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Interfacial reactions between lithium silicate glass-ceramics and Ni-based superalloys and the effect of heat treatment at elevated temperatures

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Two lithium silicate glasses (S- and BPS-glass) were sealed to four different Ni-based superalloys (Inconel 600, Inconel 718, Haynes 230, and Hastelloy C-276) and the effects of long-term heating at 700–900°C on the chemical, microstructural, and mechanical properties of sealed interfaces were studied. The presence of a small amount of ZnO in the BPS-glass leads to the formation of a thin interfacial second phase layer and a less rough alloy interface compared to the ZnO-free S-glass. Inconel 718 was found to be the most reactive of the alloys, with Cr and Nb diffusing into the glass and forming a coarse glass-ceramic microstructure at the interface. Heat treatment of all the reaction assemblies at 900°C for 100 h in air resulted in degradation of the seals and their spontaneous failure. Heat treatments at 700 or 800°C did not cause any interfacial coarsening in BPS sealed to Inconel 600, Haynes 230, and Hastelloy C-276 alloys and did not alter the bond strength of Haynes 230 bars, sealed with a thin layer of BPS-glass, demonstrating the potential of these material combinations for applications up to 800°C.

1. Introduction

Glass-ceramics have a number of advantages over glasses or ceramics as materials for hermetic metal-insulator seals. Glass-ceramics generally have superior chemical and mechanical properties to glasses and seals can be formed in fewer, less complicated processing steps than conventional ceramic-to-metal seals. Glass-ceramic seals are produced from glasses that are heat-treated to form crystallized material with the desired set of properties.

Glass-ceramic sealing materials with thermal expansion coefficients (CTE) in the range 100–200 × 10^{-7}/°C have been prepared from lithium silicate glasses and have been found to be suitable for hermetically sealing Ni or Ti-based high temperature alloys [1–3]. The glasses are heat treated to form crystalline lithium silicates and cristobalite materials for CTE-matched hermetic seals to superalloys for a variety of pyrotechnic and electronic applications [4]. Most conventional applications for such seals rarely exceed operational temperatures beyond 100–200°C, however, similar glass-ceramics have been used in seals to Inconel 718 up to 700°C in nuclear reactor and turbine engine parts [5]. Glass-ceramic enamel coatings have also been proposed to improve the long-term, oxidation resistance of metals at the elevated temperatures encountered by some electronics packaging [6] and other engine applications [7]. More recent applications where thermally stable glass-ceramic-to-metal seals are desired include hermetic seals for solid oxide fuel cells (SOFC's), for which effective sealants must maintain hermeticity between materials with CTE's that can range between 80 and 130 × 10^{-7}/°C for extended times at temperatures as high as 850°C [8, 9].

A variety of parameters that affect the quality of seals made between Li-silicate glass-ceramics and Ni-based superalloys have been identified by previous studies including heat treatment times and temperatures, glass composition, pressure, pre-oxidation of the metal, and amount of water dissolved in the glass [4]. The effect of long-term exposure to potential service conditions (700–900°C in air) is also of interest for a variety of technological applications, including SOFC's, that require robust, hermetic seals to survive at elevated temperatures. The aim of the present study was to form a strong and reliable seal between Ni-based superalloys

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and lithium silicate glass-ceramics through an understanding of,

- the nature of chemical and microstructural interactions at Ni-based superalloy/Li-silicate glass-ceramic interfaces,
- the effect of the composition of superalloys and glass-ceramics on these interactions, and
- the effect of long-term heating at potential service temperatures on microstructure and bond strength.

