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High-temperature metallizing

Part 1. *The mechanism of glass migration in the production of metal–ceramic seals*

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The method of making strong metal–ceramic seals to alumina and beryllia ceramics by first sintering a coating containing a molybdenum or tungsten powder on the ceramic and then brazing to it, is reviewed. Evidence in the literature shows that the strongest seals are generally formed on debased aluminas when glass migrates from the alumina into the metallized layer and forms a dense glass/metal structure. A hypothesis, based on a capillary flow mechanism between two porous beds, is proposed which describes how the experimental variables affect the glass migration. The relative importance of the different variables is predicted for varying circumstances.

1. Introduction

Ceramics are now used extensively instead of glass in the manufacture of high-performance electronic components, because of their better electrical and mechanical properties. In most applications the ceramic has to form a strong vacuum-tight seal with a metal. The usual method of making such a seal is to apply a thin layer of a molybdenum (or tungsten) metal paint to the surface of the ceramic and then fire it at about 1500° C in a reducing atmosphere. When successful this forms a strongly adherent coating on the ceramic which can be brazed to the metal component. If the brazing is done with Ag/Cu eutectic alloy the metallizing is usually coated with nickel before brazing. This can be done either by applying an NiO paint and reducing the oxide in hydrogen at about 950° C, or by electroplating.

This high-temperature metallizing process was first developed in Germany during World War II using steatite ceramics [1]. Addition of a small proportion of manganese or manganese dioxide to the molybdenum paints was found to improve seal strengths and the method is often referred to as the moly-manganese process, though a number of manufacturers no longer use manganese additives. As the electronics industry developed, steatite was replaced by high-alumina ceramics which have better mechanical and dielectric properties. This change caused considerable difficulties in producing satisfactory seals. Although most of these difficulties have been overcome, some problems still occur from time to time. It was, therefore, considered to be worthwhile to try to understand the underlying mechanisms.

This paper starts with a critical review of previous work and then goes on to describe the development of a hypothesis explaining the formation of strong metal–ceramic seals. More detailed experimental work on the effect of variables on the strength of metal-ceramic seals is described in Parts 2 and 3.

2. A review of previous work on metal–ceramic seals

As relatively few problems occur during brazing, this review will deal only with the metallizing. Initially, most emphasis in investigating the metallizing process was on the role of manganese, its conversion to MnO and subsequent reaction with the alumina at the metal–ceramic interface. Later more emphasis was given to the importance of a glassy phase being present in the metallizing layer [2]. In 1961 Cole and Sommer [3] showed that in order to form seals strong enough for most electronic applications, it was essential to form a dense Mo/glass composite metallizing layer similar to that shown in Fig. 1. They found that strong seals with this type of structure could be produced on a debased alumina (e.g. of the type shown in Fig. 2) both with pure molybdenum metallizing

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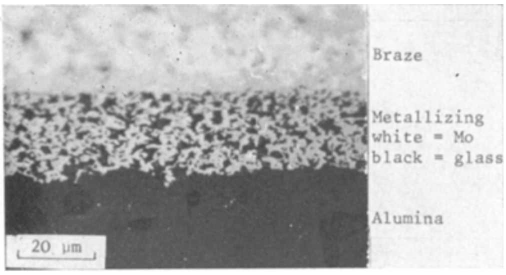

Figure 1 Photomicrograph of a good seal structure (reflected light).

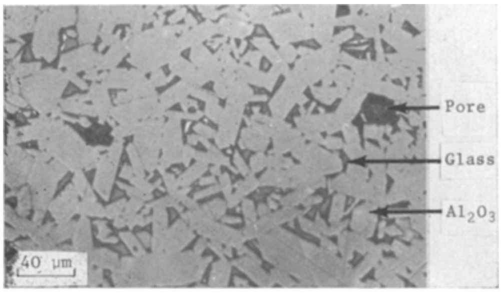

Figure 2 Photomicrograph of a debased alumina (reflected light).

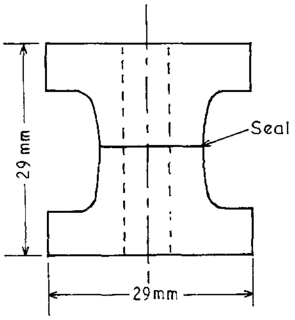

Figure 3 ASTM tensile test assembly.

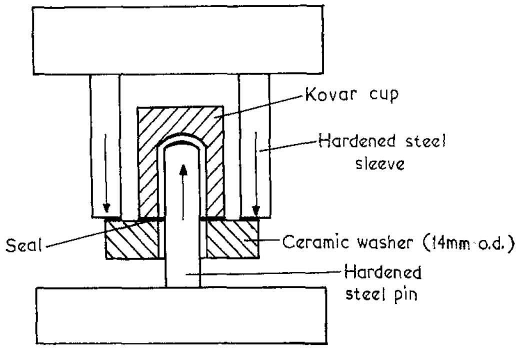

Figure 4 Cup and washer tensile test assembly.

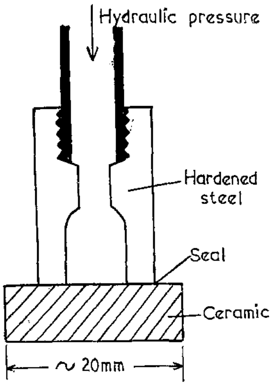

Figure 5 Hydraulic test specimen.

paints as well as with Mo/Mn or Mo/Ti compositions, but if the same paints were applied to a pure alumina (> 99 % Al_2O_3) unsatisfactory seals were formed in which the metallizing layer was penetrated by braze. They concluded that during the firing of a debased alumina, glass migrates from the alumina into the metallizing layer and thus increases the strength of the metallizing and improves the adherence. Subsequent work has confirmed the importance of glass in the metallizing and even before 1961, processes which involved adding glass to the metallizing paint had been used for metallizing pure aluminas (> 99% Al_2O_3) [2]. Despite the apparent simplicity in using metallizing paints containing glass, they are rarely used for metallizing debased aluminas, and often do not give satisfactory results on pure aluminas or pure beryllias for which there are no real alternatives. Details of a study of this problem are given in Part 3.

