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On the mechanical weakness of glass seals to nickel-plated Remendur (Fe–Co–2 to 3% V) wire

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Poor surface quality of wire can result in leaking glass-to-metal seals in sealed reed contacts. Nickel plating of Remendur reeds can be effective in eliminating this problem. However, the mechanical strength with nickel plated Remendur seals is significantly inferior to that for unplated reed seals. Measurement of breaking loads required for various types of sealed contacts, followed by examination of the fracture interfaces in a scanning electron microscope, indicates that the greater strength of seals with unplated reeds is due to a chemical bond at the Remendur/glass interface caused by interaction of constituents in the alloy with the glass. Furthermore, evolution or production of gases from the nickel plating during sealing causes the formation of large bubbles at the nickel/glass interface which reduce the area of contact and contribute to weakening. Outgassing of the nickel-plated Remendur reeds prior to sealing is impractical because the temperature required to achieve this results in degradation of the magnetic properties of the reeds. Seals made with barium oxide glasses, regardless of the reed material, appear to be stronger than those with the conventional lead oxide glass.

1. Introduction

It is generally known in glass-to-metal sealing practice that poor surface quality of the metal can lead to defective seals. Numerous factors can cause cracking, gouging, galling and other defects which may contribute to poor surface quality of the metal. The character of and potential causes for certain surface defects in Remendur (Fe–Co–2 to 3%V) wire have been described [1]. A correlation of such wire defects with leaking glass-to-metal seals in Western Electric 238A remreed contacts has also been attempted [2]. Sealed reed contacts are widely used in the communications industry and the remreed is a self-latching type contact due to the use of Remendur, which is a semipermanent magnetic alloy, as the base material. Several measures can be taken to salvage or reclaim such defective wire and reeds [3]. One approach for salvaging defective Remendur reeds was plating the entire reed with nickel. The nickel plating filled surface crevices, producing a smooth surface for overplating with the contact material and for sealing. This approach was very effective in eliminating the leaking problem but led to mechanical weakness of the seals. Although the seal strength of nickel-plated reeds using the standard lead oxide glass (Corning no. 9362) were equivalent to standard product 238A seals when subjected to tensile (axial) loading, they were significantly inferior when transverse loads were applied to the reed shank. This paper reports an investigation of the cause for this weakness and whether or not the problem could be circumvented.

2. Procedure

The approach used was to measure the transverse load required for breaking glass-to-metal seals and to examine the nature of the fracture interfaces. The transverse loading apparatus is illustrated in Fig. 1. Test samples included: (1) standard 238A contacts (Remendur); (2) nickel-plated 238A con-

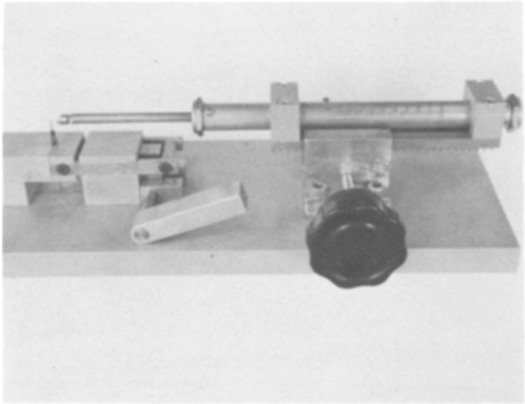

Figure 1 Transverse loading apparatus for measuring strength of glass-to-metal seals.

tacts; (3) heat-treated standard 238A contacts; (4) heat-treated nickel-plated 238A contacts; (5) standard 237B contacts (52 alloy = Fe–52 wt % Ni); (6) other manufacturers' sealed contacts.

After the seals were broken, both the reed shank in the seal region and the corresponding glass surface (after vapour deposition of 100 to 200 Å of Au) were examined in a scanning electron microscope equipped with an energy dispersive X-ray analyser (SEM-EDAX).

The normal processing for unplated and nickel-plated Remendur reeds includes an ageing anneal of 3 h at 600° C in hydrogen. Prior to sealing, some of both types were given an additional anneal of 6 h at 600° C in hydrogen or vacuum, or 3 h at 900° C in vacuum.

The influence of glass type was also examined with the nickel-plated reeds. The glasses used were the standard Corning lead oxide type with an expansion coefficient of 9.15×10^{-6} °C^{-1}, a modified version of the lead oxide glass with a coefficient of 8.85×10^{-6} °C^{-1}, and a special barium oxide–potassium oxide glass also made by Corning.

Samples of Western Electric 237B contacts, Philips R130 contacts, and Fujitsu FDR-8A contacts were also tested and examined for comparison. The 237B and Philips contacts employ soft magnetic reeds (52 alloy) whereas the Fujitsu contact has semihard magnetic reeds (Nibcolloy = 85% Co–12% Fe–3% Nb). The 237 contact uses the same lead oxide glass as the 238 contact while the Philips and Fujitsu contacts use barium oxide–calcium oxide and barium oxide–potassium oxide glasses, respectively, as determined by SEM-EDAX.

Samples of standard 238A and nickel-plated 238 contacts were exposed to a 1 HNO_3 : 3 H_2O solution for a time sufficient to dissolve the 0.535 mm diameter Remendur reeds leaving only the glass envelope. A smaller diameter drill bit (0.51 mm diameter) was inserted into the hole of the envelopes and a transverse load applied until breaking occurred. This was an attempt to determine the strength of the glass only.