2. Experimental procedure

Compositions of the materials used in this study are given in Table I. The superalloy Inconel 600 (I600) was obtained from Special Metals Inc., Huntington, WV, Inconel 718 (I718) from Huntington Alloy Products Division, Huntington, WV, Haynes 230 (H230) from Haynes International, Kokomo, IN, and Hastelloy C-276 (HC276) from Cabot Corporation, Kokomo, IN. Two types of sealing glasses were used: S-8070, equivalent of Sandia S-glass and S-8073, equivalent of Sandia-BPS glass, both of which were obtained from Schott Glass Technologies, Duryea, PA. These materials were selected because of the substantial amount of previous research on these glass-ceramic/metal systems; e.g., see references [2, 4, 10] and the references therein. The S-glass composition was originally formulated for components prepared by a 'batch' sealing process whereas the BPS-glass was formulated for seals produced by a continuous (belt) process [10]. Metal coupons approximately 5 × 10 mm in size were cut and polished down to 600 grit SiC paper. Thin sections (1–1.5 mm) of glass were sliced with a slow speed diamond cutter. After ultrasonically cleaning the samples in acetone, the glass sections were laid down on the polished surfaces of the superalloys. These assemblies were secured in graphite boats.

The assemblies were heated under flowing argon to 950°C at a rate of 19°C/min, held for 20 min at 950°C, cooled to 800°C at 5°C/min, held for 90 min at 800°C, and then furnace cooled to ambient temperature. This heat treatment provides sufficient flow to the glass for sealing and transforms the glass into a glass-ceramic. This heat treatment also produces a glass-ceramic with a lower thermal expansion coefficient ($\sim 130 \times 10^{-7}$ vs. 160×10^{-7}/°C for the 1000°C nucleated sample) [2] and it has the advantage of preventing the occurrence of excessive chemical reaction at the alloy interface [1, 3].

X-ray diffraction of glass-ceramic and reacted powder mixtures was performed with a Scintag powder diffractometer. Scanning electron microscopy (SEM) was performed with a Hitachi S-570 scanning electron microscope and energy dispersive X-ray spectroscopy (EDS) was performed using a JEOL JSM-35CF scanning electron microscope with an EDS attachment.

Four-point bend testing was used to study the joint strength between BPS-glass ceramics and H230 alloy in the as-sealed condition as well as after exposure of the sealed couples to 700 and 800°C for 100 h. H230 bars with the dimensions 25 × 4 × 3 mm were butt-sealed using a BPS-glass sample with a thickness of 0.5–0.7 mm. 8 samples were tested for each condition. An Instron multi-testing machine was used with a standard MTS 4-point bend fixture with upper span of 40 mm and lower span of 20 mm in accordance with ASTM standard C 1161-02.

3. Results and discussion

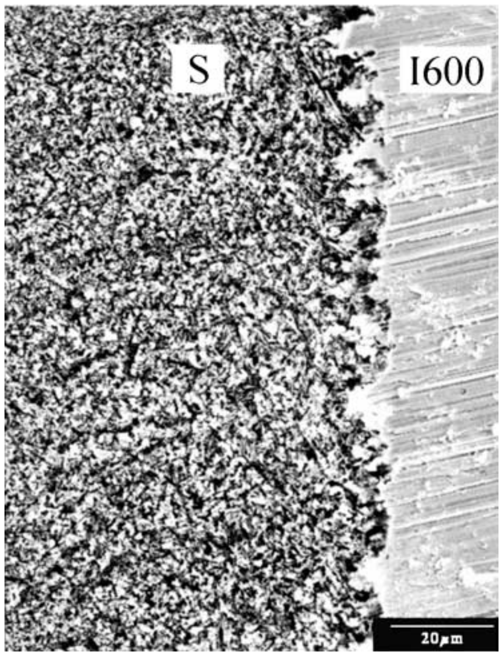
3.1. As-sealed couples

Some of the reaction assemblies did not develop strong seals and separated after the initial sealing step or during prolonged heating. S-glass successfully bonded to I600 but not to the other three superalloys under the same

TABLE I Nominal chemical compositions of Ni-based superalloys and sealing glasses used[a]