Most of the studies of metal–ceramic seals have used either a tensile or peel test to assess the strength. Fig. 3 shows the American Society for Testing Materials (ASTM) tensile test sample [4]. Fig. 4 shows another tensile test method which requires simpler test pieces and was used by Rees and Holladay for work on beryllia [5]. Floyd [6] had previously used a similar test joint (Fig. 5), in which the stress was applied by hydraulic pressure. Peel tests can also be made on discs by sealing a thin metal strip to the perimeter and then measuring the force required to initiate and/or continue peeling the metal strip.

The minimum tensile strength of a satisfactory commercial seal appears to be 55 to 70 MN m^{-2} (8000 to 10 000 lbf in^{-2}) as below this, in addition to being weak, the seals also tend

TABLE I Composition of alumina ceramics with similar average grain size

Ceramic	Composition (%)				Average grain diameter (µm)
	Al_2O_3	SiO_2	CaO	MgO	
Body A	94	4.50	0.50	1.00	6.3
Body B	94	3.00	2.00	1.00	7.1
Body C	94	1.50	1.50	3.00	6.1

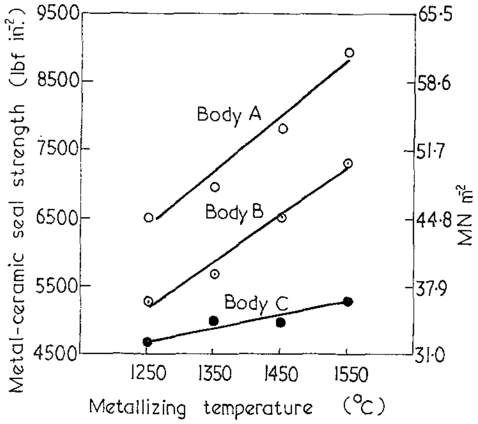

Figure 6 Effect of ceramic flux composition and metallizing temperature on metal-ceramic seal strength.

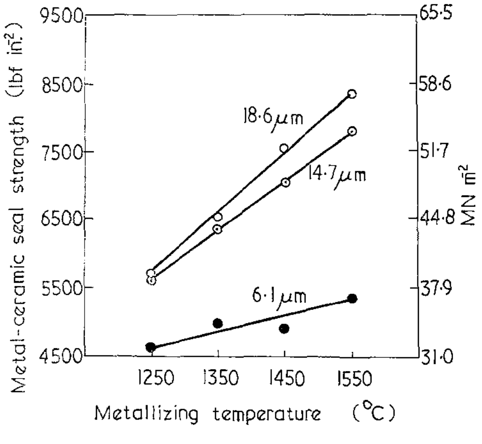

Figure 7 Effect of alumina grain size and metallizing temperature on metal-ceramic seal strength (body C).

to leak. When seals become stronger than this, tensile failure tends to occur in the ceramic and consequently the results become less meaningful.

In a study of the effect of several parameters on the metal-ceramic seal strengths, Floyd [6] found that the strength of the seals formed at a particular metallizing temperature depended upon the type of flux present in the alumina.

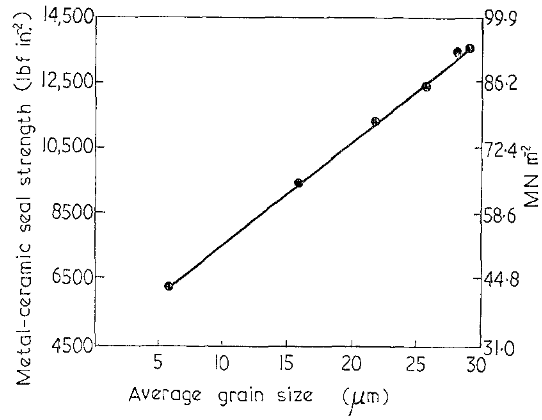

Figure 8 Effect of alumina grain size on metal-ceramic seal strength when metallized at 1550°C (body F).

The strengths increased with increasing temperature. The composition of three aluminas which were used by Floyd are shown in Table I, and the seal strengths versus metallizing temperature in Fig. 6. Fig. 7 shows that when the average grain size of body C was increased the seal strength also increased. Fig. 8 shows the increase in seal strength for a different alumina, body F, at a fixed metallizing temperature (1550°C), when the grain size of the alumina was varied over a wide range. Floyd observed that an increase in seal strength was accompanied by an increased proportion of glassy phase in the metallizing, and that in the weaker seals, the metallizing layer remained porous or became filled by the nickel plating. It is interesting that when the grain size of body F was increased to 56 µm (not included in Fig. 8), the surface of the metallizing was flooded with glass, and the seals became weak because of the failure of the nickel coating to bond to the metallizing.

