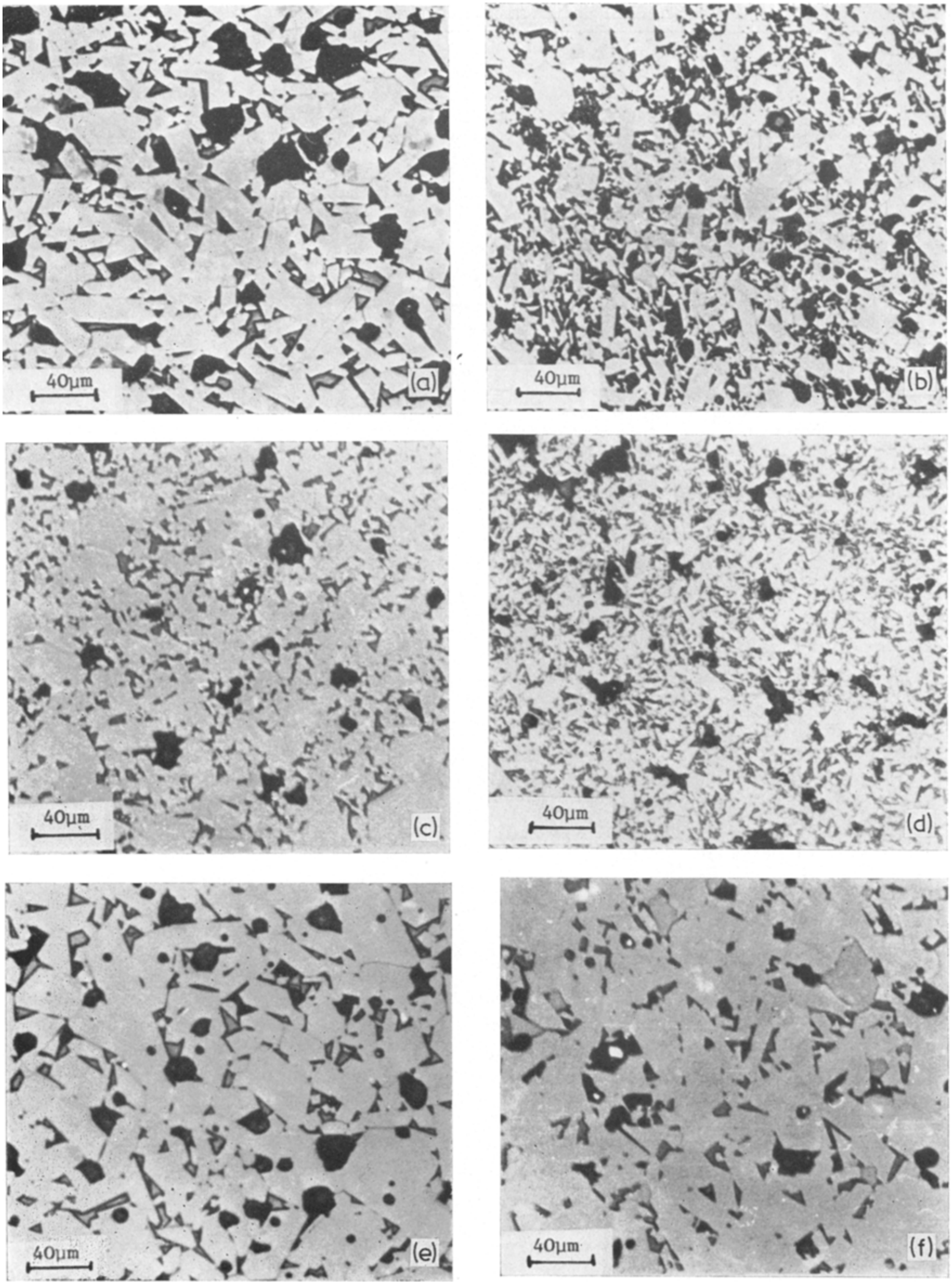

Figure 9 Photomicrographs of aluminas (reflected light): (a) alumina A; (b) alumina B, high glass; (c) alumina B, low glass; (d) alumina C; (e) alumina D; (f) alumina E. Black = void, dark grey = glass, pale grey = Al_2O_3.