	Amount present (wt%)					Amount present (wt%)	
Element	Inconel 600	Inconel 718	Haynes 230	Hastelloy C-276	Oxide	BPS-glass	S-glass
Ni	72.0[b]	50.0–55.0[b]	57.0	55.5 (balance)	SiO_2	74.1	71.7
Cr	14.0–17.0	17.0–21.0	22.0	15.5	Li_2O	13.4	12.6
Fe	6.0–10.0	17.8 (balance)	3.0	5.5	Al_2O_3	3.7	5.1
W	–	–	14.0	3.75	K_2O	2.9	4.9
Nb	–	4.75–5.50[c]	–	–	B_2O_3	1.1	3.2
Mn	1.0 max	0.35 max	0.5	1.0 max	P_2O_5	2.8	2.5
Mo	–	3.05	2.0	16.0	ZnO	2.0	–
Co	–	1.0 max	5.0 max	2.5 max			
Ti	–	0.65–1.15	–	–			
Si	0.50 max	0.35 max	0.4	0.08 max			
Cu	0.50 max	0.30 max	–	–			
Al	–	0.20–0.80	0.3	–			
C	0.15 max	0.08 max	0.1	0.01 max			
S	0.015 max	–	–	–			
P	–	0.015 max	–	–			
B	–	0.006 max	–	–			
La	–	–	0.02	–			
Zr	–	–	0.015 max	–			

[a]Manufacturer's data.
[b]Contains some Co.
[c]Contains some Ta.



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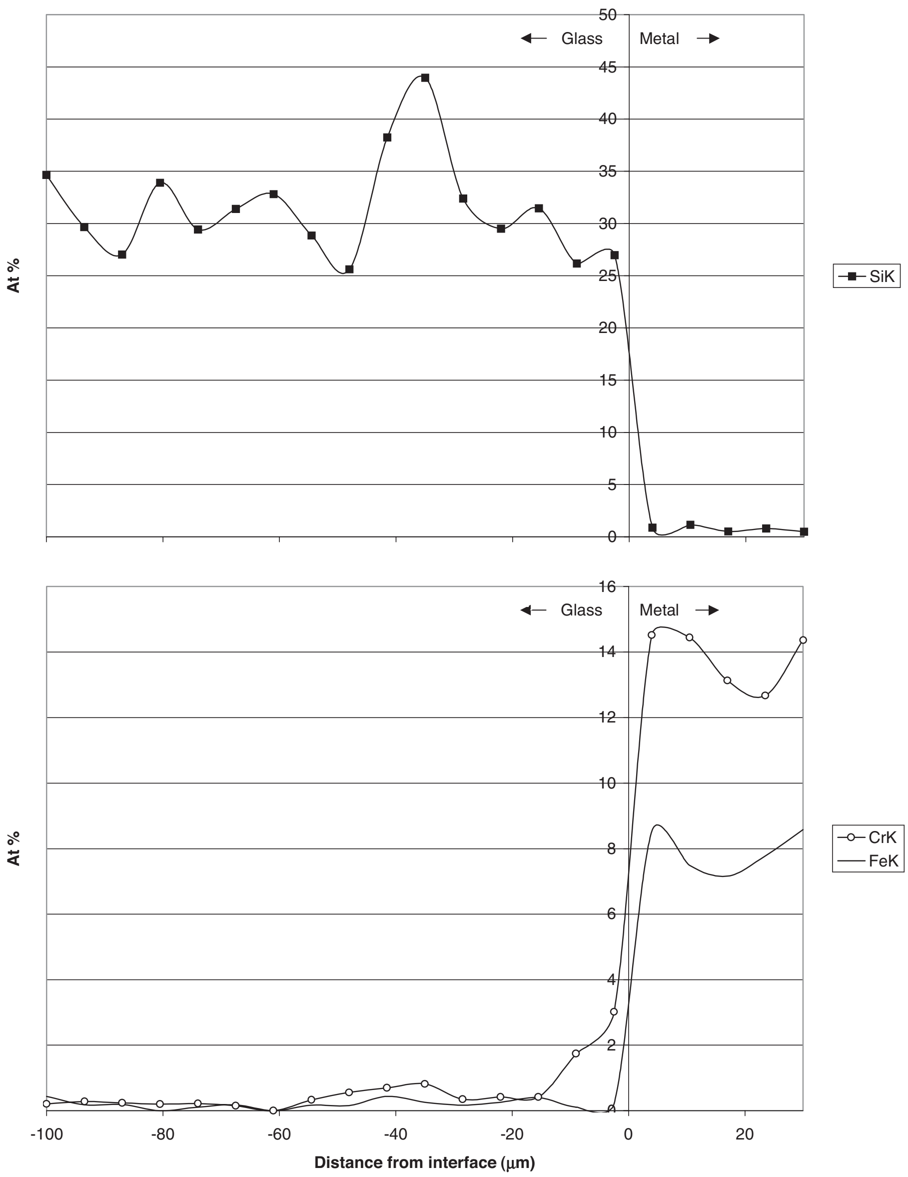


