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High-temperature metallizing

Part 3 *The use of metallizing paints containing glass or other inorganic bonding agents*

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Several metallizing paints containing molybdenum and "glass" powders have been fired on both pure and debased aluminas. Examination of the metallizing layer showed that the paints can be divided into two types: (1) those in which the glass is absorbed by the alumina, and (2) those in which the glass does not readily penetrate the alumina but builds up a reaction layer at the alumina interface. Investigations on type (1) paints have shown that the difficulty in forming strong seals with these paints is in forming a glass/Mo composite layer which is not porous and which bonds well to the braze. The rate at which the alumina absorbs "glass" increases with increasing metallizing temperature and sometimes appears erratic. ASTM tensile test samples with strengths > 55 MN m^{-2} have been prepared to a debased alumina which is normally difficult to metallize, using a metallizing paint, containing 60% molybdenum and 40% by wt of a calcium aluminosilicate glass, fired at 1400°C.

1. Introduction

In Parts 1 and 2 of this work the investigations described were concerned with seals to debased aluminas in which glass migrates from the alumina into the metallizing layer and forms a dense metal/glass composite layer which adheres well to the alumina and which can be brazed. With pure aluminas ($>$ 99% Al_2O_3) or pure beryllias ($>$ 99% BeO) there is insufficient glass to migrate and the metallizing remains porous and has little adhesion to the ceramic. To overcome this problem it is possible to add glass or other inorganic bonding agents that melt when the metallizing paint is fired. Several paint compositions have been described for producing seals to pure alumina and/or beryllia [1-7]. The bonding agents are either mixtures of oxides which have been pre-fritted to form a glass or mixtures which will melt at the metallizing temperature. Common constituents are TiO_2, MnO, CaO, MgO, aud SiO_2, with SiO_2 being common to most compositions. For convenience all additives of this type will be referred to as glasses, though in some cases the bond may be crystalline. Photomicrographs of good seals with glass additives [4, 7] appear similar to good seals produced by glass migration.

While the literature reports indicate no special difficulty about making strong seals to pure aluminas or pure beryllias, commercial seals made with glass additives have the reputation of being more inconsistent than corresponding seals to debased aluminas or debased beryllias made with paints containing only Mo or W. This varying quality of seals produced from metal/glass paints was confirmed recently in a survey conducted by Rees and Holladay [7] in which a variety of different types of beryllia ($>$ 99% BeO) were metallized by seven commercial metallizers and then brazed by Rees and Holladay to form tensile-test samples. Although good seals were produced by some of the metallizers on some of the beryllias, many of the seals were weak.

As some debased aluminas are also difficult to metallize using the glass migration method, the aim of the investigation described here was to make seals to both pure and debased aluminas and to see what factors cause inconsistencies in the seal strength.

2. Experimental

2.1. Preparation of peel test samples

The initial experiments were done using a simple peel test in which a copper strip (14 mm × 10 mm × 10 mm) was brazed with Ag/Cu eutectic

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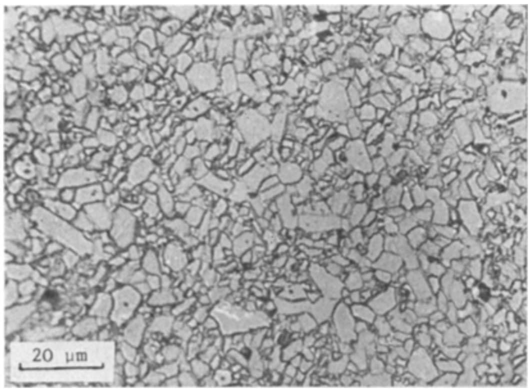

Figure 1 Alumina G, polished section, thermally etched.