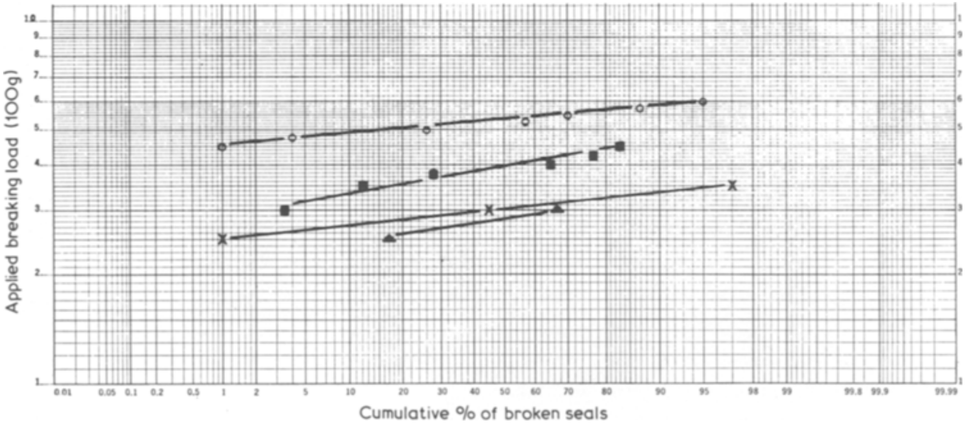

Figure 2 Results of transverse loading tests on 238-type sealed contacts with reeds annealed for 3 h at 600° C in H_2 prior to sealing. ○, Unplated Remendur, PbO glass (91.5×10^{-7} ° C^{-1} exp. coeff.) 100 samples; ▲, nickel-plated Remendur, PbO glass (91.5×10^{-7} ° C^{-1} exp. coeff.) 200 samples; ×, nickel-plated Remendur, PbO glass (88.5×10^{-7} ° C^{-1} exp. coeff.) 100 samples; ■, nickel-plated Remendur, BaO glass, 56 samples.

3. Results and discussion

3.1. Seal character of normally processed plated and unplated reeds

It can readily be seen from the plot of applied breaking loads versus the cumulative percent of broken seals (Fig. 2) that seals to standard (unplated) Remendur reeds were stronger than any with nickel-plated reeds. Of the three types of contacts with nickel-plated reeds, those employing the barium oxide glass had significantly stronger seals.

It was hypothesized that the observed weakness of seals to nickel with lead oxide glass was due to the inability of the nickel/glass interface to transfer shear stresses as does a Remendur/glass interface. This could be the result of a difference between a "mechanical" or friction bond and a "chemical bond". Evidence to support this hypothesis was found in the SEM-EDAX results.

Fig. 3 illustrates the typical surface character of unplated and nickel plated Remendur reeds after the ageing anneal (600° C for 3h in hydrogen) but prior to sealing. Surface smoothness appears the same. The EDAX spectrum in Fig. 3a shows the positioning (energies ranging from 0 to 10 keV) and typical relative intensities of the V, Fe,

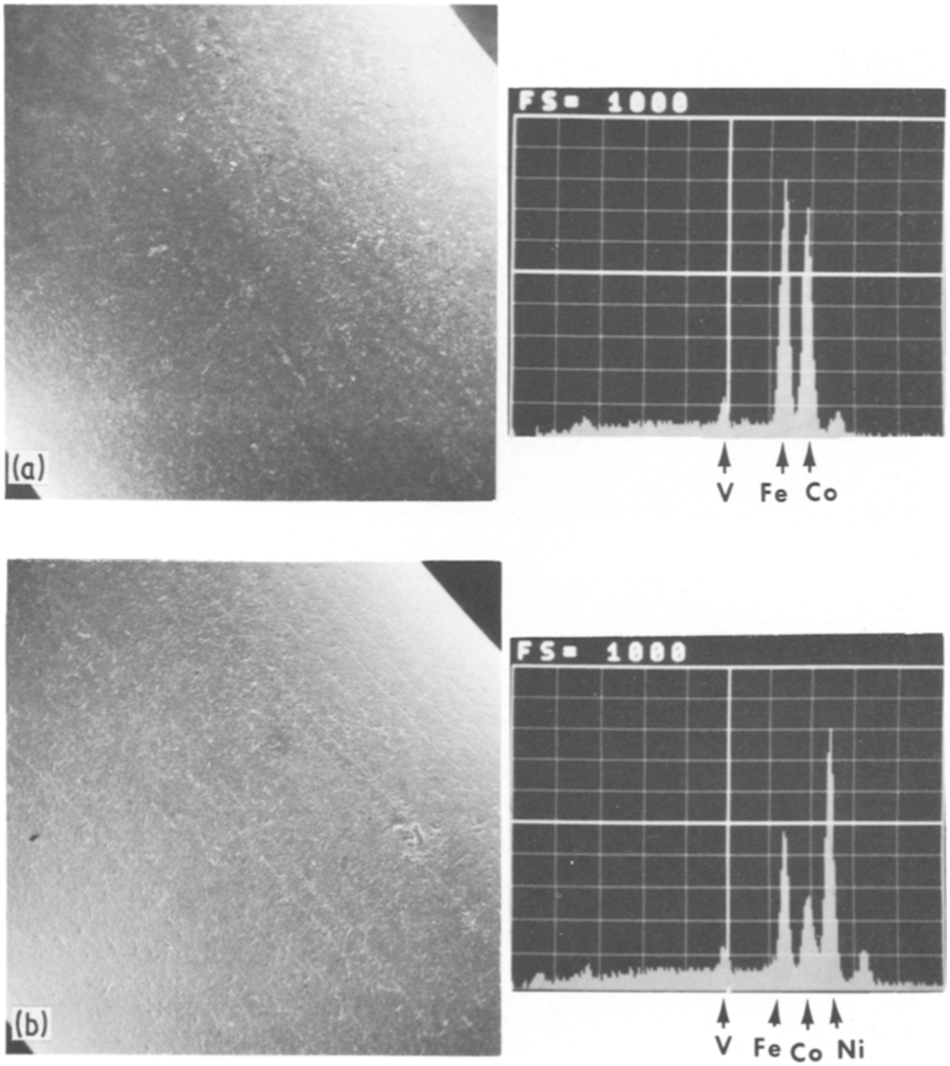

Figure 3 Typical surface character of unplated and nickel-plated Remendur reeds (SEM micrographs and EDAX analyses). (a) Unplated reed shank (× 200) and corresponding X-ray scan. (b) Nickel-plated reed shank (× 200) and corresponding X-ray scan.

and Co $K\alpha$ peaks for Remendur. In this spectrum and all others in this paper, labelling of the β peaks has been omitted for clarity. The spectrum in Fig. 3b shows that the nickel-plated reeds have a nickel-rich and not a pure nickel surface after ageing. The ageing anneal after plating causes interdiffusion of the nickel with components of the reed.