Reed [7] also found that the composition of the glassy phase affected the temperature at which strong seals were produced. Using his "941" alumina (Al_2O_3, 94%; SiO_2, 3%; CaO, 3%) strong seals were produced at a metallizing temperature of 1425°C, but with his "942" alumina (Al_2O_3, 94%; SiO_2 4%; CaO, 2%) strong seals were not formed until 1600°C. He ascribed this difference to the greater fluidity of the glass in the "941" body. A low seal strength was also obtained with the "941" body, metallized at 1425°C, when the average grain size was relatively small (mean diameter 5.6 µm). Otherwise, no correlations between the seal

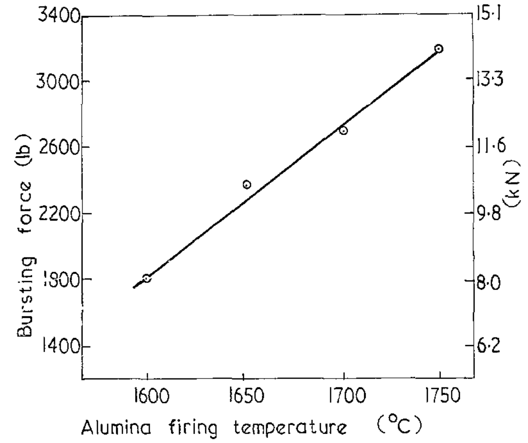

Figure 9 Bursting force for metal–ceramic seal versus original firing temperature of the alumina.

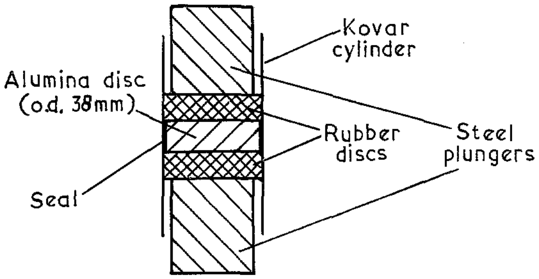

Figure 10 Metal–ceramic seal test.

strengths and grain sizes of the "941" or "942" aluminas were found.

Cole and Hynes [8] found that the strength of seals to a debased alumina increased, as the original firing temperature of the alumina was increased. Their results are shown in Fig. 9. The strengths were assessed by a rather unusual method, illustrated in Fig. 10. Pressure was applied to the two metal plungers which caused the rubber discs to exert a pressure on the walls of the test sample. The force was increased at intervals of 200 lb (890 N) and the seal leak-tested after each increment. The bursting force was the force which made the seal leak. Comparison of the photomicrographs of the alumina samples, given by Cole and Hynes, indicates that the average grain size increased with successively higher firing temperatures. This brings the results into line with those obtained by Floyd (Fig. 8).

Cole and Hynes also studied the seal strength as a function of the flux content in the alumina. Fig. 11 shows that the seal strength increased up to a flux content of 12%, and then decreased at higher flux contents. A corresponding curve, for the modulus of rupture of the alumina versus flux content, shows that the seal strength and modulus of rupture of the alumina are not related.

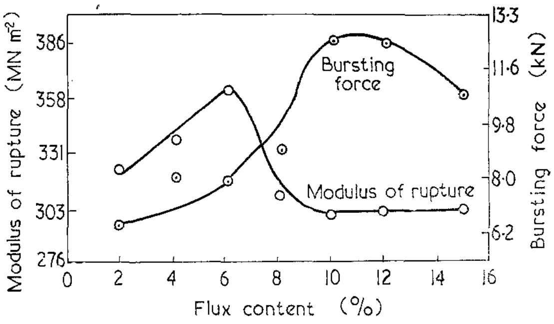

Figure 11 Modulus of rupture and metal–ceramic seal bursting force versus flux content.

No systematic study has been made of the effect of molybdenum particle size or metallizing thickness on seal strength, but small particle size is preferred and the metallizing thickness is traditionally 15 to 25 μm. Reed [7] found that a metallizing paint containing molybdenum (mean diameter 1.65 μm) formed strong seals at a lower metallizing temperature than a similar paint containing molybdenum (mean diameter 5 μm). Tungsten powders have also been used by several workers in place of molybdenum [9, 10].

Both molybdenum trioxide and tungsten trioxide have been used in metallizing paints as a source of the metals, as in a reducing atmosphere conversion to the metal is complete above 750° C. Tentarelli *et al.* [11] claim that such paints can be used to produce seals with strengths of over 70 MN m^{-2} at temperatures between 900 and 1100° C, which are too low for glass to migrate. A subsequent investigation by Martin and Popper [12] has confirmed that fairly good adherence can be obtained by this process, but only by burnishing the metallizing layer before brazing. Strengths of ~ 70 MN m^{-2} were obtained on a pure alumina but the results obtained were very erratic, and seals frequently leaked. Reed [7], on the other hand, found that maximum strength with molybdenum oxide paints was developed at a somewhat higher temperature (1300° C), but in most of his work the paints were fired to temperatures normally used for metal paints. The texture which he shows of metallizing produced by an oxide paint fired at 1425° C is very similar to that shown in Fig. 1, which was produced from a pure metal paint.

Brymner and Calvert [13], however, have recently reported that oxide paints have been used satisfactorily in a commercial process, at a metallizing temperature of 1100°C. A description of the paint preparation mentioned the use of porcelain grinding media so that adhesion may be aided by milling porcelain into the paint.

The situation with the oxide paints is thus not really clear and it is possible, though not certain, that the metallizing–ceramic adhesion involves different bonding mechanisms to those produced with metal paints. The rest of the work is concerned only with metal paints.

The atmospheres used in metallizing furnaces appear to vary from 100% H_2 to mixtures of nitrogen with only 10% H_2. Dry gases are reported to produce weak seals, and it is usual to bubble the gases through water before passing them into a furnace. Dew points of the furnace gas may be up to 30°C or possibly higher. Recently Arthur and Fussel [14] have investigated the effect of metallizing temperature, soak time and furnace gas composition on the strength of seals to Coors AD 94 alumina. The dew point of the furnace gas was maintained constant at approximately 4°C. The most striking feature of the investigation was the very high and narrow range of strengths which were obtained, despite the fact that 270 samples were fired under a total of twenty-seven different combinations of conditions. An interesting observation, however, was the very short soak time (8 min) that can be used to produce an adequate seal strength.