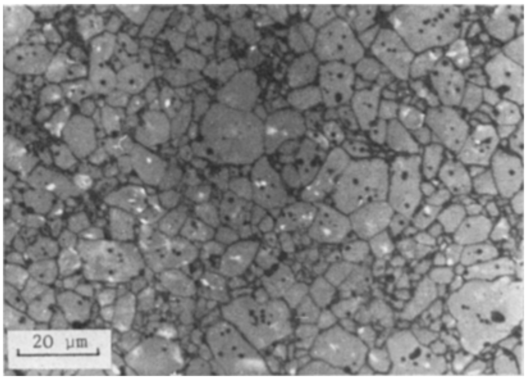

Figure 2 Alumina H, polished section, thermally etched.

alloy to a flat surface of the ceramic which had been metallized and coated with nickel. (The nickel was applied as NiO paint (Wesgo 532) and fired in dry H_2 for 30 min at 950°C). The strength was assessed by attempting to pull the copper strip off the ceramic using a pair of pliers. Strong seals failed by the copper tearing while with weak seals the copper was easily peeled off the ceramic. Two types of pure alumina ($\sim$ 99% Al_2O_3) G and H (Figs. 1 and 2) were used, and the debased alumina X (95% Al_2O_3), described in detail in Part 2. The metallizing paints were prepared from a commercial molybdenum powder (Lamp Metals Co) which was milled to a median particle diameter (Coulter counter) of approximately 5 µm. Two manganese glasses were prepared by melting mixtures of MnO_2, SiO_2 and Al_2O_3. The nominal compositions were: glass 1 MnO 50%; SiO_2 30%; Al_2O_3 20%; and glass 2 MnO 54%; SiO_2 46%. However, analysis of glass 2 showed that it also contained an appreciable concentration of potassium which is present in the technical grades of manganese dioxide. The analytical figures were MnO 45.2%; SiO_2 46.8%; and K_2O $\sim$ 5%. After melting, the glasses were poured into water and milled until the median particle size was below about 2 µm as determined by scanning electron microscopy. The glass and the molybdenum powders were then mixed in the desired proportions with a 5% solution of ethyl cellulose in 2-ethoxyethanol on a triple roll mill. A brushable paint was produced with approximate solids content of 1.6 g ml^{-1} of solution.

The metallizing was fired in a horizontal tube furnace by slowly pushing the samples, in an alumina boat, into the hot zone, soaking them for 30 min and then pushing them out. The temperature-time profile for the samples was similar to that shown in Part 2 (Fig. 3).

Two experimental metallizing paints were also obtained from a valve manufacturer. Both paints contained 80% Mo + 20% by wt of bonding agent. The first bonding agent contained 50% by wt CaO + 50% Al_2O_3 (calcium aluminate) and the second 52% MnO; 13% Al_2O_3, 35% SiO_2.

2.2. Preparation of ASTM tensile test samples

After the initial experiments using peel tests, quantitative tests were done using the ASTM tensile test [8]. The metallizing was coated with Ni by reduction of a layer of NiO paint and samples were brazed with Ag/Cu eutectic alloy. Four types of alumina were used for these tests, three debased aluminas A, B and E, which were described in Part 2, and alumina H (99.5% Al_2O_3, Fig. 2). Paints were prepared as for the peel tests using the manganese silicate glass, and also a calcium aluminosilicate glass (CaO, 30%;

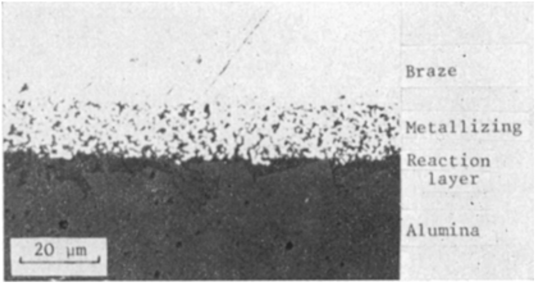

Figure 3 Section of a seal prepared with a metallizing paint containing calcium aluminate, fired on alumina H.

