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Thermal Expansion and Adhesion of Ceramic to Metal Sealings: Case of Porcelain–Kovar Junctions

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Abstract

Glass to metal sealings necessitate a pre-oxidation of the metal, producing a thin superficial oxide layer. In the case of porcelain–kovar junctions a glassy interphase is necessary, which reacts and dissolves the oxide layer during the bonding thermal treatment. In the interfacial zone this leads to a good fitting of the thermal expansion coefficients of the phases present: in the alloy the superficial part is impoverished in iron and its thermal expansion coefficient is close to that of the FeO-rich glass which has dissolved the oxide layer. The resulting buffer zone limits the effect of strains appearing during cooling at the end of the bonding thermal treatment. Moreover, the FeO-rich glass penetrates the open porosity of the superficial alloy layer (due to its pre-oxidation) providing a good physical adherence of glass to kovar. At the porcelain–glass interface there is no problem because of the similarity of dilatometric behaviour of the two materials.

1 Introduction

Glass to metal sealings necessitate a preliminary oxidation treatment of the metal. The resulting oxide layer reacts subsequently with glass to make a strong junction between glass and metal. This bonding thermal treatment is achieved at temperatures near to that of glass softening, and during cooling the difference in thermal expansion between glass and metal may generate interfacial strains strong enough to break the junction. To prevent this, special alloys and glasses are used, their main characteristic being the similarity in their thermal expansion.

On the basis of this very simple theoretical approach, a technology has long been developed industrially, and many various pieces for a wide range of applications are currently produced. Nevertheless many questions remain unanswered, such as: why are the conditions (sealing time, temperature, etc.) of the alloy pre-oxidation so important, or why must the duration of the joining thermal treatment be so sharp? In spite of the industrial importance of these questions a limited number of papers is available in the literature,[1–6] and the know-how remains in the factories.

Some studies[1–4] have shown that a good junction depends on the degree of preoxidation, sealing time and temperature. It has been shown[5,6] that iron diffusion into the glass produces a modification in the thermal expansion behaviour of glasses. According to Ikeda and Samalima[5] the glass thermal expansion increases, while according to Mayer *et al.*[6] it decreases.

In order to shed some light on the mechanism of the glass to metal junction, we decided to study each step of the process, by working on the example of porcelain–kovar joining with a glass interphase. We have already our published results on the oxidation of kovar.[7] This material which is the one most used for glass junctions, is a Fe–Co–Ni alloy, but its oxidation layer is mainly composed of iron oxides. The underlying oxide is enriched in cobalt and nickel and presents an important porosity. During the reaction with glass, the oxide layer of the alloy is dissolved by the glass, and this improves its wetting quality and produces good junctions.[8]

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Table 1. Measured thermal expansion coefficients, α

Material	*Kovar*	*Glass*	*Porcelain*
α ($\times 10^7$)	50	52	52

Table 2. Main impurities of the metallic powders

	Iron	*Nickel*	*Cobalt*
Al	0·007	0·008	0·005
Ca	0·001	<0·001	0·005
Ni	0·02		0·05
Si	0·1	0·02	0·03
Sr	<0·001	<0·001	
Ti	0·01		
Cr		0·001	
Cu		0·005	0·04
Fe		0·001	0·01
Mg		0·001	
Mn			0·005

The aim of this work was to study what the effects of these treatments are on the thermal expansion of the interfacial zone in order to understand better the origins of the bonding.

2 Materials and Methods

The materials used have very similar measured thermal expansion coefficients, as shown in Table 1.