The micrographs and spectra in Figs. 4 to 6 represent the topography and composition of the interfaces in seal areas after breaking. The interface characteristics in these figures are typical of those observed for the kinds of broken contacts plotted in Fig. 2. In Fig. 4a the most significant characteristic of the unplated reed seal area is the presence of lead globules on the surface which are the light particles in the micrograph. The overall scan analysis indicates the presence of the lead particles as well as an apparent increase in cobalt and decrease in iron content of the reed surface. The mating glass surface in Fig. 4b has small voids which could be due to gas porosity and/or breaking away of the lead globules. The analysis of the glass surface reveals a significant enhancement of iron in the seal region (intensity of 5.0 versus intensity of 1.0 for a glass fracture surface away from the seal area) and also the presence of vanadium. In all glass analyses in this paper, the

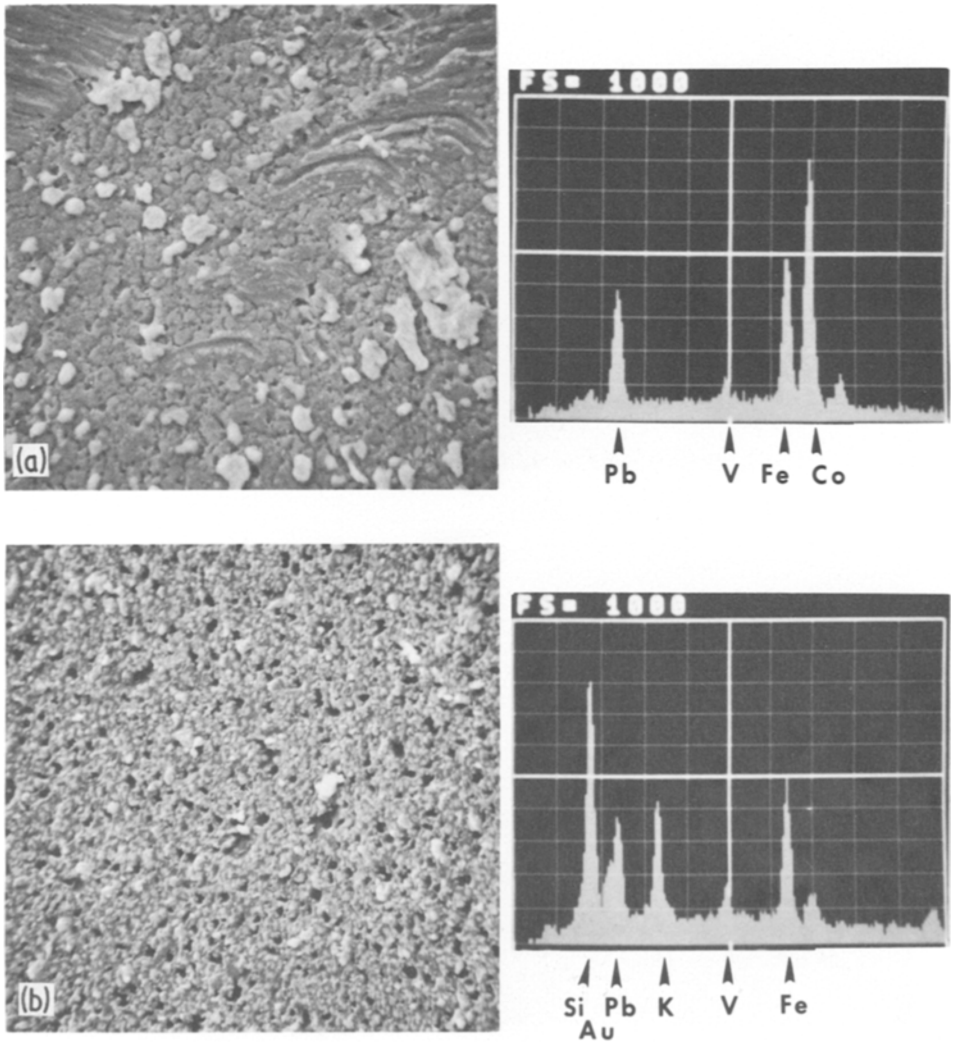

Figure 4 Broken seal fracture surfaces from standard 238A sealed contact (SEM-EDAX). (a) Unplated Remendur seal area (X 2000) and corresponding X-ray scan. (b) Mating PbO_2 glass seal area (X 2000) and corresponding X-ray scan.

major gold peak (from the conductive vapour deposited layer) is almost coincident with the major lead peak. These results indicate a definite chemical interaction at the interface. It is believed that the glass sealing operation at 1000° C causes reduction of the lead oxide in the glass primarily by iron or iron oxide (FeO) corresponding to the following reactions:

$$\mathrm{Fe(s) + PbO(s) \rightarrow Pb(1) + FeO(s)}$$
$$\Delta G^\circ = -19 \text{ kcal}$$

or

$$\mathrm{3FeO(s) + PbO(s) \rightarrow Pb(1) + Fe_3O_4(s)}$$
$$\Delta G^\circ = -14 \text{ kcal.}$$

From tabulated data [4] and a standard free energy diagram for the formation of oxides [5] these reactions are thermodynamically feasible at 1000° C as indicated. These reactions result in a mutual transfer of components, especially lead and iron oxide(s), across the seal interface. The authors previously reported [1] on the preferential oxidation and redistribution of iron and vanadium to the surface of Remendur when heated to 1000° C and this further supports the observation that iron and vanadium oxides transfer to the glass leaving a cobalt-rich reed surface. A similar redistribution has been reported for glass seals to Kovar (54% Fe–31% Ni–17% Co) when the alloy was intentionally pre-oxidized [6].