Al_2O_3, 39.5%; and SiO_2, 30.6%) which was previously used for the contact angle measurements described in Part 1. Two grades of molybdenum powder were used with median particle size 5 and 2 μm. A number of the ASTM tests were also made with screen-printed metallizing paints. These were prepared similarly to the brush paints but using 2-butoxyethanol in in place of 2-ethoxyethanol.

The metallizing was fired in a similar way to the peel test samples but omitting a soak period.

3. Results

3.1. Peel tests

The results of the peel tests are summarized in Table I. Although the results are erratic the strong seals had good seal structures, in that the metallizing was not extensively penetrated by the braze, while weak seals showed a deficiency of glass and the metallizing was extensively penetrated by braze. However, one exception to this were the seals prepared with the paint containing calcium aluminate, as failure occurred due to the erratic adhesion of an interfacial layer which was formed between the metallized layer and the alumina. A section of a seal is shown in Fig. 3. Microscopic examination of the layer at first indicated that it was mainly amorphous with a few large lathlike crystals, but etching with HF indicated the presence of submicron crystals. The composition of the layer was determined by electron probe microanalysis (EPMA) and corresponded approximately to 2CaO, $3Al_2O_3$.

The variable structures of the metallizing containing the manganese glasses indicated that the molten glasses were migrating into the aluminas. EPMA of the alumina showed that the migration took place along the grain boundaries. The depth of glass penetration was measured by analysing the alumina with the electron probe at gradually increasing distances from the Mo/Al_2O_3 interface. Counts were taken for Si on strips 12 μm × 180 μm parallel to the Mo/Al_2O_3 interface, and for Mn on strips 16 μm × 170 μm. Results are shown in Table II calculated as oxides. The concentrations of SiO_2 and MnO in the centre of the sample (6 mm) can be assumed to represent the background levels of these oxides in the alumina. The concentration of both SiO_2 and MnO have increased in the alumina up to distances of ~ 150 μm from the metallizing thus confirming considerable movement of the glass.

TABLE I Results of peel tests using Mo + glass metallizing paints

Alumina	Glass content of paint (% by wt)*	Firing temperature (°C)	No of samples	Strength, and seal structure
H	30% MAS	1500	5	Two strong, good seal structures. Three weak, metallizing extensively penetrated by braze.
H	30% MS	1300	2	Strong, plenty of glass in metallizing.
H	30% MS	1400	1	Strong, slight braze penetration in isolated parts of metallizing.
G	30% MS	1300	2	One strong, one weak.
G	30% MS	1400	2	One strong, good structure. One weak, ext. penetrated by braze.
G	30% MS	1500	3	Two strong, good structure. One weak, ext. penetrated by braze.
H	20% CA†	1500	7	Three strong, four weak, metallizing not penetrated by braze. Seal failure at Mo/Al_2O_3 interface.
H	20% MAS†	1400	2	Weak, metallizing soaked with braze.
X	30% MAS	1375	1	
X	30% MAS	1400	1	

*MAS = manganese aluminosilicate glass.
MS = manganese silicate glass.
CA = calcium aluminate glass.
†Valve manufacturers paint.

TABLE II Analysis showing the penetration of silicon and manganese into alumina G, from a metallizing paint containing manganese aluminosilicate glass (sample fired for 30 min at 1500 °C)

Distance from metallized surface (μm)	Concentration of Si as SiO_2 (%)	Distance from metallized surface (μm)	Concentration of Mn as MnO (%)
Metallized layer	4.6	Metallized layer	1.0
0– 12	1.4	0– 16	0.4
12– 24	0.8	16– 32	0.3
24– 36	1.0	32– 48	0.2
36– 48	0.6	48– 64	0.2
48– 60	0.5	64– 80	0.3
60– 72	0.7	80– 96	0.3
72– 84	0.7	96–112	0.4
84– 96	0.7	112–128	0.4
96–108	0.5	128–144	0.2
108–120	0.6	144–160	0.2
132–144	0.7		
136–168	0.5	6 mm	0.0 (± 0.03)
180–192	0.5		
204–216	0.4		
228–240	0.4		
252–264	0.3		
300–312	0.4		
600–612	0.3		
6mm	0.3 (± 0.02)		