Kovar was provided by Imphy SA (ref. 08D1006), porcelain by KPCL S.A. (ref. CM10) and glass was made from a Cerdec S.A. frit.[9]

When kovar is oxidized, the composition of the alloy near the interface is very different from that of the bulk[7] and gives the approximate compositions of the metallic phase existing in the interfacial zone. From Fig. 1, it is obvious that the thermal expansion of the interfacial zone is certainly strongly perturbed by the composition modifications due to the bonding reaction as well in the alloy[7] as in the oxide and glassy phases.[9] This induces local coefficient values very different from those given in Table 1. It was impossible for us to determine directly these values on real pieces of complex morphology, and the only feasible way was to make different samples having compositions corresponding to those followed by EDX analysis across the interface in the case of a strong and vacuum-tight junction.

For the alloy, bars were prepared from metallic powders of iron, cobalt and nickel provided by Cerac Inc. mixed for 4 h in a Turbula mixer (Prolabo S.A.). Table 2 presents the main impurity contents of these powders. They were then heated in an alumina crucible at 1420°C under a flow of pure argon (L'Oxygène Liquide S.A., quality U) for 1 h in a graphite furnace. After cooling, small bars (4 × 4 × 35 mm) were cut and polished. The iron oxide–glass mixtures were made with iron monoxide (from Cerac Inc.) since it has been shown that the iron oxide scale, initially composed of Fe_3O_4 and Fe_2O_3, becomes only iron monoxide above 900°C.[9] Elemental composition is given in Table 3 and the composition of the glass frit, provided by Cerdec S.A., in Table 4.

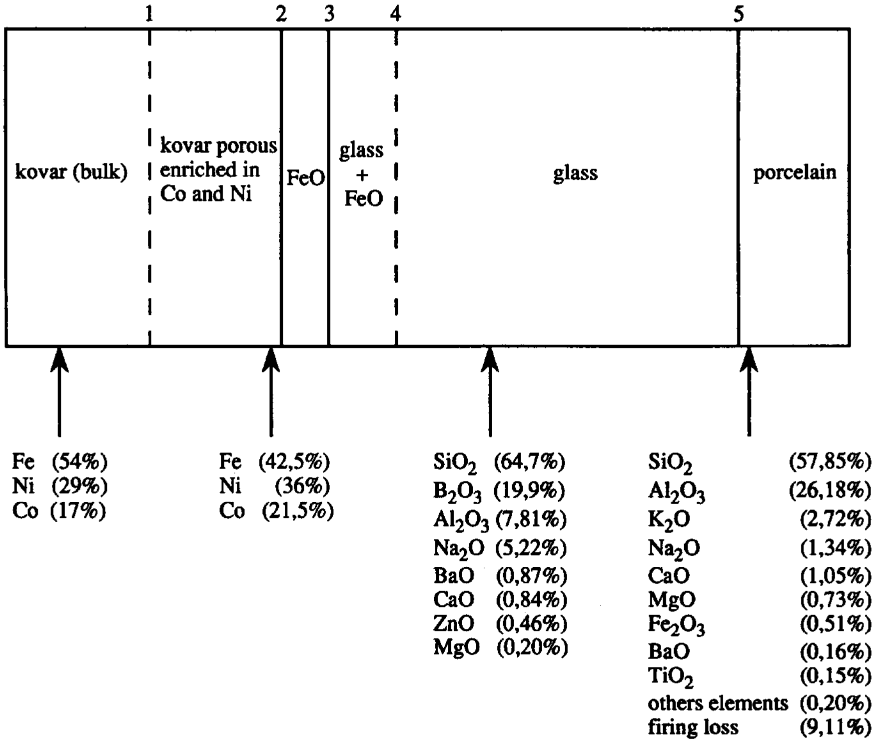

Fig. 1. Major components of the interfacial zone after bonding.