The results in Fig. 5 dramatically illustrate the

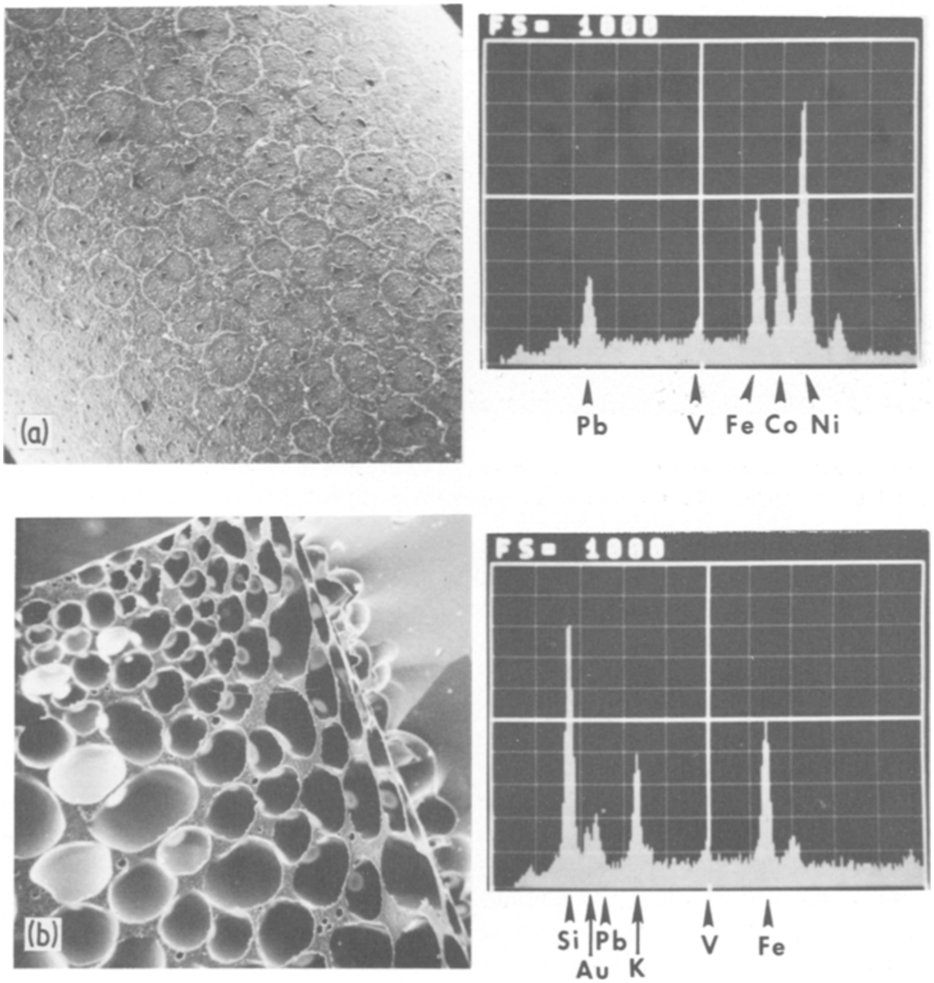

Figure 5 Broken seal fracture surfaces from a nickel-plated 238-type sealed contact (SEM-EDAX). (a) Nickel-plated Remendur seal area (X 200) and corresponding X-ray scan. (b) Mating PbO_2 glass seal area (X 200) and corresponding X-ray scan.

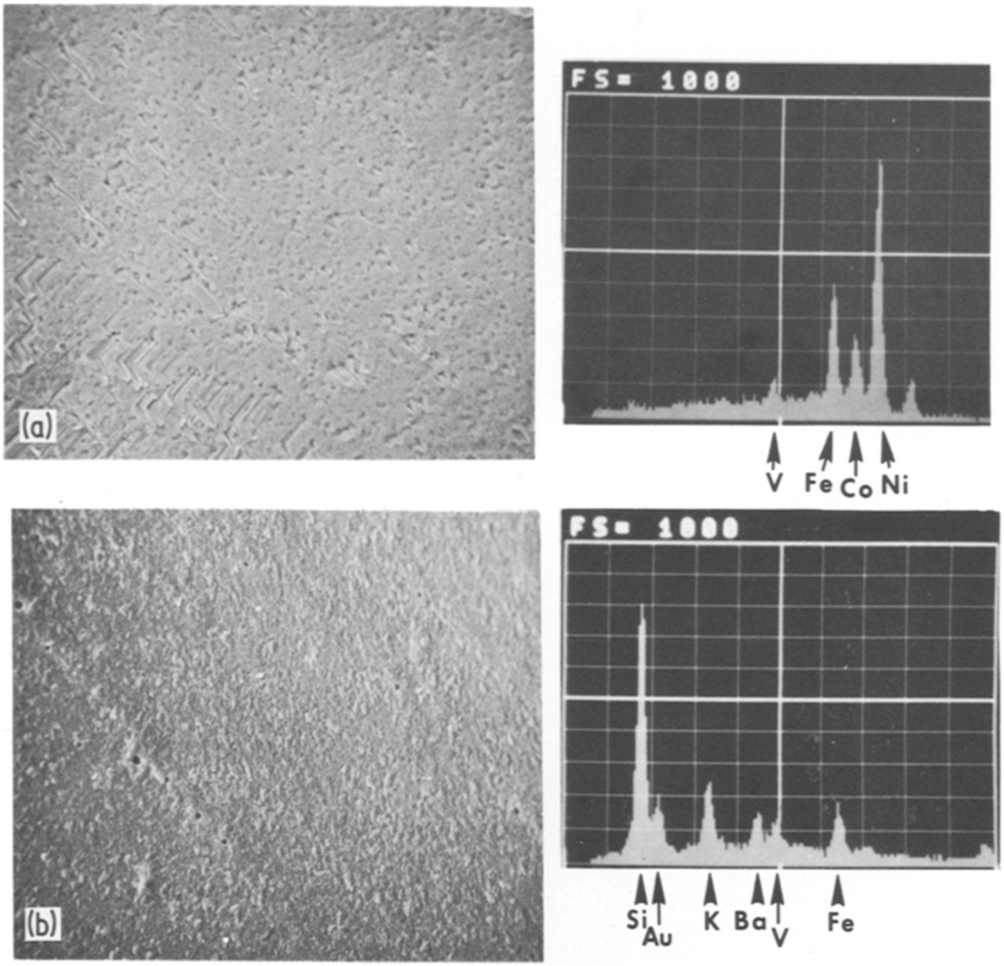

Figure 6 Broken seal fracture surfaces from a nickel-plated 238-type sealed contact (SEM-EDAX). (a) Nickel-plated Remendur seal area (X 1000) and corresponding X-ray scan. (b) Mating BaO glass seal area (X 1000) and corresponding X-ray scan.