TABLE VI Characterization of ASTM alumina samples by microscopy and density determination

Alumina	Nominal Al_2O_3 content (%)	Nominal density (mg m^{-3})	Density range (five samples) (mg m^{-3})	Microscopic examination (single specimens)		
				Glass* (%)	Porosity* (%)	Mean grain intercept (μm)
A	95	3.68	3.45 ± 0.00	10.2	18.0	13.3
B	94.0	3.67	3.54-3.62	16.2	6.8	5.5
				8.5	6.8	8.5
C	95	3.76	3.68-3.69	11.2	8.1	5.5
				9.5	8.0	5.8
D	97.6	3.76	3.70-3.75	6.9	4.1	20.4
E	97.5	3.79	3.77-3.78	5.3	6.6	18.5

*Determined by a point-count analysis.

TABLE VII Chemical and X-ray analyses of ASTM alumina samples

Alumina	Nominal Al_2O_3 content (%)	Chemical analysis					X-ray diffraction analysis secondary phases
		% Al_2O_3	Main glass-forming components				
			% SiO_2	% CaO	% MgO	% ZrO_2	
A	95	94.5	3.19	0.73	0.71	0.63	Trace ZrO_2 + trace $CaO.Al_2O_3.2SiO_2$
B	94	94.2	4.20	0.78	0.55	n.d.*	None
C	95	94.8	2.66	2.00	0.03	n.d.	None
D	97.6	96.8	1.55	1.17	0.17	n.d.	Trace $2CaO.Al_2O_3.SiO_2$
E	97.5	96.7	1.68	0.47	0.94	n.d.	Little $MgO.Al_2O_3$, trace $CaO.Al_2O_3.2SiO_2$

*Not determined.

Alumina C was very badly finished and the base of the samples tended to be very rough, and some samples were rejected because they showed extensive dye absorption. Photomicrographs of aluminas C, D and E are shown in Fig. 9d to f.

4.2. Comparison of the seal strength of metallizing fired at 1500° C

The results for metallizing fired at 1500° C are shown in Table VIII. Good seal structures and comparatively high-strength seals were produced with both the coarse- and fine-grained metallizing on the two coarse-grained aluminas A and D, e.g. Figs. 10 and 11, but only the fine-grained metallizing paint produced strong seals to the fine-grained aluminas. Alumina B behaved like a fine-grained alumina. Alumina E was different to the other aluminas as, although it is coarse, weak seals were produced with both the coarse- and fine-grained metallizing paints, and there was very little glass present in the metallized layers. The failure to obtain strong seals with alumina E was not unexpected as the manufacturers suggested a metallizing temperature of about 1650° C. The failure of the glass to migrate is probably connected with the relatively low concentration of flux present in this alumina and its extensive devitrification to spinel ($MgO.Al_2O_3$).

In general, the strong seals were vacuum tight whereas the weak seals tended to leak. The tensile failure of the weak seals tended to occur at the Mo/Al_2O_3 interface, while the strong seals failed in the alumina about 1 mm from the Mo/Al_2O_3 interface. The seals to alumina A were unusual in that most of the sample broke in the neck of the alumina test-piece. This was presumably because the alumina was made weak by its high porosity.

Alumina B appeared to be just on the borderline for giving satisfactory metallizing with the fine-grained metallizing paint as although the strength was satisfactory, there was considerable penetration of braze into parts of the metallizing, and four out of five samples leaked. The results were more consistent than expected in view of the variability of this batch of alumina.

TABLE VIII ASTM tensile tests, Cu/Ag braze (metallizing fired at 1500°C in 90% N_2 + 10% H_2, dew point 20°C)

Alumina	Mean grain intercept (µm)	ASTM tensile strength*				Comments
		Fine Mo paint median diameter 2 µm		Coarse Mo paint median diameter 5 µm		
		(lbf in^{-2})	(MN m^{-2})	(lbf in^{-2})	(MN m^{-2})	
A	13.3	8 580 ±1 740	59.2 ±12.0	8 020 ±1 290	55.3 ± 8.9	Weak Al_2O_3, neck breaks, good metallizing textures
B	5.5, 8.5	10 600 ±2 300	73.1 ±15.9	4 250 ± 820	29.3 ± 5.6	Fine: some good textures + some braze pen. Coarse: metallizing soaked with braze
C	5.5, 5.8	10 190 ±1 510	70.3 ±10.4	7 220 ±1 130	49.7 ± 7.8	Fine: good texture Coarse: some braze pen.
D	20.4	10 240 ±2 980	70.6 ±0.5	10 040 ±1 380	71.6 ± 9.5	Good textures
E†	18.5	5 220‡ ±1 220	36.0‡ ± 8.4	1 670§ ± 98	11.5§ ± 5.5	Fine: very dense Mo, little glass Coarse: metallizing soaked with braze

*Mean for five seals ± standard deviation, except where indicated.
†Fired in 100% H_2, dew point 40°C.
‡Mean for four seals.
§Mean for three seals.