Table 3. Metallic elements content of the iron monoxide powder

Fe	*Al*	*Ca*	*Co*	*Cr*	*Cu*	*Mg*	*Ni*	*Ti*
77·28	0·02	<0·01	<0·01	<0·01	0·001	0·1	0·02	<0·02

Table 4. Composition of the glass frit

Oxide	SiO_2	Al_2O_3	B_2O_3	Na_2O	*MgO*	*CaO*	*BaO*	*ZnO*
% (pds)	64·7	7·81	19·9	5·22	0·20	0·84	0·87	0·46

Iron monoxide and glass powders were mixed in an agate mortar and then put in a silico-alumineous crucible previously covered with kaolin to avoid any bonding between glass and crucible. They were heated to over 900°C in accordance with the bonding thermal treatment.[9] After cooling, the pellets were cut with a diamond saw to obtain small bars for dilatometry. Great attention was paid to avoid the presence of kaolin traces, and finally the samples were carefully polished. The dimensions of the pieces were about 4 × 4 × 40 mm. Dilatometry measurements were carried out in a Netzsch 402E-3 differential dilatometer, coupled to a computer which processed the signal. Bars were heated under an argon flow to 1000°C at the rate of 2°C min^{-1} for the alloy bars and until the dilatometric softening point.

3 Results

In order to determine the composition of the alloy sample and that of the glass–FeO mixtures, we obtained the concentration profiles of the elements present in the interfacial zone after short thermal treatments.[9] Figure 2 shows that, in the interfacial zone from kovar to glass, there are four distinct domains:

- the original alloy with its nominal composition (part I);
- the Fe-impoverished alloy zone (part II) extending for about 8 μm where the alloy composition was of 42·5 wt% Fe, 21·5 wt% Co and 36 wt% Ni at 2 μm from the interface with oxide or glass;
- a narrow range (2 μm) containing both glass and iron oxide partially or entirely dissolved (part III);
- a large domain extending 30 μm in which iron diffuses into the glass.

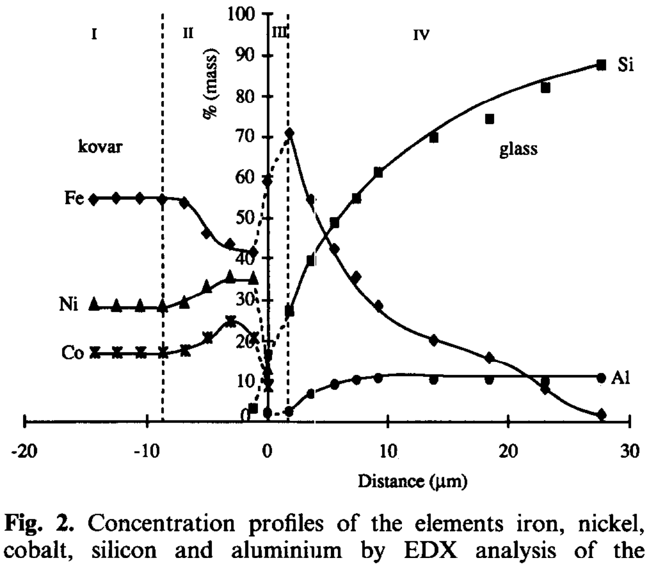

Fig. 2. Concentration profiles of the elements iron, nickel, cobalt, silicon and aluminium by EDX analysis of the kovar/glass interface after 15 min at 910°C.

Based on these observations we prepared an alloy sample with the same composition as measured near the alloy surface (Fe: 42·5 wt%; Co: 21·5 wt%; Ni: 36 wt%) and three FeO–glass mixtures with weight ratios of 20–80%, 40–60% and 60–40% respectively.

Dilatometric measurements were carried out on samples having these compositions and Fig. 3 presents their dilatometric curves between 20 and 1000°C together with those of original glass, kovar and porcelain.

One can see that the glass expansion and the softening temperature grow appreciably with increasing FeO content. The relevant values as well as the thermal expansion coefficients of kovar, prepared alloy and porcelain are given in Table 5. One can also notice, examining Fig. 3, that the increase in thermal expansion due to the glass transition becomes smaller with increasing FeO content in the glass. Concerning the prepared alloy, which contains less iron than kovar, its thermal expansion is greater than that of porcelain and of kovar.