(B)

Figure 1 (A) SEM micrographs of as-sealed I600-S reaction assembly and (B) EDS line profile showing Si, Cr, and Fe concentration throughout the seal.

sealing conditions. I600 differs from the other superalloys primarily by its higher Ni content (Table I). BPS-glass bonded to all superalloys that were investigated. As seen in Table I, the main difference between S- and BPS-glass is the presence of 2 wt% ZnO in the latter.

The microstructures of as-sealed I600/S and I600/BPS couples and corresponding EDS line profiles are shown in Figs 1 and 2. It is evident that the I600/S interface is much rougher than the I600/BPS interface. A distinct interfacial second phase (arrows, Fig. 2A) is seen at the interface of I600/BPS. X-ray diffraction (XRD) of sealed (and later on cleaved) interfaces of S as well as BPS glass-ceramics indicates two major phases on the glass side: lithium disilicate (LS2) and lithium chromium silicate (LCS) as demonstrated in Fig. 3. EDS analysis indicates that the second phase at the I600/BPS interface is enriched in Cr (Fig. 2B) but the amount of Cr diffusion beyond this layer is quite small. In the case of I600/S, on the other hand, a higher amount of Cr penetrates into the glass side but does not concentrate at the glass/metal interface (Fig. 1B). For example, in the case of I600/BPS, the highest relative