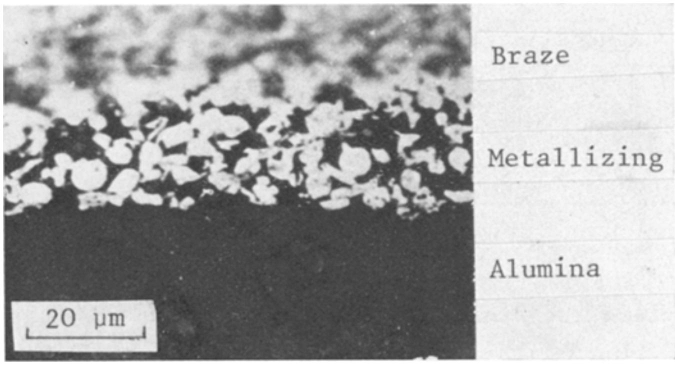

Figure 10 Section of a seal to an ASTM sample of alumina A, coarse molybdenum.

4.3. The effect of metallizing temperature on seal strengths

In addition to the sample fired at 1500°C, metallized samples of alumina D were also fired at 1400 and 1450°C. The results are shown in Table IX. Dense glass/Mo metallizing layers were produced with the fine-grained paint at 1400 and 1450°C, but the strengths were considerably less than those produced at 1500°C, even though the failure occurred just within the alumina. The coarse-grained metallizing also formed weaker seals when fired at 1400 and 1450°C, but this was caused by the inadequate migration of glass into the metallizing.

5. Effect of refiring of alumina on its metallizing properties

In addition to the alumina samples which have

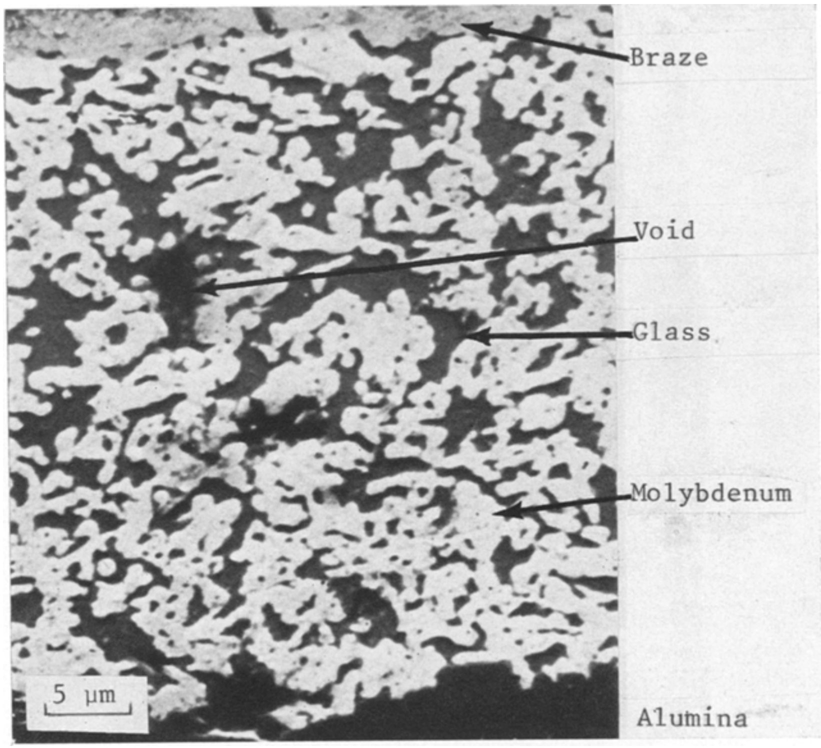

Figure 11 Section a seal to an ASTM sample of alumina D, fine Mo (SEM, polished section).