3.2. ASTM tensile tests

As it had been established that one of the problems in forming strong seals with metallizing paints containing glass is the loss of glass into the alumina, it was decided to investigate whether the glass movement is affected by the particle size distribution of the metal in the paint or by the type of glass. Results are shown in Table III for three types of alumina and four screen-printed metallizing paints fired in 90% N_2 + 10% H_2, dew point 20°C, at 1400°C (residence time in hot zone 15 to 20 min). The firing temperature was chosen so that it was sufficiently high to melt both types of glass in the paints but not sufficiently high for glass already present in the two debased aluminas to become very mobile. The results are remarkably consistent for all the samples and indicate little difference between the two types of glass or the different molybdenum particle sizes. Examination of the seal structure by microscopy showed metallizing regions with a good glass/Mo composite structure as well as metallizing penetrated by braze. In a few samples, presumably in regions where the glass had not migrated into the alumina, there was excess glass in the metallizing layer which caused local failure of the seals at the metallizing/nickel interface. A scanning electron micrograph (SEM) of the paint containing 30% manganese silicate and the fine molybdenum fired on sapphire showed an excess of devitrified glass covering the molybdenum particles (Fig. 4). As the glass is not able to penetrate the sapphire, because of the absence of grain boundaries, this confirms that there is more than sufficient glass to form a dense metal/glass composite layer.

An unsatisfactory feature of the screen-printed metallizing paints which were prepared, was that it did not appear possible to increase the thickness of paint, which was applied to the alumina in a single printing, without producing very rough coatings. The fired metallizing layers tended to be very thin (~ 8 μm) and it was considered that this might have been a contributory factor in producing relatively weak seals. A few alumina samples were therefore double or triple printed with the metallizing paints containing the coarse molybdenum and either the calcium aluminosilicate or manganese silicate glasses. Brush paints of the same composition were also made up and used to produce thicker metallizing layers (~ 25 μm). The seal strengths were not significantly different from the single printed samples.

The unevenness in the structure of the metallized layers on the ASTM samples and the erratic nature of the results obtained with peel tests

TABLE III ASTM tensile strengths on samples metallized with paints containing glass

Alumina	Paint type*		Mean strength ± S.D.		Leak test†		Main region of failure
	Mo	Glass	(lbf in^{-2})	(MN m^{-2})	(a)	(b)	
A	F	Mn	5480 ± 1670	37.8 ± 11.5	5	0	Mo/Al_2O_3 + thin Al_2O_3
	C	Mn	6660 ± 1270	45.9 ± 8.8	5	1	Mo/Al_2O_3
	F	Ca	6800 ± 960	46.9 ± 6.6	5	0	V. thin Al_2O_3 + Mo + Mo/Al_2O_3
	C	Ca	6930 ± 1450	47.8 ± 10.0	5	1	Mo/Al_2O_3
B	F	Mn	6180 ± 1050	42.6 ± 7.2	4	0	Mo/Al_2O_3
	C	Mn	5520 ± 1390	38.0 ± 9.6	5	1	Mo/Al_2O_3
	F	Ca	4970 ± 1270	34.3 ± 8.8	4	1	Mo/Al_2O_3 + v. thin Al_2O_3
	C	Ca	6360 ± 1120	43.5 ± 7.7	5	0	Mo/Al_2O_3
H	F	Mn	6230 ± 1360	42.9 ± 9.4	4	0	V. thin Al_2O_3 + Mo/Al_2O_3
	C	Mn	5430 ± 2060	37.5 ± 14.2	4	1	Mo/Al_2O_3
	F	Ca	6000 ± 750	41.4 ± 5.2	4	0	V. thin Al_2O_3 + Mo/braze
	C	Ca	4880 ± 1430	33.6 ± 9.9	4	1	Mo/Al_2O_3

*F = Fine-grained molybdenum.
C = Coarse-grained molybdenum.
†(a) = No. of specimens tested.
(b) = No. of specimens leaky.