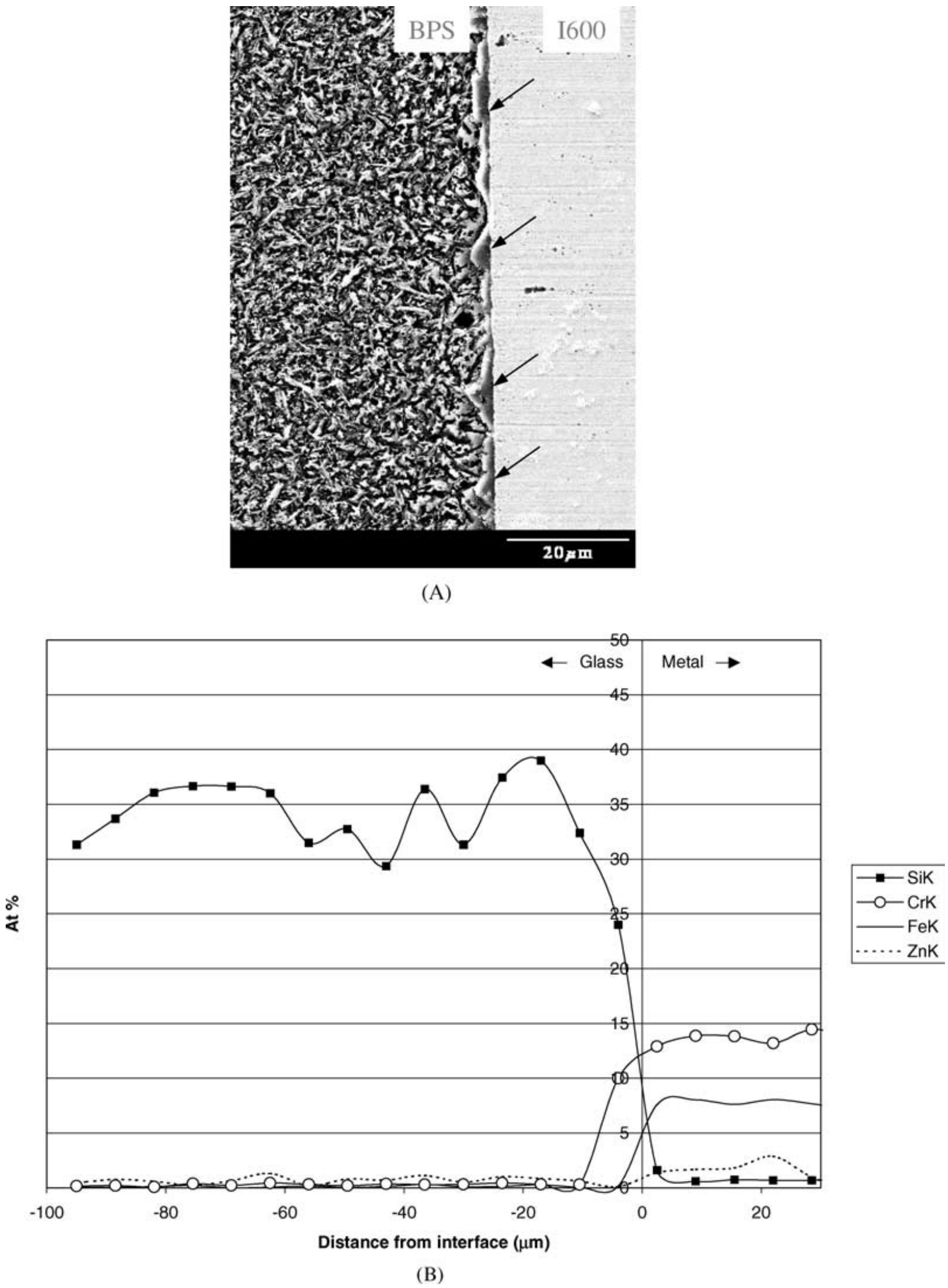