different character of the seal interface when nickel plated Remendur is used with the same lead oxide glass. The nature of the seal can be described best as "gassy". The cavernous voids in the glass indicate that a significant amount of gas(es) was generated during the sealing operation and presumably was entrapped at the interface as the molten glass hardened. Obviously, the resultant area of glass-to-metal contact in the seal area was minimized and as could be expected such seals had lower strength. The scan analysis indicates there was a similar interaction between iron of the reed and lead oxide of the glass with mutual transfer. It is significant to note that there was no evidence of the more abundant nickel playing a part in this interaction, i.e. no indication of nickel on the glass surface of the seal area.

The interface character of a seal made to nickel-plated Remendur with a barium oxide glass is considerably different from one made with the lead oxide glass. Fig. 6 shows that neither the reed nor the glass indicate any reactivity or mutual transfer of components. Furthermore, there is a lack of porosity or gas bubbles in the glass. It would appear that such seals, although lacking an apparent chemical bond, are stronger by virtue of the maximum interface contact and presumably the radial compressive stress at the interface.

3.2. Effects of additional heat-treatments of reeds

Generally, bubbles in glass-to-metal seals are due to evolution of dissolved gases in the metal. Nickel, iron, and their alloys can be especially gassy if not vacuum-melted [7]. It is recommended that prior to sealing, such metal parts be degassed and/or decarburized in vacuum or wet hydrogen at a temperature above that used in the sealing process [7] such as 900 to 1100° C [8]. Rather than subject the reeds to such temperatures, which are deleterious to the magnetic character of the reeds, [9, 10] they were given an extended anneal (6 additional hours) at the normal ageing temperature [10] (600° C) in cylinder hydrogen or vacuum. In addition, the glass envelopes were given a moderate anneal (400° C, 30 min) prior to the sealing operation. Fig. 7 shows the breaking test results on contacts made after such treatment as well as control samples. They reveal that the extended 600° C treatments had no effect on improving seal strength of nickel-plated reeds with lead oxide glass as all datum points fall on the same curve. Nor was any effect noted on the seal strength to unplated Remendur. Examination of the broken seal interfaces likewise indicated no significant differences in appearance between the treated samples and the controls; the interface characteristics were the same as shown in Figs. 4 and 5. This was true despite the fact that the surface concentration of both Fe and Co had increased relative to Ni for the extended annealing time.

These results prompted the use of a more severe treatment (900° C, 3 h, vacuum), despite the effect on magnetic properties, in order to see if seal strength could be improved. As seen in Fig. 8 this treatment did not affect seals with unplated reeds but it did increase the strength of seals with nickel-plated reeds when the data for the latter are compared with corresponding data in Fig. 2 and 7. The scanning micrographs in Fig. 9 show that the glass surface for this nickel-plated reed seal, although still pocked, is much less so than one which had not been heated at 900° C (cf. Fig. 5b). Further examination of the micrographs and analyses in Fig. 9 reveals there has been considerably more interaction and mutual transfer of components, especially lead and iron, when again compared with those in Fig. 5; it is important to note that there is still no evidence of nickel transfer. The analyses of the reed seal areas illustrate that the higher temperature treatment (Fig. 9a) had so promoted interdiffusion that the surface was nickel-deficient rather than nickel-rich and thus resulted in a seal having characteristics like those with unplated Remendur (Fig. 4a) rather than nickel-plated Remendur (Fig. 5a).

A monopole mass spectrometer with a high vacuum system was utilized to monitor the outgassing of various reeds upon heating to temperatures above 1000° C. It was found that nickel-plated reeds with only the usual 600° C anneal,

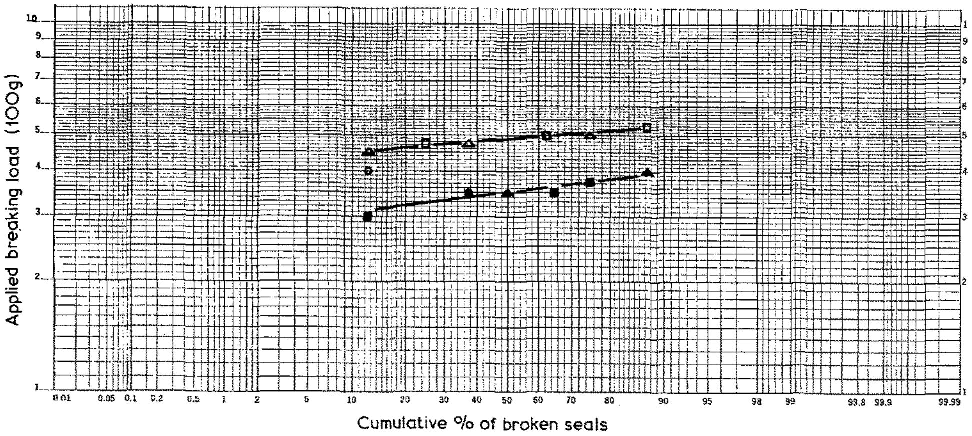

Figure 7 Results of transverse loading tests on 238-type sealed contacts after 6 h additional annealing at 600° C of reeds prior to sealing. Unplated Remendur, PbO glass (91.5×10^{-7} °C^{-1} exp. coeff.): ○ control, no additional anneal; △, hydrogen anneal, 8 samples; □, 10^{-5} Torr vacuum anneal, 8 samples. Nickel-plated Remendur, PbO glass (91.5×10^{-7} °C^{-1} exp. coeff.): ●, control, no additional anneal, 12 samples; ▲, hydrogen anneal, 8 samples; ■ 10^{-5} Torr vacuum anneal, 8 samples.