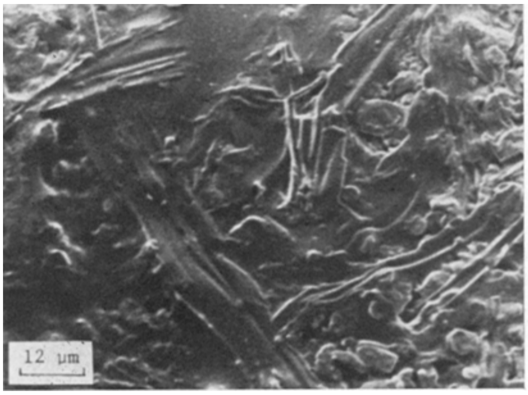

Figure 4 Surface of a metallizing paint containing 30% wt of manganese silicate glass fired on sapphire (SEM).

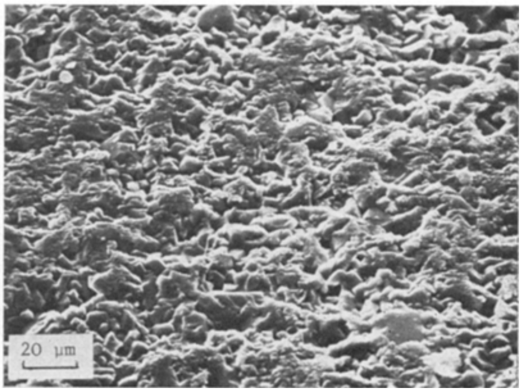

Figure 5 Ground surface of a debased alumina (SEM).

suggested that loss of glass from the metallizing could be partly connected with variable amounts of surface damage on the alumina. Examination of a ground surface of a debased alumina by SEM shows that the surface is divided up into relatively smooth burnished areas where the alumina and glassy phase have flowed and rough areas where grains have been pulled out (Fig. 5). As these rougher areas will probably absorb glass more readily than the burnished areas an attempt was made to seal the surfaces of the debased aluminas by simply refiring the debased aluminas at 1500°C or by applying a coating of the calcium aluminosilicate glass (3 mg cm^{-2}) before refiring. The aluminas were then metallized at 1400°C as before. No increase in seal strength occurred when compared with the results for the untreated aluminas and the seal structures also appeared unaltered with regions of metallizing penetrated by braze. The layers of glass which had been fired on the aluminas were not visible in the seal sections and presumably had soaked into the alumina.

As the seal strengths and structures were unsatisfactory with metallizing paints containing

TABLE IV ASTM tensile strengths of seals prepared with a metallizing paint containing 60% by wt of molybdenum and 40% calcium aluminosilicate glass on alumina E (97.5% Al_2O_3)

Metallizing temperature (°C)		ASTM tensile strength (lbf in^{-2})	ASTM tensile strength (MN m^{-2})	Region of failure
1400		10230	70.5	Mo/Ni interface
		7040	48.5	
		6820	47.0	
	Mean	8030	55.3	
1450		8030	55.4	Mo/Ni interface
		8360	57.6	
		9570	66.0	
	Mean	8653	59.6	
1500		6875	47.4	Mixed, in Al_2O_3, Mo, and at Mo/Ni interface
		6875	47.4	
		5500	37.9	
	Mean	6416	44.2	

30% glass, a paint containing 40% by wt glass was also prepared. Tests were done on alumina E (97.5% Al_2O_3)*. The results are shown in Table IV for three firing temperatures. The strengths are significantly greater than for the corresponding paint containing 30% glass. An interesting point is that whereas samples fired at 1400 and 1450°C failed entirely at the metallizing/Ni interface, samples fired at 1500°C failed in several parts of the seal and were weaker. Comparison of the seal structures showed that less glass remained in the metallizing fired at 1500°C than in the samples fired at 1450 or 1400°C. This is illustrated by the seal sections shown in Figs. 6 and 7.