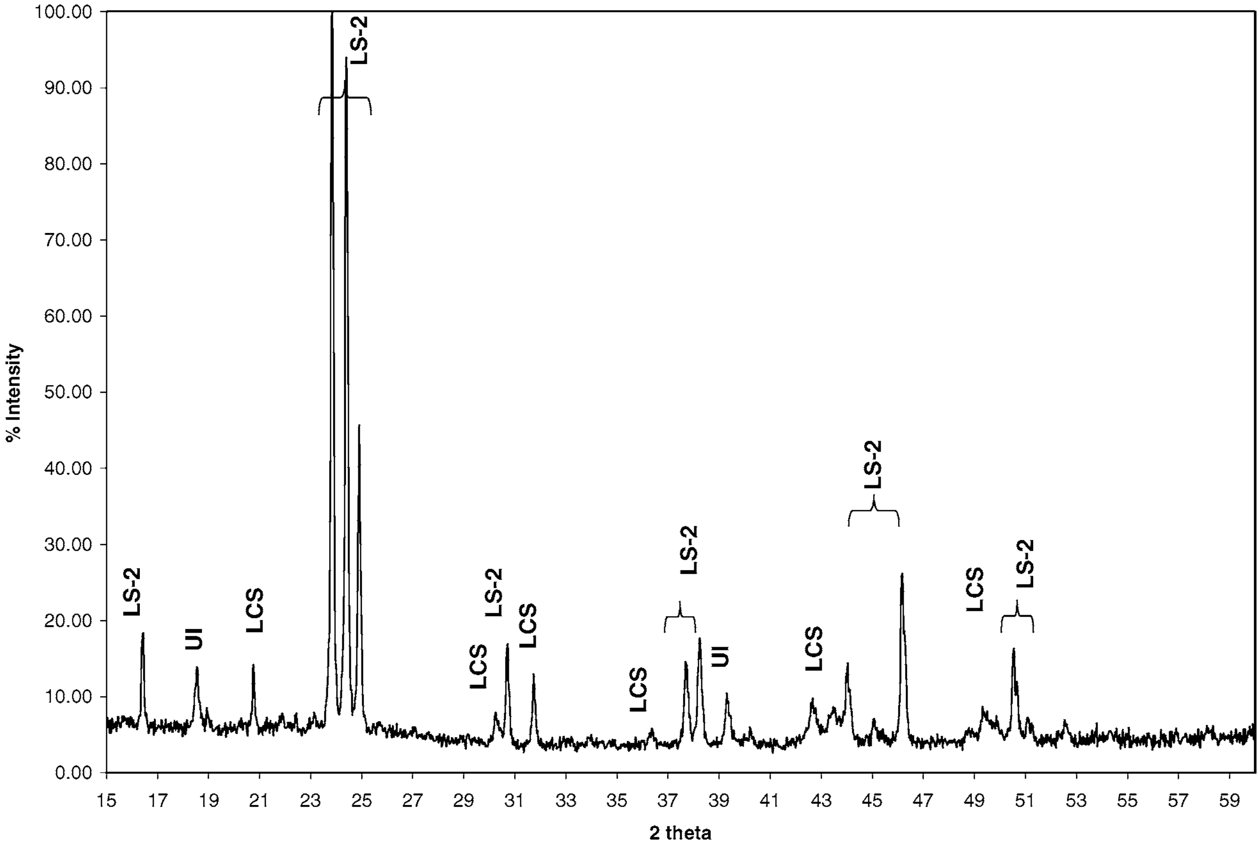