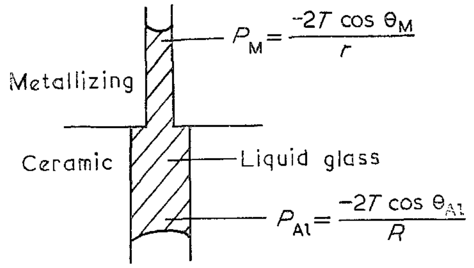

Figure 12 Twin capillary model showing the pressure of the glass in the metallizing and in the ceramic.

Despite the tradition of adding manganese or manganese dioxide to metallizing paints, it is not really clear why (or even whether) such additives are beneficial. Thermodynamic data and experimental observations [3] indicate that under typical metallizing conditions MnO_2 and Mn are both converted to MnO, and it has been shown that the manganese oxide can react with alumina to form a manganese spinel ($MnAl_2O_4$) [6]. It has been suggested that it is the spinel that produces the adhesion between the molybdenum and the alumina. Helgesson, for example, supports such a view and discounts the theory of glass migration [15]. His results, however, only go up to a maximum seal strength of 40 MN m^{-2} which is well below the value for a good commercial seal. Floyd [6] also obtained similar strengths for seals which had a layer of spinel present at the metal/ceramic interface, but unlike Helgesson, Floyd went on to show that if more suitable metallizing conditions are used the spinel layer disappears and stronger seals (> 70 MN m^{-2}) are formed by migration of the glassy phase from the alumina into the metallizing layer.

Electron microprobe analyses of seals prepared with paints containing manganese additives show that the manganese can dissolve in the glassy phase of the alumina and may migrate quite large distances into the ceramic [16, 17].

The bulk of the evidence in the literature thus indicates that strong metal–ceramic seals (tensile strength > 70 MN m^{-2}) are only produced when the metallizing layer consists of a dense metal/glass composite layer. The addition of manganese to the metallizing paint has a modifying effect in the production of such seals but is not essential for the formation of strong seals.

3. The development of a theory of glass migration

The evidence from the literature survey shows that the metallizing variables affect the strength of a metal–ceramic seal by determining the extent of the glass migration into the metallizing layer. The most probable mechanism of glass migration is one of capillary flow, in which the driving force is the surface tension of the liquid glass. However, as the movement of liquids in porous solids is a fairly complicated process, it is convenient to start by representing the glass flow in the alumina and the metallizing by a simple model system of twin capillaries, as shown in Fig. 12. The pores in the metallizing are represented by a cylindrical capillary tube, radius *r*, and glass-filled pores in the alumina by a cylindrical capillary of radius *R*. When glass is fluid at the metallizing temperature, glass will flow from the alumina capillary into the metallizing capillary, if the capillary pressure in the metallizing is greater than that in the alumina.

$$\text{i.e. if } \frac{2T\cos\theta_{M}}{r} > \frac{2T\cos\theta_{Al}}{R}$$

where T = surface tension of the glass, θ_M = glass/molybdenum (or tungsten) contact angle, θ_{Al} = glass/alumina contact angle.

Failure to get the necessary migration of glass into the metallizing could therefore occur if

$$\frac{\cos\theta_{M}}{r} \ngtr \frac{\cos\theta_{Al}}{R}$$

either because the pores in the metallizing are not small, relative to the glass-filled pores in the alumina, and/or if there is poor wetting between the glass and the metallizing and $\cos\theta_M$ is small. Alternatively, the system could fail to reach equilibrium because of the glass having a very high viscosity and insufficient time being allowed for the glass to migrate. By studying the order of size in which the pores in the metallizing become filled, we can establish whether the glass flow is limited by equilibrium or dynamic factors. According to Washburn [18] the rate of penetration of a liquid into a horizontal or short vertical capillary tube under its own capillary pressure is

$$\frac{dl}{dt} = \frac{aT\cos\theta}{\eta 4l}$$

where l = length of the column of liquid at time t, a = radius of the capillary, η = viscosity of the liquid, T = surface tension of the liquid, θ = contact angle between the liquid and the walls of the capillary.

The rate of penetration should, therefore, increase with increasing radius of the capillary, and thus large pores should become filled before small pores. If the glass flow is limited by the equilibrium conditions, then the large pores may not fill at all. Examination of several samples of porous metallizing, into which only a small amount of glass had migrated showed that glass was present in only the smallest pores or neck spaces between the molybdenum particles, thus indicating that the glass flow was limited by equilibrium rather than kinetic factors.

To explain why glass flow into the metallizing improves by using a wet atmosphere in preference to a dry atmosphere, and also improves with increasing metallizing temperatures, it is necessary for $\cos\theta_M/r$ to increase relative to $\cos\theta_{Al}/R$. The most obvious way is for $\cos\theta_M$ to increase. Reed [7] has measured the contact angles of nine calcium aluminosilicate glasses on both molybdenum and sapphire in $H_2/3N_2$ at

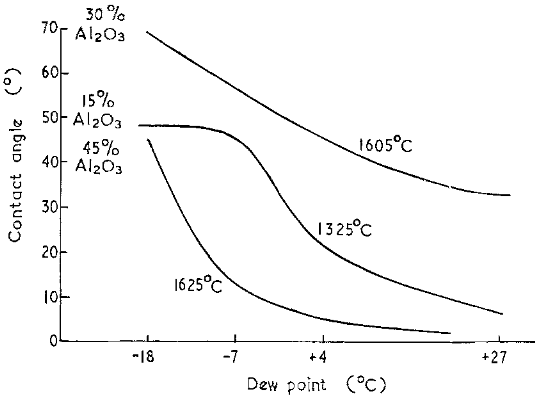

Figure 13 Contact angle versus dew point of 1:1 SiO_2/CaO melts on molybdenum.