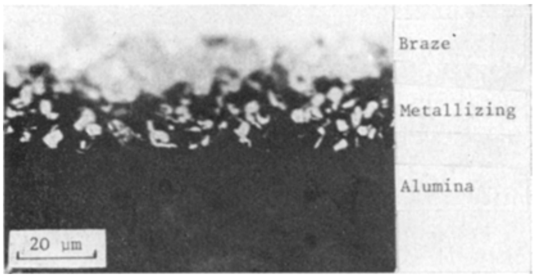

Figure 6 Section of a seal prepared with a metallizing paint containing 40% calcium aluminosilicate glass fired on alumina E at 1400°C.

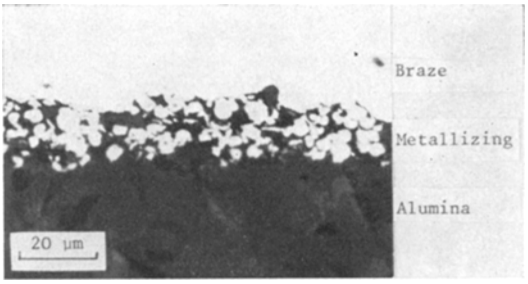

Figure 7 Section of a seal prepared with a metallizing paint containing 40% calcium aluminosilicate glass fired on alumina E at 1500°C.

4. Discussion

Examinations of the seal structures which were produced with metallizing paints containing glass show that the paints may be divided into two types: (1) those which contain glasses which penetrate the grain boundaries of the alumina, e.g. manganese silicate, manganese aluminosilicate and calcium aluminosilicate glasses, and (2) those which contain glasses which do not readily penetrate the alumina but build up a reaction layer at the alumina interface, e.g. calcium aluminate. Both types of paint appear to have disadvantages as the reaction layer produced by the calcium aluminate gave poor

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* For a detailed description of this alumina see Part 2.

adhesion to the alumina,* while with the type (1) paints it was difficult to allow for loss of glass from the metallizing layer.

The results of the peel tests show that it is possible to produce some relatively satisfactory metallized layers with the type (1) paints with 30% by wt glass, but the results were not consistent as the amount of glass which was absorbed by the alumina appeared variable. The reason for this variability was not discovered and did not appear to be connected with the surface condition of the alumina although this was strongly suspected. Results obtained with the ASTM samples were much more consistent and show that the absorption of glass is not prevented by changing from a manganese silicate glass to a calcium aluminosilicate glass, nor by reducing the particle size of the molybdenum paint.

The failure to consistently obtain metallizing with a dense glass/metal composite structure with paints containing 30% wt of glass was somewhat surprising as Reed [5] obtained strong seals to a pure alumina with two paints containing only 20% by wt of glass (64% MnO + 36% SiO_2, and 80% $CaSiO_3$ + 20% Al_2O_3) and Klomp and Botden [3] also obtained strong seals with molybdenum paints containing 20% by wt of glass using several glasses. If the weight concentrations of the glasses are converted to volume concentrations, 20, 30 and 40% by wt become respectively approximately 50, 60, and 70% by vol. Judged purely from considerations of the particle packing of the molybdenum, 50% by vol of glass should be sufficient to form a dense glass/metal composite structure with slight exposure of the molybdenum particles at the surface, while 60 and 70% by vol of glass should be too high and tend to coat the surface of the metallized layer with glass. There was thus some reluctance to increase the glass concentration to 40% by wt. However, this produced the strongest seals, although tensile failure tended to occur at the Ni/metallizing interface. Even with this high glass concentration, too high a metallizing temperature (1500° C) produced metallized layers which were porous before brazing and thus formed weak seals.

Fulrath and Hollar [6] also found that the strongest seals to a 99% alumina were produced with a molybdenum metallizing paint containing 70% by vol of glass (manganese aluminosilicate) but unlike the present results, seal failure only occurred at the metallizing/braze interface when the molybdenum concentration was reduced to 10% by vol.