4 Discussion

During the joining reaction, the oxide layer of the kovar reacts and is progressively dissolved into the glass.[8] As a consequence, near the interface 3 (Fig. 1)

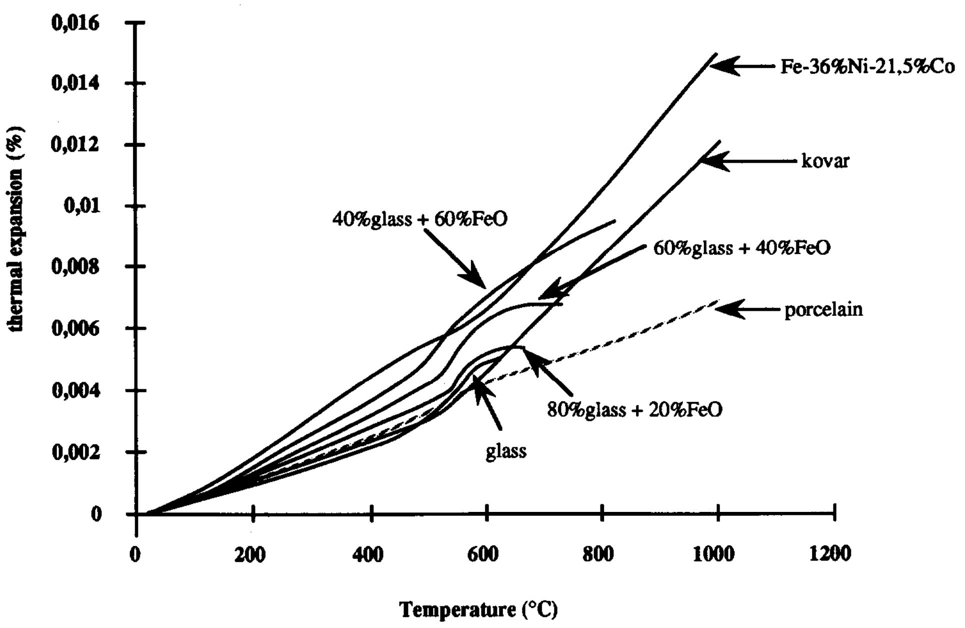

Fig. 3. Dilatometric curves of glass, prepared alloy, glass and FeO, kovar and porcelain.

the FeO content of the glassy phase increases rapidly: to a certain extent a kind of continuity may occur at this interface between the dilatometric behaviour of FeO and that of the glassy phase rich in FeO. On the dilatometric curves of Fig. 3 and considering Table 5, we actually observe that the thermal expansion of the FeO-rich glassy phases tends to approach the value[10] of pure FeO ($\alpha = 12{\cdot}2 \times 10^{-6}$ °C^{-1}), and therefore the behaviour of the glass tends towards that of a cristallized phase with the narrowing of the glass transition zone.

We have previously shown,[8] on the basis of the examination of the pseudo ternary phase diagrams of FeO–Al_2O_3–SiO_2[11] and FeO–Na_2O–SiO_2[12] (the FeO–B_2O_3–SiO_2 phase diagram is not available) that the effect of FeO dissolution in the glass is a lowering of the temperature of apparition of the liquid phase, the optimum being reached for FeO content of about 50 wt%, and, consequently, we have observed that FeO dissolution noticeably improves the wetting of the glassy phase. There is a double beneficial effect of the FeO dissolution in the glass which fits the dilatometric characteristics of glass and oxide layer at the interface 3 (Fig. 1) and which contributes to good wetting.

At the beginning of the dissolution process, there is a significant dilatation gap between the reaction zone and the bulk of the glass, because the diffusion area of FeO is still very restricted. For this reason this zone is very brittle and may crack when cooling. It is necessary therefore to prolong the treatment time at the joining temperature to allow the FeO dissolution gradient to attain an optimal width to avoid this problem.