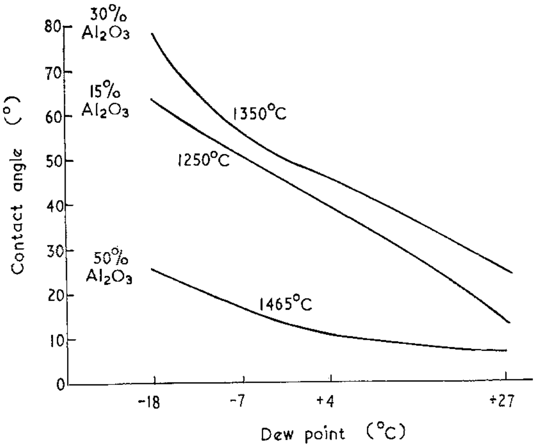

Figure 14 Contact angle versus dew point of 2:1 SiO_2/CaO melts on molybdenum.

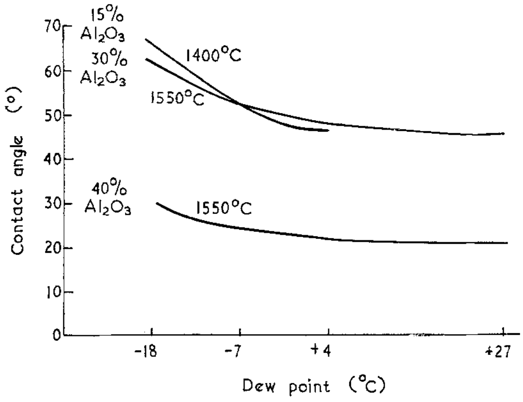

Figure 15 Contact angle versus dew point of 3:1 SiO_2/CaO melts on molybdenum.

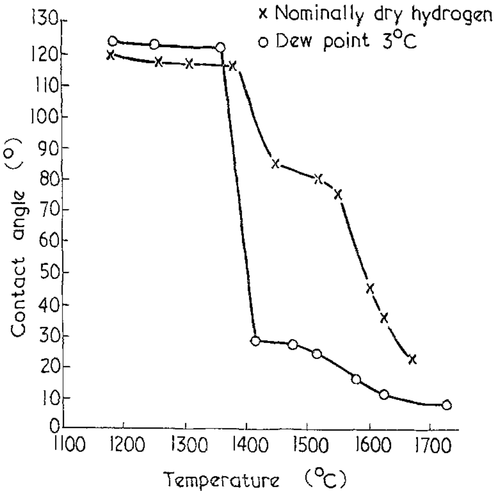

Figure 16 Contact angle versus temperature for a calcium aluminosilicate glass on molybdenum in nominally dry hydrogen and at 3° C dew point.

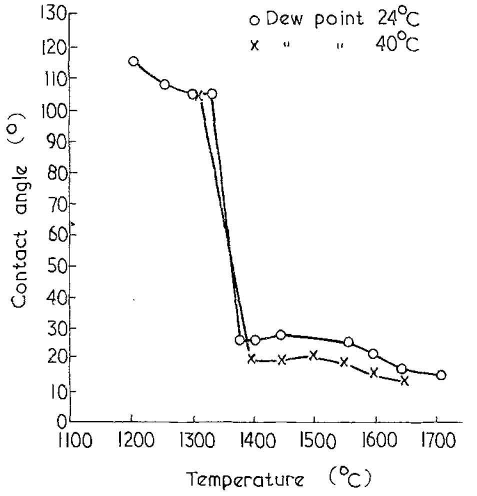

Figure 17 Contact angle versus temperature for a calcium aluminosilicate glass on molybdenum in hydrogen, dew point 40 and 24° C.

various humidities. The glass/molybdenum contact angles which are shown in Figs. 13 to 15 for each glass at a single temperature, decrease markedly with increasing humidity. The corresponding glass/sapphire contact angles (not shown) were less dependent on humidity and were always below 30° over the same range of humidities.

Additional contact angle measurements were made during this work to establish the trend with increasing temperature. Figs. 16 and 17 show contact angles on molybdenum for a similar type of glass (CaO, 30.0%; SiO_2, 30.6%; Al_2O_3, 39.5%) measured over a range of temperatures and humidities in a hydrogen atmosphere. A striking feature of the results in Figs. 16 and 17 is that in wet hydrogen the glass/molybdenum contact angle drops to quite low values at relatively low temperature (~ 1400° C). Thus, above 1400° C a large increase in $\cos \theta_M$ cannot occur ($\cos 20° = 0.94$, $\cos 0° = 1$). This suggests that an additional reason is necessary to explain why glass migration continues to increase up to very high temperatures (~ 1700° C) for aluminas containing glasses of a similar composition. The greater ease of glass migration could be caused by an increase in the volume of glass which is produced either (i) by dissolution of an increased amount of alumina at the high temperature and/or (ii) by a higher thermal expansion of the glass relative to the alumina. At present there is little evidence concerning (i) and it seems unlikely in view of the slowness with which alumina dissolves when aluminosilicate glasses are prepared.

Evidence in favour of (ii) is shown in Table II. The composition of glass 6 is very similar to that of the glass used in the contact angle measurements of Figs. 16 and 17. Thus, if an alumina containing this type of glass is heated, between 1400 and 1600° C, the glass volume expands by 2.9% while the alumina expands by only 0.6%. The net expansion of the glass (2.3%) is therefore quite significant, and could be accommodated by the glass penetrating the alumina grain boundaries and expanding the whole body, or it could exude from the surface of the body. The latter effect is perhaps most likely to occur when the alumina has a very large grain size and would explain why, in exceptional circumstances, the surface of the metallizing can become flooded with glass as observed by Floyd [6].