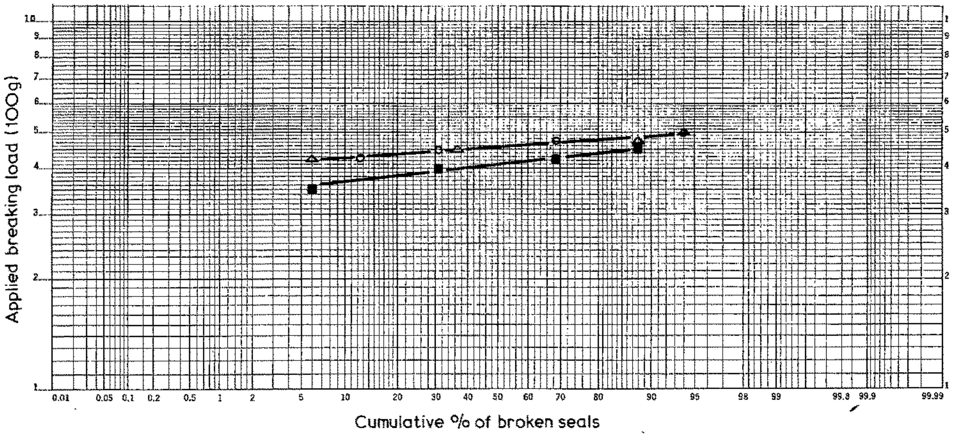

Figure 8 Results of transverse loading tests on 238-type sealed contacts after 3 h additional vacuum anneal at 900° C of reeds prior to sealing. ○, Unplated Remendur, PbO glass (91.5 × 10^{-7} ° C^{-1} exp. coeff.) no additional anneal, 16 samples; △ unplated Remendur, PbO glass (91.5 × 10^{-7} ° C^{-1} exp. coeff.) 10^{-5} Torr vacuum, 16 samples; ■, nickel-plated Remendur, PbO glass (91.5 × 10^{-7} ° C^{-1} exp. coeff.) 10^{-5} Torr vacuum, 16 samples.

exude 5 to 10 times more gas, primarily H_2, CO and CO_2, than nickel-plated reeds which had an additional 900° C anneal or those without nickel plating. Attempts to determine what gas(es) was trapped in the bubbles at the interface by actually breaking the seals in the vacuum chamber were inconclusive. Nevertheless, these results confirm that a major cause of gassy seals, particularly with nickel plating, is the evolution of dissolved impurities from the nickel.

The results indicate that heat-treatment of nickel-plated Remendur reeds is an impractical approach to preventing gassy seals to lead oxide-type glass. The high temperature required for effective degassing would alter the desired magnetic character of the Remendur.

3.3. Comparison with other types of sealed contacts

For comparison with the standard and nickel-plated Remendur seals, samples of other type dry reed contacts were tested. The mechanically soft reeds (52 alloy = Fe–52 wt % Ni) used in the Western Electric 237B and the Phillips R130 bent at transverse loads under 100 g in this manner. At the other extreme the Fujitsu contacts, employing 0.60 mm diameter Nibcolloy (85% Co–12% Fe–3% Nb) reeds in a barium oxide–potassium oxide glass, had seal strengths considerably greater than any other contact tested and greater than the 650 g loading limit of the test fixture. Although quantitative data on the breaking strengths were not generated for these contacts, interesting characteristics of these seal interfaces warrant discussion.

The interface of the 237B seal, although not illustrated, was very similar to that of the standard 238A as pictured previously in Fig. 4. One observes the mutual transfer of iron and lead but, significantly, no transfer of nickel. The interface of the Philips seal was considerably different in terms of topography from any other seal examined as seen in Fig. 10. The barium oxide–calcium oxide glass conformed exactly to the surface of the 52 alloy reed and the glass separated by the fracture revealed a replica of the reed surface. There was no evidence of transfer of any of the components. The Philips sealing procedure and the use of the barium oxide–calcium oxide glass appears to produce a strong compression-type seal.

A somewhat puzzling contrast was provided by the Fujitsu contact seals. The micrographs and spectra in Fig. 11 illustrate that, as with the other seals employing barium oxide glasses, there was no transfer of glass components to the reed and only a small transfer of iron and cobalt to the glass. However, these much stronger seals had many small voids (3 μm or less in diameter) in the glass surface. It is presumed that these were due to dissolved gases or carbon in the Nibcolloy. It