In the alloy region (interface 2 of Fig. 1) the results of Fig. 3 are also very interesting. One can see that the impoverishment in iron of this zone corresponds to an increase in its thermal expansion coefficient since Table 5 shows that the Fe(42·5 wt%)–Ni(36 wt%)–Co(21·5 wt%) alloy has a thermal expansion coefficient nearly twice that of kovar and close to that[10] of FeO. Between interfaces 1 and 2 (Fig. 1) there is certainly a regular increase of the thermal expansion related to the changes of composition of the alloy in this domain. This constitutes a buffer zone which tends to fit the dilatometric behaviour of kovar and

Table 5. Thermal expansion coefficients of the different compounds present in the interfacial zone and softening temperatures of the glassy phases

	Glass	*80% glass + 20% FeO*	*60% glass + 40% FeO*	*40% glass + 60% FeO*	*Kovar*	*42·5% Fe +36% Ni +21·5% Co*	*Porcelain*
α (300°C) $\times 10^7$	52	61	78	84	50	102	52
Softening temperature (°C)	620	654	733	832			

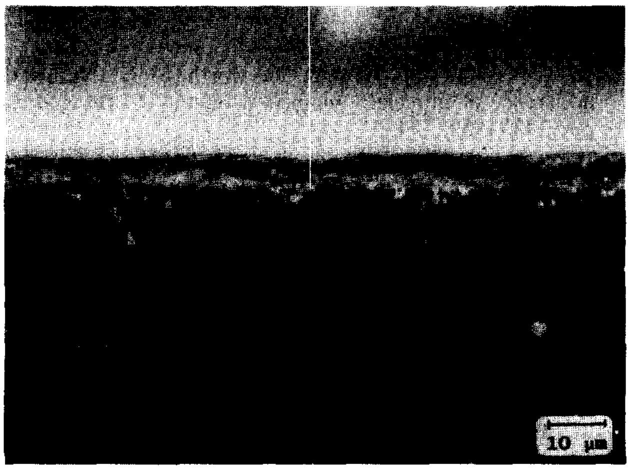

Fig. 4. Micrograph of a kovar/glass interface.

FeO-rich glass or FeO phase. It would seem improbable that the joining can be strong if the FeO phase is present, because its porosity constitutes a low resistance zone. This result has been experimentally confirmed.[9]

In these conditions a good bonding is reached when the entire iron oxide layer has reacted with the glass. At this point the interfaces 2 and 3 meet and there is a good fitting of thermal expansion coefficients on both sides. A good fitting is also found between interfaces 1 and 2 due to the smooth change of the composition of the alloy in this zone. This condition is also fulfilled in the glassy phase through the FeO diffusion space. If the thermal treatment is too long, FeO diffusion leads to a complete homogenization of the glassy phase. In this case we have a small FeO concentration in the glass and we find again a thermal expansion coefficient similar to that of the original glass resulting once again in a dilatation gap at the interface 2/3 (Fig. 1). This result is consistent with experimental results[9] and with industrial know-how, as far as it can be ascertained.

Looking at the interface 5 (Fig. 1), there is never any dilatation problem in this region because the glass quantity is sufficient to avoid any dilatometric change when FeO is dissolved, and the values of the thermal expansion coefficients do not differ from those of Table 1.

At this point, one important question arises: if the result of this precise treatment is only to obtain a good fitting of thermal expansion coefficients in the interfacial zone, why are they necessary, since the original materials (Table 1) had already very similar dilatometric behaviour? We propose two answers: first, the glass wetting improvement as previously shown,[8] and second, the achievement of a physical adhesion through the penetration of glass into the alloy. Indeed the pre-oxidation treatment creates some superficial open porosity in the alloy that glass invades during FeO dissolution as shown in Fig. 2. Here one may observe that there is some silicon located in the iron-impoverished alloy (part II), and otherwise it is well illustrated by the micrograph of Fig. 4 which shows the glass penetration in the open porosity of the iron-impoverished alloy. Our experiments do not allow any assertion to be made about an eventual chemical process, which is possible, but not proved.