So far the twin capillary model has been useful in focusing attention on the effect of the relative pore sizes and the glass/molybdenum contact angle in controlling the glass migration. The increased volume of the glass in the alumina is less easily assimilated in the hypothesis, although it may be considered that the high expansion of the glass causes R to increase and thus lowers the capillary pressure in the alumina. A further difficulty, when applying the twin capillary model, is that the flow of glass does not appear to be reversed during cooling in cases

TABLE II Coefficients of cubical expansions of some calcium aluminosilicate glasses [19]

Glass	Composition (%)			Coefficient of cubical expansion at 1600°C
	CaO	Al_2O_3	SiO_2	$\times 10^{-6}$ °C^{-1}
1	39	19	42	223
2	35	10	55	280
3	34	30	36	183
4	30	25	45	192
5	30	10	60	291
6	29	40	31	144
7	25	20	55	246
8	25	10	65	260
9	23	15	62	298
10	15	20	65	219
Solid alumina	—	100	—	10

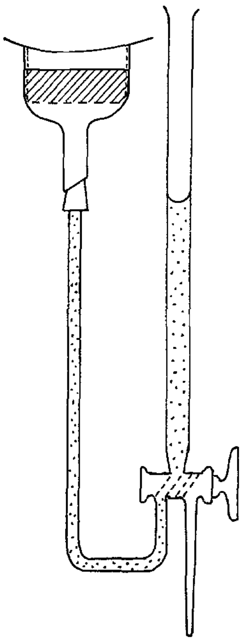

Figure 18 Apparatus for measuring relation between pressure difference and moisture content.

when one would expect to pass through the stage again, when

$$\frac{\cos\theta_M}{T} < \frac{\cos\theta_{Al}}{R}.$$

To overcome these problems it is preferable to use a more realistic model and to make use of observations on other solid-liquid systems.

In the new model we will consider the alumina and the metallizing as two beds of powder, in which the capillary pressure of the molten glass in the pores is able to set up a pressure difference which brings about a redistribution of the glass. Similar pressure differentials in aqueous systems have been measured experimentally.

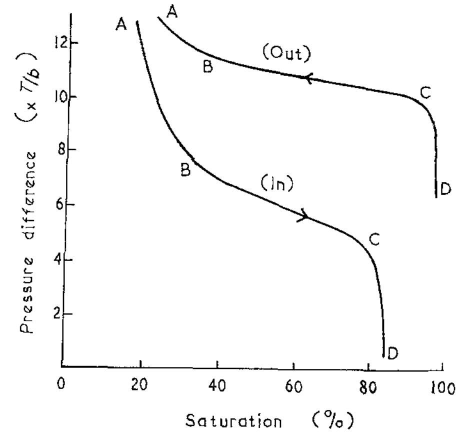

Figure 19 Relation between percentage saturation of the pore space in a bed of sand and pressure difference (expressed in terms of T/b where T = surface tension and b = average radius of the sand grains).

Fig. 18 shows an apparatus which was used by Haines [20] to relate the degree of saturation of a powder bed with the pressure difference across the bed, when one surface of the bed is in contact with water. The pressure difference is measured from the height of the powder/water interface above the free surface of the column of water. The percentage saturation of the powder is calculated from the volume of the bed, the total amount of water in the apparatus and the volume of water present in the space below the bed. The percentage saturation can be adjusted by adding or taking water from the apparatus. Fig. 19 shows typical results for a bed of sand. Two distinct curves were obtained, depending on whether the bed started off virtually dry (in) or 100% saturated (out). The shape of the curves can be explained roughly by considering the three stages in the distribution of a liquid in a bed of regularly packed spherical particles. These are shown in Fig. 20. At low liquid concentrations the liquid exists only as isolated wedges in the necks between the particles (pendular stage). As more liquid is added, the wedges build up until they just meet (funicular stage); both the air and water exist as continuous phases. The radii of curvature of the liquid menisci increase in passing from the pendular to the funicular stages, and the

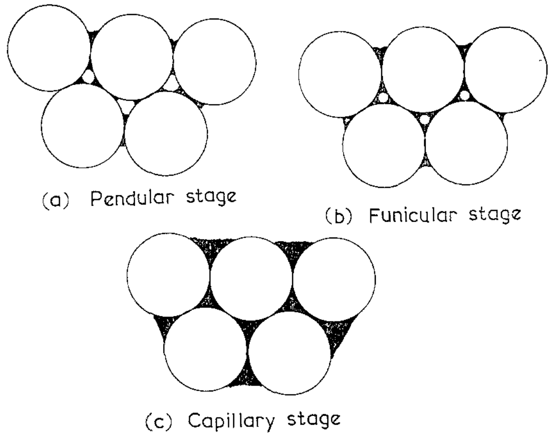

Figure 20 Stages in the distribution of a liquid in a powder bed: (a) pendular stage; (b) funicular stage; (c) capillary stage.

capillary pressure in the liquid therefore decreases. In the case of the sand bed and other powder beds in which there is a wide distribution of pore sizes, the three stages may co-exist in the partially saturated beds. The curves in Fig. 19 can be split into three regions: the steep parts (AB) at low saturation correspond roughly with the transition to or from the pendular stage and the filling or emptying of very small pores; the low gradient portions (BC) during which the bulk of the pores are filled or emptied, correspond mainly with the funicular and capillary stages; the almost vertical portion of the "out" curve (CD), near 100% concentration, probably corresponds with the uptake of a small amount of surplus water separating the particles, and the steep part of the "in" curve (CD), near 80% saturation, exists because virtually all the pores have become full except for some air bubbles which have become trapped (in much thinner beds such as the metallizing layer it seems probable that a higher degree of saturation can be reached). As the magnitude of the pressure difference in the various parts of the curve depends primarily on the capillary pressure within the pores, beds of fine particles give larger pressure differences than beds of coarse particles. In the metallizing situation in which the temperature and furnace humidity affect the glass/metal contact angle and also the volume of liquid glass, we would expect the pressure difference curves to change both with temperature and furnace humidity.