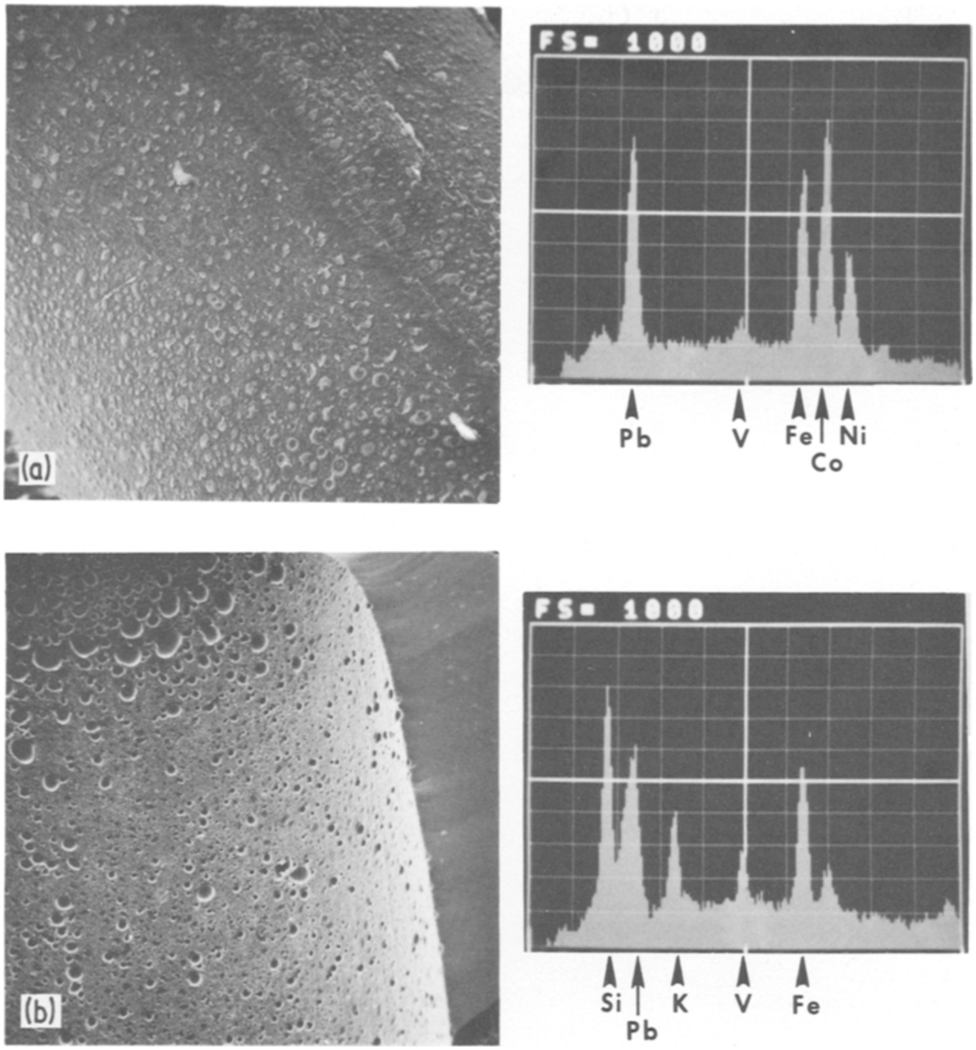

Figure 9 Broken seal fracture surfaces from a nickel-plated 238-type sealed contact with 3 h additional vacuum anneal (900° C) of reeds prior to sealing (SEM-EDAX). (a) Ni-plated Remendur seal area (X 200) and corresponding X-ray scan. (b) Mating PbO_2 glass seal area (X 200) and corresponding X-ray scan.

may be that the greater strength of these seals is due to the higher strength and better mechanical adherence of the barium oxide glass, despite the reduced area of seal contact due to the voids. The larger diameter Nibcolloy reed and surrounding mass of glass may also have some influence on the apparent greater strength of such seals.

One conclusion which can be drawn from all the foregoing is that no matter whether Remendur or 52 alloy is used or what sealing procedure followed, seals made with barium oxide glasses are stronger. An attempt was made to determine whether this was due to the barium oxide glass being inherently stronger. Fig. 12 shows the results of breaking tests on glass envelopes where the original plated or unplated Remendur reeds were dissolved out and a slightly smaller rod inserted for applying the transverse load. This admittedly qualitative test does suggest that the barium oxide glass made by Corning is stronger than their lead oxide glass. The authors were advised that the barium oxide glass should not be inherently stronger and it was suggested that the apparent difference between the two glasses was more likely

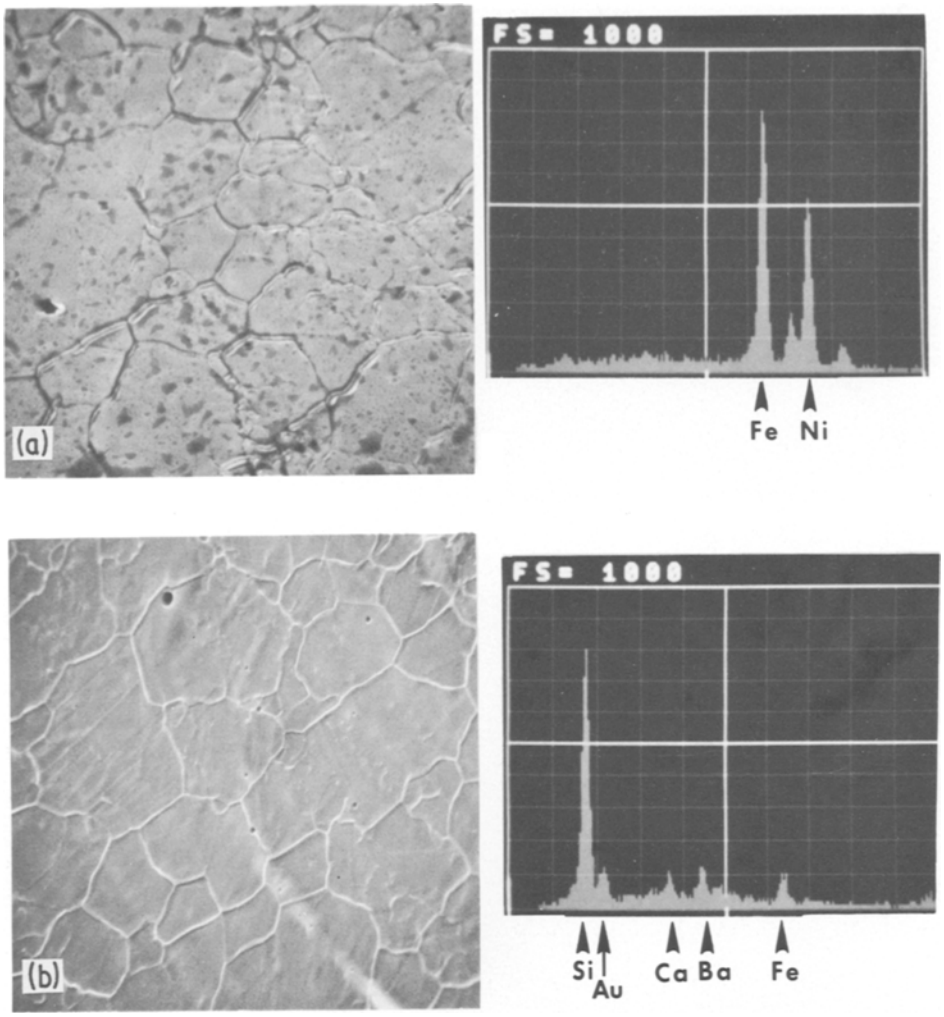

Figure 10 Broken seal fracture surfaces from a Philips R130 sealed contact (SEM-EDAX). (a) 52-alloy seal area (× 2000) and corresponding X-ray scan. (b) Rating BaO glass seal area (× 2000) and corresponding X-ray scan.

due to differences in stress risers in the glass surface such as microcracks and pits caused by differences in the sealing procedure and by the acid dissolution of the reeds [11].