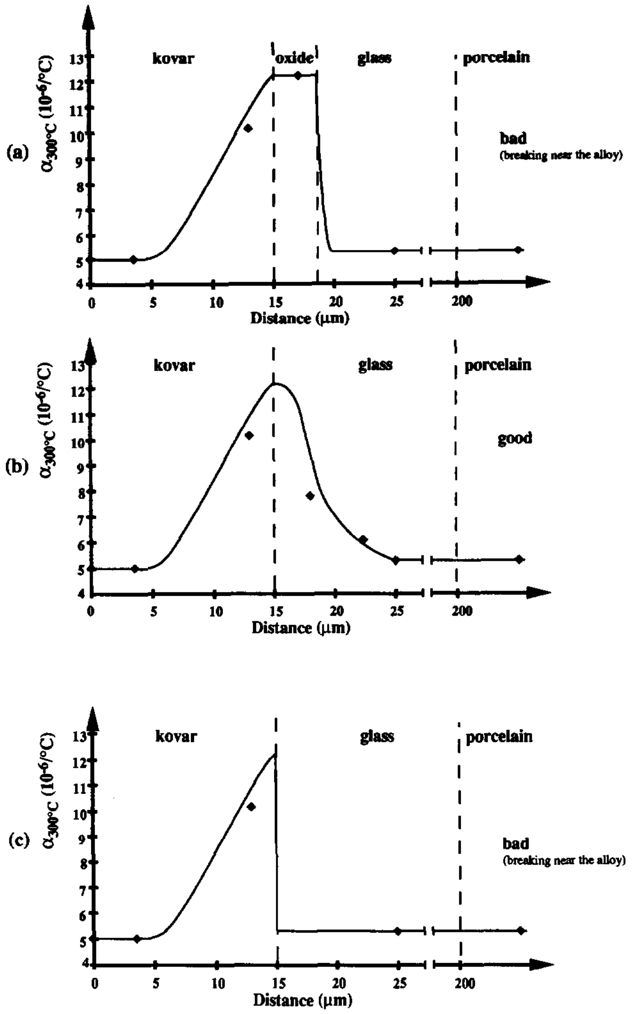

Fig. 5. Dilatometric profile of the interfacial zone: (a) oxide layer slightly dissolved; (b) oxide layer almost totally dissolved; (c) the whole oxide layer is dissolved.

5 Conclusion

This work sheds some light on the role of the pre-oxidation of the alloy in the glass to metal sealings. Not only does it improve the glass wetting[8] but it is also responsible for the fitting of thermal expansion coefficients in the interfacial zone. In fact the formation of the oxide layer creates an iron-impoverished zone whose thermal expansion is higher than that of underlying alloy, and the oxide dissolution into the glass increases the thermal expansion of the glass to values approaching those of the iron-impoverished alloy. At last, the pre-oxidation creates open porosity in the alloy[7] in which FeO-rich glass penetrates during bonding treatment, so creating a strong physical adhesion.

The duration of the bonding thermal treatment is very important and its role is well summarized in Fig. 5 which presents diagrams describing the thermal expansion coefficients evolution in the interfacial zone according to the time of thermal treatment. If it is too short (Fig. 5(a)), the brittle oxide layer remains and the FeO-dissolved gradient is very strong, so that the bonding is weak. If the treatment duration corresponds to that of a complete reaction or dissolution of the FeO layer in the glass (Fig. 5(b)), it is the best case where there is a large gradient of FeO in the glass, hence a good fitting of the thermal expansion coefficients in the interfacial zone, and a sufficient penetration of the glass in the superficial porosity of the alloy. For too long times (Fig. 5(c)) homogenization of the glass leads to a significant gap of the thermal expansion coefficients at the glass to alloy interface and the bonding breaks during cooling at the end of thermal treatment.

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