Although the factors that affect the rate of glass absorption have not been properly established, it seems reasonable to assume that absorption takes place by some type of capillary flow mechanism along the grain boundaries of the alumina. Two mechanisms are possible depending upon the state of the grain boundaries. In mechanism (1) it is assumed that there is a liquid phase in the grain boundaries of the alumina (e.g. a debased alumina near its normal metallizing temperature) and that the glass absorption is essentially the reverse of the normal glass migration process described in Part 1. The amount of glass removed from the metallizing layer will depend upon the relative suction pressures of the metallizing and the alumina. In mechanism (2) it is assumed that the grain boundary phase is relatively immobile (e.g. a pure alumina, or a debased alumina below the softening point of its secondary phase) and that the rate of capillary flow is determined largely by the rate of dissolution of the grain boundary phase. Glass absorption which takes place via mechanism (2) will obviously be much slower than that which takes place by mechanism (1), and this offers a better opportunity of controlling the metallizing structure. Differences in the rate of dissolution of different grain boundary phases in pure aluminas or pure beryllias by the various glasses in the metallizing paints could explain why some paints containing glass are more suited to some ceramics than to others.

5. Conclusions

Investigations using metallizing paints containing molybdenum plus glass have shown that the paints can be divided into two types: (1) those containing glasses which penetrate the alumina grain boundaries and (2) those in which the glass does not readily penetrate into the alumina but builds up a reaction layer at the alumina interface. Preliminary experiments with a type (2) paint containing calcium aluminate produced weak seals due to poor adhesion at the metallizing/Al_2O_3 interface.

The main difficulty in forming strong seals

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* In contrast to this observation, it was stated during a discussion at the meeting on "High-Temperature Metallizing" held at the *B. Ceram. R.A.*, 5 June, 1974, that calcium aluminate is being used very successfully in the lighting industry to seal tungsten to alumina.

with type (1) paints appears to be in allowing for the absorption of the glass by the alumina, so that there is not too much or too little glass in the metallized layer (i.e. to form a similar structure to the good seals produced by glass migration). The rate of glass absorption from the metallizing by a pure alumina was not markedly affected by the particle size of the molybdenum but increased with increasing metallizing temperature.

Glass was also absorbed from the metallizing by debased aluminas when the metallizing was fired at temperatures below those at which the glasses already present in the aluminas become mobile. Experiments with a debased alumina, which cannot be metallized satisfactorily with pure metal paints, except at very high temperatures (~ 1650°C), showed that it is possible to produce strong seals (ASTM tensile strengths > 55 MN m^{-2}) by using a very high concentration of a calcium aluminosilicate glass in the metallizing paint (~ 70% by vol), and firing the paint at 1400 or 1450°C. Increasing the metallizing temperature to 1500°C reduced the amount of glass left in the metallizing layer and reduced the seal strength.

Considerations of the mechanisms which are involved in the glass absorption indicate that this type of metallizing process is intrinsically difficult to control and that further knowledge is required to develop a process or processes which will give consistently strong seals on a wide range of aluminas.

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References

1. L. H. LA FORGE, *Bull. Amer. Ceram. Soc.* **35** (1956) 117.
2. A. MEYER, *Ber. Deutsch. Keram. Ges.* **42** (1965) 452.
3. J. T. KLOMP and P. J. BOTDEN, *B. Ceram. R.A. Spec. Publ.* **48** (1965) 129.
4. L. REED and R. A. HUGGINS, *J. Amer. Ceram. Soc.* **48** (1965) 421.
5. L. REED, A.D. 636, 950 (1966).
6. R. M. FULRATH and E. L. HOLLAR, *Bull. Amer. Ceram. Soc.* **47** (1968) 493.
7. G. H. REES and C. O. HOLLADAY, Brush Wellman Report, Ohio, 1972.
8. AMERICAN SOCIETY FOR TESTING AND MATERIALS, ASTM F19-64 (reapproved 1971).

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