4. Conclusions

(1) With lead oxide glass, normally processed unplated Remendur reeds produce stronger seals than normally processed nickel-plated Remendur reeds. This can be attributed to (a) a chemical bond at the Remendur–glass interface due to interaction of constituents in the glass and alloy, and (b) reduced area of contact from large bubbles formed at the nickel–glass interface due to evolution or production of gases from the nickel plating.

(2) Outgassing by heat-treatment of nickel-plated Remendur reeds prior to sealing is impractical because the temperature required to adequately improve the strength of seals with lead oxide glass degrades the magnetic properties of the reeds.

(3) Seals made with barium oxide glasses, regardless of reed material, appear to be stronger than those with lead oxide glass. It is uncertain whether this is due to inherent properties of the glasses, differences in sealing procedures, or both.

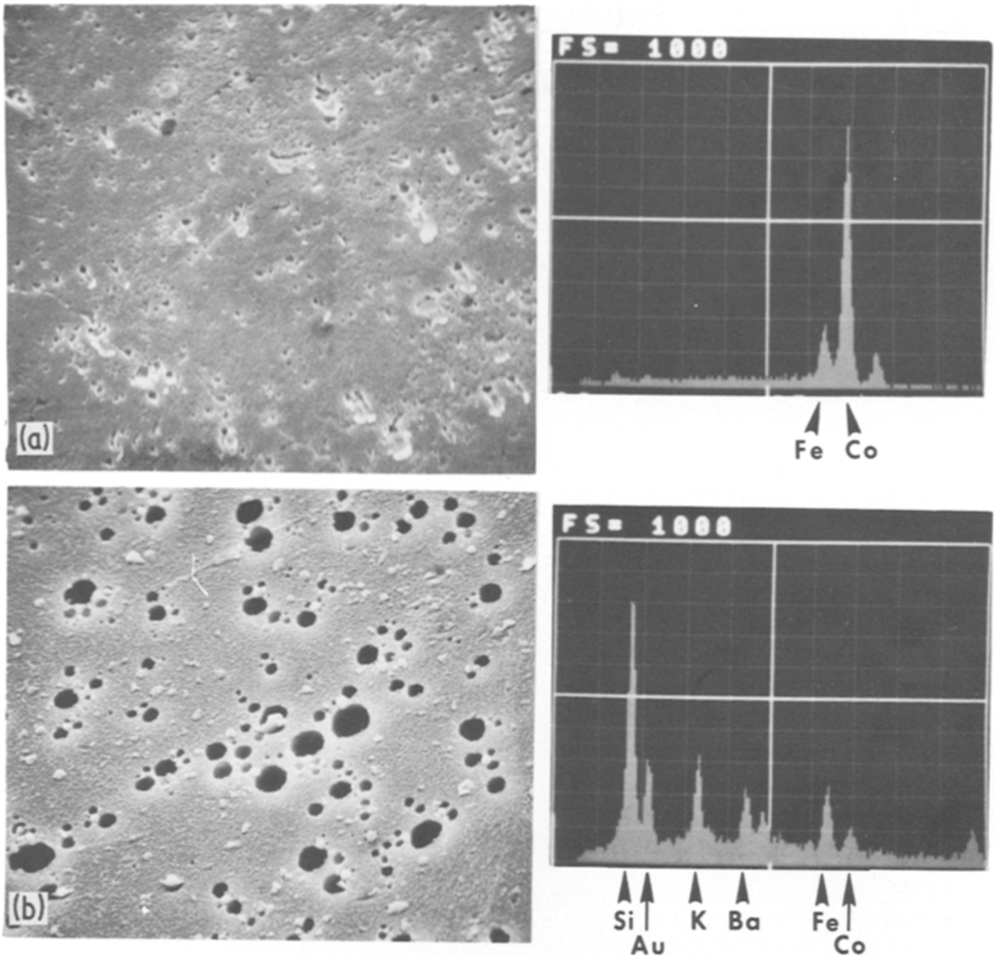

Figure 11 Broken seal fracture surfaces from a Fujitsu FDR-8A sealed contact (SEM-EDAX). (a) Nibcolloy seal area (X 2000) and corresponding X-ray scan.. (b) Mating BaO glass seal area (X 2000) and corresponding X-ray scan.

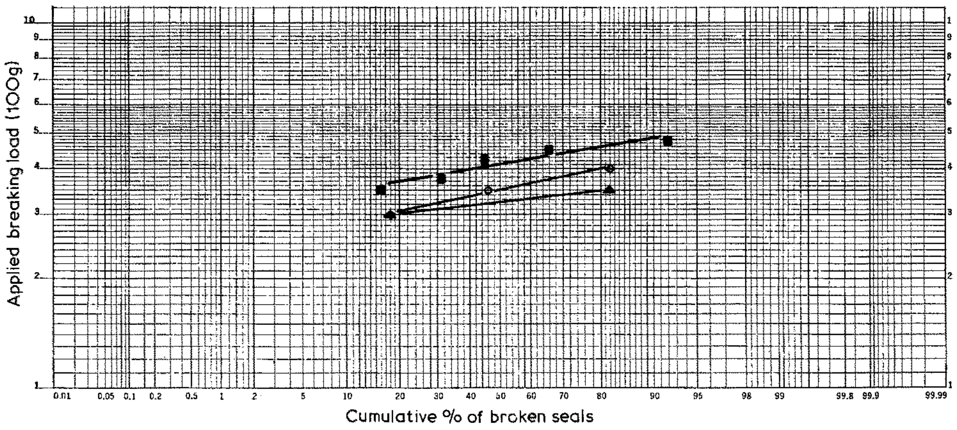

Figure 12 Results of transverse loading tests on 238-type sealed contacts after dissolving out and replacing reeds with smaller diameter rod. ○, Unplated Remendur, PbO glass (91.5×10^{-7} ° C^{-1} exp. coeff.) 11 samples; ▲ nickel-plated Remendur, PbO glass (91.5×10^{-7} °C^{-1} exp. coeff.) 11 samples; ■, nickel-plated Remendur, BaO glass, 12 samples.

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