TABLE IX Effect of metallizing temperature on the strength of seals to alumina D (samples fired in 90% N_2 + 10% H_2, dew point 20° C)

Temperature (° C)	ASTM tensile strength fine Mo		Region of failure	ASTM tensile strength coarse Mo		Region of failure
	(lbf in^{-2})	(MN m^{-2})		(lbf in^{-2})	(MN m^{-2})	
1400	6 300*	43.4	Al_2O_3	3 280*	22.6	Mo/Al_2O_3
1450	7 700*	53.1	Al_2O_3	5 240*	36.1	$Mo/Al_2O_3 + Al_2O_3$
1500	10 240†	70.6	Al_2O_3 + Mo	10 400†	71.6	Al_2O_3 + Mo

*Mean of three samples.
†Mean of five samples.

already been described, several samples of alumina were received which had been taken from batches which some valve manufacturers had not been able to metallize satisfactorily. Previous batches had been metallized satisfactorily (without difficulty) at temperatures below 1550° C. One batch was of alumina A, two were alumina and one alumina X. In all cases the average grain intercepts were < 6 µm. Attempts to metallize them at 1500° C with either the coarse- or fine-grained metallizing paint, described in Section 2.1, also produced weak seals with little glass in the metallizing layer. With the coarse-grained paint, the metallizing was extensively penetrated by braze, while the fine-grained metallizing showed excessive (metal–metal) sintering, and had poor adhesion. As it is believed that the difficulty in metallizing these batches of alumina is caused primarily by their small grain size, an attempt was made to establish the type of refiring conditions which are necessary to increase the grain size of a typical debased alumina. Experiments were done on a second batch of ASTM samples of alumina B. The grain size was again small with an average grain intercept of 6.0 µm, 7.6% glass and 7.0% pores. Unlike the first batch of ASTM alumina B samples the density was consistent at 3.62 to

TABLE X Effect of heat-treatment on the average grain intercept of alumina B (batch 2) and on strength of seals (coarse Mo, fired at 1500°C in 90% N_2 + 10% H_2, dew point 20°C)

Heat-treatment			Mean grain intercept (μm)	ASTM tensile strength		Region of failure
Time (h)	Temperature (°C)	Atm		(lbf in^{-2})	(MN m^{-2})	
as-received		—	6.0	5010	34.5	Mo + Mo/Al_2O_3
21	1500	90% N_2 + 10% H_2	7.0	5940	41.0	Mo + Mo/Al_2O_3
7	180	air	7.7	4980	34.3	Mo + Mo/Al_2O_3
25	1740	air	21.5	7350	50.7	Mo + Al_2O_3 + braze

TABLE XI Comparison of the ASTM tensile strengths of seals to alumina B (batch 2) using Mo and Mo/Mn paints

No. of samples	Paint composition	Metallizing tempetature (°C)	Mean seal strength	
			(lbf in^{-2})	(MN m^{-2})
2	100% Mo	1500	5010	34.5
2	100% Mo	1550	4580	31.6
1	90% Mo + 10% MnO_2	1500	3300	22.8
2	90% Mo + 10% MnO_2	1550	3520	24.3

*Samples fired in 90% N_2 + 10% H_2, dew point 20°C.

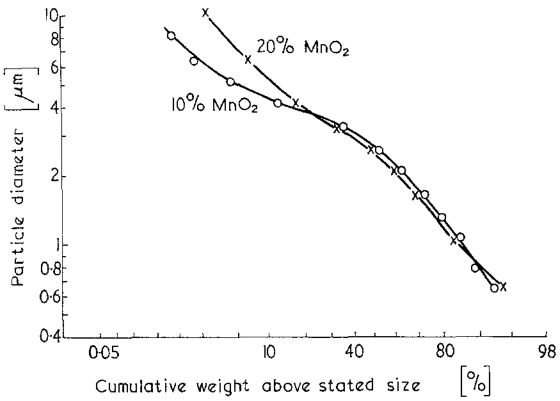

Figure 12 Particle size distribution of two moly/manganese paints.

3.63 mg m^{-2}.

The first refiring experiments were tried in the metallizing furnace but as this proved inadequate, further firings were done in a gas-fired furnace. The average grain intercepts of the refired samples are shown in Table X, together with ASTM tensile strengths of samples metallized with the coarse-grained metallizing paint. No significant increase in seal strength occurred when the average grain intercept was increased up to 7.0 or 7.7 μm, and the metallizing layers contained little glass. When the grain size was increased to 21.5 μm, the seal strength increased and the metallizing layer was well filled with glass. The seal strengths however were slightly low, probably because of a rather large number of bubbles in the braze. The cause of the bad brazing was not discovered.