To explain the glass migration, it is convenient to consider the pressure difference as a suction pressure (i.e. a negative pressure) that the "powder" bed (alumina or metallizing) can exert at a particular temperature, and percentage saturation, and in a particular furnace atmosphere. There will be two sets of suction pressures for each bed, depending upon whether liquid is flowing into the bed *P* (in) or whether it is flowing out, *P* (out). Thus, when the metallizing layer and the debased alumina are in contact at the metallizing temperature, glass will migrate from the alumina into the metallizing layer until the suction pressure of the metallizing layer P_M (in) becomes equal to the suction pressure letting glass out P_{Al} (out). In a favourable metallizing situation the two suction pressures will not become balanced until the metallizing is practically saturated with glass,

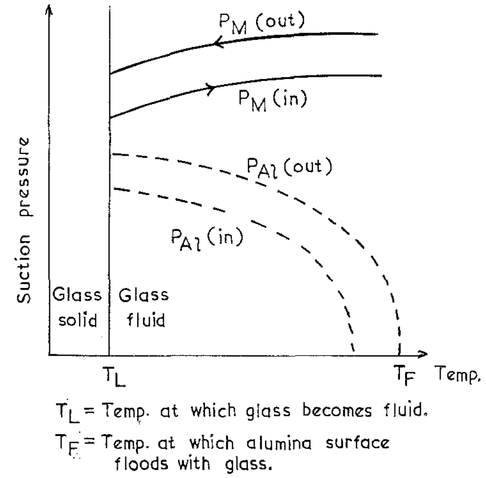

Figure 21 Ideal metallizing conditions.

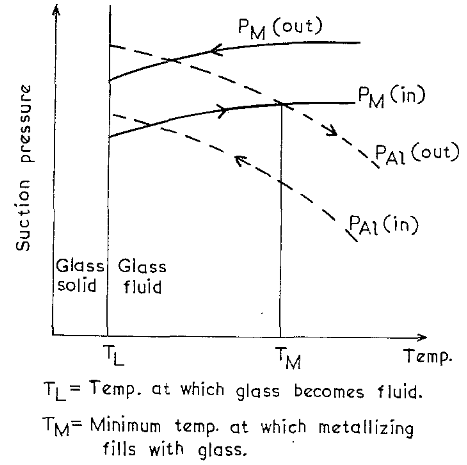

Figure 22 Favourable metallizing conditions.

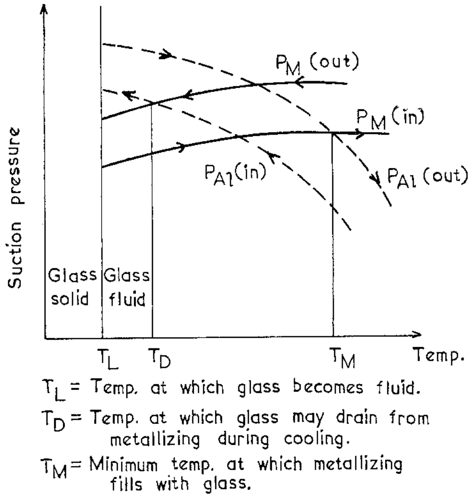

Figure 23 Unsatisfactory metallizing conditions (drainage).

while in an unfavourable situation they will become balanced when the metallizing layer is only partially saturated. In order to understand the effect of the metallizing temperature on the equilibrium, some possible relationships between the suction pressures are illustrated in Figs. 21 to 23. The suction pressures are plotted as a function of the metallizing temperature. The scales are arbitrary. The curves are different to the pressure difference curves in Fig. 19 as we are considering the effect of temperature on only one point from each curve. Thus the suction pressures in Figs. 21 and 23, P_M (out) and P_M (in), refer to the suction pressures the metallizing layer can exert when it is practically saturated with liquid glass, i.e. points corresponding to C in Fig. 19. In Figs. 21 to 23 it is assumed that the furnace atmosphere has been chosen to give the best wetting between the glass and the metallizing at a particular temperature, but that increasing the temperature further improves the wetting (i.e. a slight increase in cos θ_M) and hence increases the suction pressure of the metallizing. At high temperatures P_M (out) and P_M (in) assume constant values as cos $\theta_M \rightarrow 1$.

The suction pressure of the alumina P_{Al} (in) and P_{Al} (out) also refer to the alumina at near saturation level as under normal circumstances only a small proportion of the glass in the alumina is required to fill all the pores in the metallizing. The values of P_{Al} (out) and P_{Al} (in) are assumed to decrease with increasing temperature as the glass expands more than the alumina and ultimately at a very high temperature (T_F) it is possible for the glass to expand out of the alumina and flood the surface of the alumina.

Fig. 21 shows the relationship between suction pressures which gives the ideal metallizing conditions, and which will generally be associated with very coarse grained aluminas. On heating, the glass becomes fluid at a temperature T_L. At T_L the suction pressure of the alumina P_{Al} (out) is relatively low and below that of the metallizing P_M (in), glass will, therefore, migrate into the metallizing and practically saturate it. On heating the sample to a higher temperature, P_M (in) increases slightly and at the same time the glass in the alumina expands and causes the suction pressure P_{Al} (out) to decrease. Therefore at all temperatures above T_L, P_M (in) $>$ P_{Al} (out), so that increasing the metallizing temperature above T_L has no further effect on the glass migration except if it is raised above a temperature T_F, when the glass begins to expand out of the alumina and flooding of the metallizing surface becomes possible. On cooling (excepting flooded surfaces) there is no tendency for glass to flow back into the alumina as P_M (out) is always greater than P_{Al} (in).