6. The influence of manganese dioxide on seal strengths

6.1. Description of the metallizing paints

SEM examination of the manganese dioxide powder (BDH technical grade) indicated that it was rather coarse and it was therefore premilled before making up paints with the molybdenum. Two paints were prepared containing 20 wt % of MnO_2 and 80% of premilled molybdenum (Lamp Metals), and 10 wt % MnO_2 and 90% molybdenum. The particle size distributions of the two paints measured by the Coulter counter are shown in Fig. 12.

6.2. Results of the peel tests

These tests were again done on alumina X. Each paint was fired in hydrogen at 1500°C, dew point 40°C. All samples were weak after brazing and microscopic examination showed that the metallizing was extensively penetrated by braze. Failure took place mainly at the Mo/Al_2O_3 interface or in the metallizing. There was no spinel at the Mo/Al_2O_3 interface and less glass in the metallizing layer than in the corresponding samples previously prepared from 100% Mo.

The metallizing paint containing 10% MnO_2 was also fired in 90% N_2 + 10% H_2 at 1500°C and dew points of 3, 20, and 40°C. All the seals were weak. Thus on alumina X, both the paints containing manganese dioxide were inferior to the equivalent paint containing molybdenum alone.

6.3. ASTM tensile tests

The second batch of alumina B was used for these tests (average grain intercept, 6.0 μm). The results for the 100% coarse molybdenum paint and the corresponding paint containing 10% MnO_2 are shown in Table XI for two firing temperatures. The results for the 100% Mo were similar to the results on the first batch of alumina B and showed low strengths. No improvement was obtained by adding the MnO_2 and if anything the results were worse. Samples fired at 1550°C were not appreciably stronger than those fired at 1500°C.

7. Discussion

The results confirm previous findings that when paints containing molybdenum or tungsten powders are fired on a debased alumina the strongest adhesion is developed when glass migrates from the alumina into the metallizing layer and forms a dense glass/Mo or glass/W composite structure. The glass appears to have two functions: one is to provide adhesion between the molybdenum (or tungsten) and the alumina, and the other is to strengthen the metallizing layer by filling up the pores and forming a strong composite layer. Extensive metal–metal sintering of the molybdenum or tungsten particles does not appear to be essential to form a strong seal, and glass migration tends to prevent this. Thus, when the glass did not migrate into the metallizing layer, metal–metal sintering increased. Although quite densely sintered metal layers, which were very coherent, were produced in this way, they had poor adhesion to the alumina. A highly porous metallizing layer forms a weak seal because of the low strength of the metallizing layer itself, or, if the pores are filled with braze, fails because of poor adhesion to the alumina. There is little evidence that strong adhesion is developed between molybdenum (or tungsten) and alumina, other than that which occurs via bonding with the glassy phase. This applies specifically to the high-temperature metallizing method and not to the development of metal/alumina bonds using other methods (e.g. MoO_3).

According to the predictions made from the glass migration hypothesis, which were described in Part 1 of this work, glass migration should be most favoured by applying a metallizing layer in which the pores are considerably smaller than the glass-filled pores in the alumina. If the two sets of pores become similar in size, less glass will migrate into the metallizing at the usual metallizing temperature and much higher temperatures will be required to completely fill the pores with glass. As the pore sizes are roughly related to grain size, glass should migrate more readily from a coarse-grained alumina than from a fine-grained alumina, and into a fine-grained metallizing layer more readily than into a coarse-grained metallizing layer.

Apart from results on alumina E which does not appear to contain an easily meltable "glassy phase", observations of the glass migration from other aluminas agree well with the behaviour which was predicted. Thus, both the coarse- and fine-grained metallizing layers were well filled with glass after firing them at 1500°C on the coarse-grained aluminas A, D, and B (refired), but only the fine-grained metallizing was completely filled with glass when the two grades of metallizing were fired on the somewhat finer-grained aluminas X and C.

On the very-fine-grained aluminas (mean grain intercept < 6 μm) which were received from the valve manufacturers, even the fine-grained metallizing layers failed to fill completely with glass. Alumina B (batches 1 and 2) appeared to be just on the borderline for being metallizable. Glass also filled the fine-grained metallizing on alumina X and D at lower temperatures than for the coarse-grained metallizing, and for alumina X the glass migration into the fine-grained metallizing was satisfactory over a slightly wider range of furnace atmosphere.