Fig. 22 also represents favourable metallizing conditions but in this case the metallizing temperature has to be raised to a temperature T_M or above before P_M (in) $>$ P_{Al} (out) and the metallizing layer is saturated with glass. On cooling there will be no tendency for the glass to flow back into the alumina as P_M (out) $>$ P_{Al} (in). The slight increase in P_M (out) and P_M (in) with increasing temperature is again associated with a decrease in the glass/metal contact angle, while the corresponding decrease in P_{Al} (out) and P_{Al} (in) are associated with the high expansion of the glass within the alumina.

Fig. 23 represents unsatisfactory metallizing conditions. Saturation of the metallizing layer when P_M (in) $>$ P_{Al} (out) only occurs at a very high temperature, and then as the sample cools P_M (out) becomes less than P_{Al} (in) and it is possible that some of the glass will drain out of the metallizing layer and go back into the alumina. The glass will not be totally drained from the metallizing because the suction pressure of the metallizing will rise as the degree of saturation falls, as in the sand bed (Fig. 19). The metallizing layer will, therefore, contain some glass but will be porous and weak.

The curves in Figs. 21 and 22 can also be used to explain partial filling of a metallizing

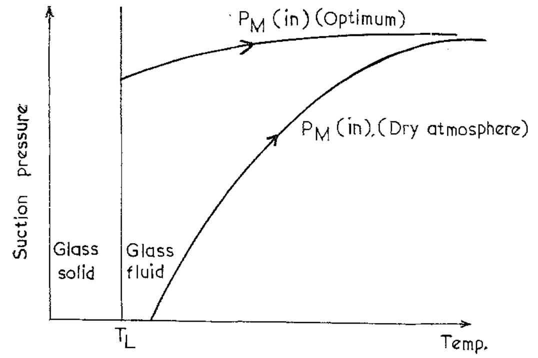

Figure 24 Comparison of the metallizing suction pressures in optimum conditions and in a dry atmosphere.

layer by glass if the curves for P_M (out) and P_M (in) are taken to represent the suction pressures at lower degrees of saturation.

Figs. 21 to 23 represent metallizing conditions in which the furnace atmosphere gives optimum wetting conditions between the glass and the molybdenum. If a relatively dry atmosphere were used instead, the suction pressure curves representing the metallizing layers would start off at zero or much lower values because of the poorer wetting which reduces cos θ_M, but would get closer to the values representing the optimum conditions at high temperatures. The comparison between two such curves is shown diagrammatically in Fig. 24. If the suction pressures of the metallizing in a dry atmosphere were substituted for P_M (out) and P_M (in) in Fig. 21 or 22, the effect would be to raise the minimum metallizing temperature T_M. The probability of getting conditions like those in Fig. 23 would also be increased. The chances of getting metal–metal sintering, which closes the pores in the metallizing layer and prevents glass migration would also be increased.

If manganese or manganese dioxide is added to the metallizing paint it is possible that the addition could be favourable or unfavourable, depending upon the particular conditions which prevail. Thus the Mn or MnO_2 could affect the initial pore size distribution in the metallizing. If the pore sizes are reduced by using very fine MnO_2 this would aid glass flow into the metallizing. However, if after the manganese oxide is dissolved in the glass the pores were larger than when Mo alone was used, this would increase the chances of drainage occurring during cooling. If manganese compounds are used with very fine grained molybdenum or tungsten paints, the addition might be favourable in preventing metal–metal sintering. It is thus not possible to predict whether the addition of manganese compounds will be beneficial.

4. Conclusions

Evidence from the literature indicates that when metallizing 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. Addition of additives to the metallizing paint, such as manganese or titanium compounds is not essential. The migration of glass is believed to take place by a capillary flow mechanism and can be explained in detail by a hypothesis which considers the relative suction pressures of the glass in the metallizing and the glass in the alumina.

The hypothesis shows that the metallizing conditions can be divided into three categories:

(1) Large grained aluminas with glass pockets very much larger than the pores in the unfired metallizing.

(2) The glass pockets in the alumina just larger or of equal size to the pores in the metallizing.

(3) Very fine grained aluminas with glass pockets smaller than the pores in the metallizing.

Provided that there is an adequate concentration of glass in the debased aluminas a good metallizing layer can be formed in category 1 at any temperature which is above the temperature at which the glass in the alumina becomes fluid, and provided that there is good wetting between the glass and the metal. This excepts very high temperatures at which it is possible for glass to flood and coat the surface of the metallizing, thus preventing a good seal being made to the braze.

In category 2 a higher metallizing temperature is required to form good metallizing but there will be a fairly large range of temperature, above the temperature at which the glass becomes fluid, when the metallizing layer will be partially, but not wholly, filled with glass. The quality of the metallizing will be much more sensitive to furnace atmosphere than in category 1.

Category 3 provides the most difficult situation as filling of the pores in the metallizing will not occur except at a high temperature.

This may be above the maximum temperature which can be reached in a normal metallizing furnace, and may cause trouble due to distortion of the alumina. Alternatively, excessive metal–metal sintering could occur which will prevent penetration of glass into the metallizing layer and reduce adhesion.

The use of titanium and manganese compounds affects the glass migration process by altering the pore structure in the metallizing, and by dissolving in the migrating glass. This will not necessarily be beneficial.

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