An unusual feature of the results was the rather low tensile strengths which were obtained when the fine-grained metallizing on alumina D was fired at 1400 or 1450°C, despite the formation of a good seal structure. Failure occurred just inside the alumina about 250 μm from the Mo/Al_2O_3 interface, indicating a weakness in the alumina itself. This could result from damage which is produced by grinding the alumina during manufacture of the test samples, and which is not healed satisfactorily at the lower metallizing temperature, or could result from a weakness produced by the metallizing process such as the selective emptying of the glass-filled pores near the alumina surface. At higher metallizing temperatures it is possible that the glass is drawn more evenly from throughout the alumina sample, and such weaknesses are, therefore, avoided.

Observations of the metallizing on alumina X fired in both hydrogen and 90% N_2 + 10% H_2 show that the addition of water vapour to the atmosphere aids the glass migration, as expected from consideration of its effect in lowering the glass/Mo contact angle. However, trends which are hardly noticeable in the contact angles appear to become magnified in their effect on the glass migration. (This may arise from the difference in composition between the glass in alumina X and that used in the contact angle measurements, or could be a real effect for all glasses.) Thus in the contact angle measurements which were described in Part 1, it was observed that the glass/Mo contact angles in hydrogen were only slightly lower at low temperatures when the dew point was 20°C, than when it was 3°C. However, when the glass migration from alumina X was compared under the same conditions the differences were considerable. Very little glass migrated into the fine-grained metallizing at 3°C dew point, except when the metallizing temperature was raised to 1500°C, whereas glass migrated readily at only 1375°C when the dew point was 20°C.

Another difference which is not fully brought out by the contact angle measurements is that a smaller concentration of water vapour is required in 90% N_2 + 10% H_2 to improve the wetting between the glass and the molybdenum, than is required in hydrogen. Although glass migration does not readily take place at 3°C dew point in hydrogen, this dew point gives good conditions in 90% N_2 + 10% H_2. The more marked effect of low concentrations of water vapour in improving the wetting of the molybdenum by glass in 90% N_2 + 10% H_2 could be related to the higher oxidation potentials (pH_2O/pH_2) which are produced, compared with 100% H_2, and which may affect the surface energy of the molybdenum. A dew point of 40°C in 90% N_2 + 10% H_2 is too high for producing satisfactory glass migration, and oxidation of the molybdenum occurs. The oxidation is in accordance with the thermodynamic data quoted by Cole and Sommer [5] which shows that oxidation of the molybdenum is possible at 1500°C, according to the reaction:

$$Mo + O_2 \rightarrow MoO_2$$

when the oxidation potential pH_2O/pH_2 is approximately 1. This is very close to the value 0.8 calculated for 90% N_2 + 10% H_2 at 40°C dew point.

The effect of temperature on the glass migration process seems most noticeable at temperatures just above the temperature at which the glass becomes mobile. On alumina X, the fine-grained metallizing was filled with glass at 1375°C while only a little glass migrated into the coarse-grained metallizing; raising the temperature to 1450 or 1500°C greatly increased the amount of glass migrating into the coarse-grained metallizing but did not completely fill the pores. However, increasing the metallizing temperature to 1550°C gave no further improvement. There was also little improvement in the amount of glass which migrated from alumina B into the coarse-grained metallizing when the metallizing temperature was raised from 1500 to 1550°C. These observations suggest that in the glass migration hypothesis slightly more emphasis should be given to the increase in suction pressure of the metallizing and perhaps slightly less to the decrease in suction pressure of the alumina as the temperature increases.

Apart from alumina E which contains a high melting glassy phase the effects of differences in glass composition and concentration on the glass migration were not very noticeable. Glass migrated slightly more readily at 1500°C from alumina C into the coarse-grained metallizing than from alumina B (batch 2) although both these aluminas had a similar average grain size. This may be because the alumina B contains a glass with a higher softening point (high SiO_2 content). The glass content of alumina D is appreciably smaller than the other aluminas, with the exception of alumina E, but glass migrated readily into both the coarse- and fine-grained metallizing at 1500°C and it is possible that its low glass content is compensated by its very large grain size. However, the glass migration into the coarse-grained metallizing at 1450 and 1400°C occurred less readily than expected in view of the large differences in the grain size of the molybdenum and alumina, and the complete filling of the fine-grained metallizing by glass at the same temperatures.

The addition of manganese dioxide to the metallizing paints tended to decrease the amount of glass which migrated into the metallizing layers on both alumina X and alumina B, and thus decreased seal strengths. It is possible that the decreased glass migration is caused by creating larger pores in the metallizing when the MnO_2 is dissolved.

Although only a few experiments were done with tungsten metallizing paints, the results are interesting in that they confirm the importance of using a fine metal grain size to aid glass migration but also show that a very fine-grained metal may sinter too readily and hence prevent glass migration.

8. Conclusions

The strongest seals are formed to a debased alumina when glass migrates from the alumina, into the metallizing layer and forms a dense metal/glass composite layer. Addition of manganese compounds to the metallizing paint is not essential to form a strong seal and in the few experiments in which manganese dioxide was added to a molybdenum metallizing paint, the seal strengths were actually reduced because of a reduction in the amount of glass which migrated into the metallizing layer, compared with using molybdenum alone.

Observations on the glass migration process appear to agree well with those predicted by the glass migration hypothesis which was put forward in Part 1 of this work, that satisfactory glass migration can be achieved at lower temperatures and over a wider range of furnace atmospheres when the alumina has a large grain size relative to the grain size of the metallizing paint. Fine-grained metallizing paints are, therefore, preferred. However, too fine a metallizing paint is undesirable as extensive metal–metal sintering can occur and prevent glass migration.

Metallizing can be fired satisfactorily either in hydrogen or in N_2/H_2 atmospheres and the addition of a small amount of water vapour promotes the glass migration. The optimum dew point for water vapour in hydrogen is higher than for $90\%\ N_2 + 10\%\ H_2$; at 40°C dew point in $90\%\ N_2 + 10\%\ H_2$ oxidation of the molybdenum tends to occur. A dew point of 3°C in $90\%\ N_2 + 10\%\ H_2$ provides satisfactory conditions but is too low in hydrogen.

Five out of six of the commercial debased aluminas which were investigated contained a glass which would migrate at 1500°C and produced strong seals when the grain size of the alumina was suitably large. However, the glass in the sixth alumina did not appear to be mobile at this temperature and formed weak seals. Problems in metallizing very-fine-grained debased aluminas can be overcome by refiring the aluminas for prolonged periods at high temperatures ($\sim$ 1700°C) to increase the grain size, but as there is a considerable danger of distorting the samples at this temperature, this should preferably be done before machining the alumina.

Although most of the results appear to agree with the predictions made from the glass migration hypothesis, the relationship between the strength and structure of the seals has not been fully established. In general, seals with tensile strengths of 55 to 70 MN m^{-2} (8000 to 10 000 lbf in^{-2}), which would be satisfactory for most industrial purposes, contain metallizing layers which consist of a dense metal/glass composite layer which is not extensively penetrated by braze and the seals usually fail in the alumina. However, when one alumina was metallized at a relatively low temperature the seals failed in the alumina at an average strength of 43 MN m^{-2} (6300 lbf in^{-2}) even though the seal structure appeared satisfactory. This indicates that the metallizing process may introduce some weakness into the alumina and further investigations should be directed towards understanding the factors which determine the highest possible seal strengths, as well as studying the necessary conditions to get satisfactory glass migration from a wider range of alumina ceramics.

Acknowledgements

This work has been carried out with the support of Procurement Executive, Ministry of Defence and is published by permission of the Director of B. Ceram. R.A. The authors wish to thank Miss R. Saunders (English Electric Valve Co), Dr D. Godfrey (Admiralty Materials Laboratory) for valuable discussions.

References

1. H. BENDER, *Ceramic Age* **63** (1954) 15.
2. AMERICAN SOCIETY FOR TESTING AND MATERIALS, ASTM F19-64 (Reapproved 1971).
3. D. B. BINNS, B. Ceram. R.A. Spec. Publ. 48, (1965) p. 173 (Alumina 13).
4. L. REED, Heat Treatment Studies on High-Alumina Ceramics, Advances in Electron Tube Techniques. "Proceedings of the Sixth National Conference, edited by D. Slater. (Pergamon, London and New York, 1963).
5. S. S. COLE and G. SOMMER, *J. Amer. Ceram. Soc.* **44** (1961) 265.

Received 7 October and accepted 30 October 1974.