Figure 2 (A) SEM micrographs of as-sealed I600-BPS reaction assembly and (B) EDS line profile showing Si, Cr, Fe, and Zn concentration throughout the seal.



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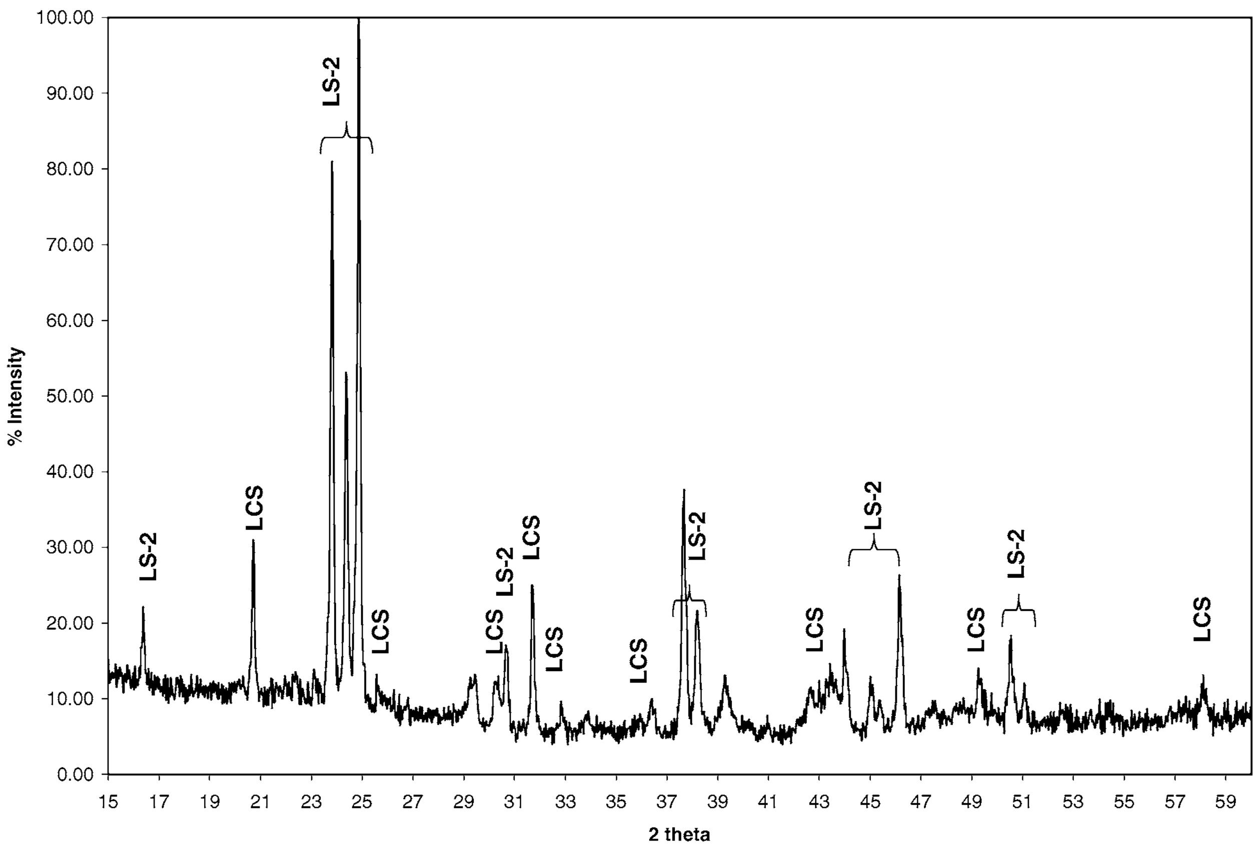
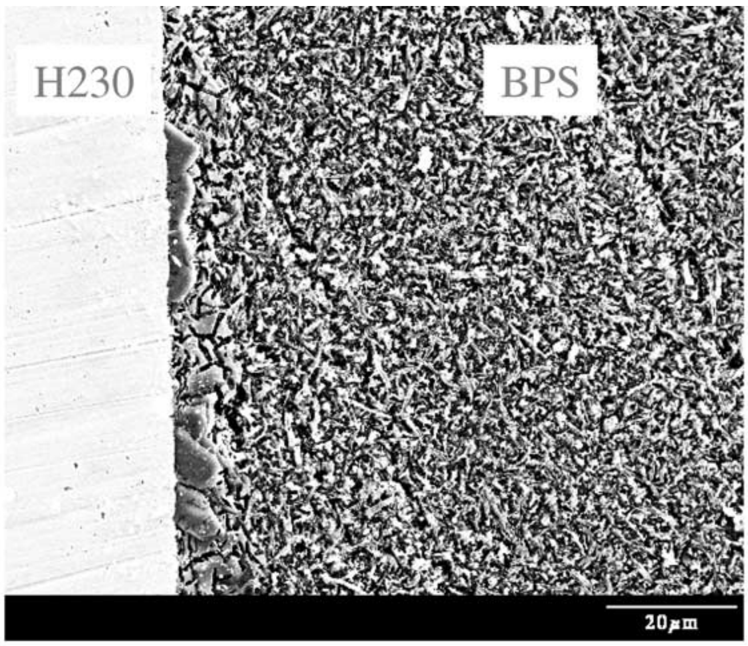


(B)

Figure 3 XRD patterns of the glass side from cleaved interfaces of as-sealed: (A) I600-S and (B) I600-BPS couples (LS-2: lithium disilicate, LCS: lithium chromium silicate, UI: unidentified).

amount of Cr detected at up to 100 μm beyond the interface is ∼1 wt% (0.4 at.%). Approximately 2 wt% (0.8 at.%) Cr was detected in the case of I600/S in the same region.

According to the patent describing BPS glass-ceramic seals, the presence of ZnO improves both the corrosion resistance of the glass-ceramic and the glass-to-metal bond strength [10], but the mechanism for improved bond strength was not discussed. The present results indicate that the formation of a thin intermediate layer at the I600/BPS interface apparently plays a beneficial role by preventing excessive reaction that leads to microstructural deterioration seen in the case of I600/S seals (Fig. 1A). According to EDS analysis, there is a small amount (∼0.3 wt%) of Zn in the interfacial second phase layer. The presence of the intermediate layer in the case of I600/BPS and its absence in the case of I600/S points out that Zn helps the formation of this layer. This may explain the stronger bonding between the superalloys and the glass in the presence



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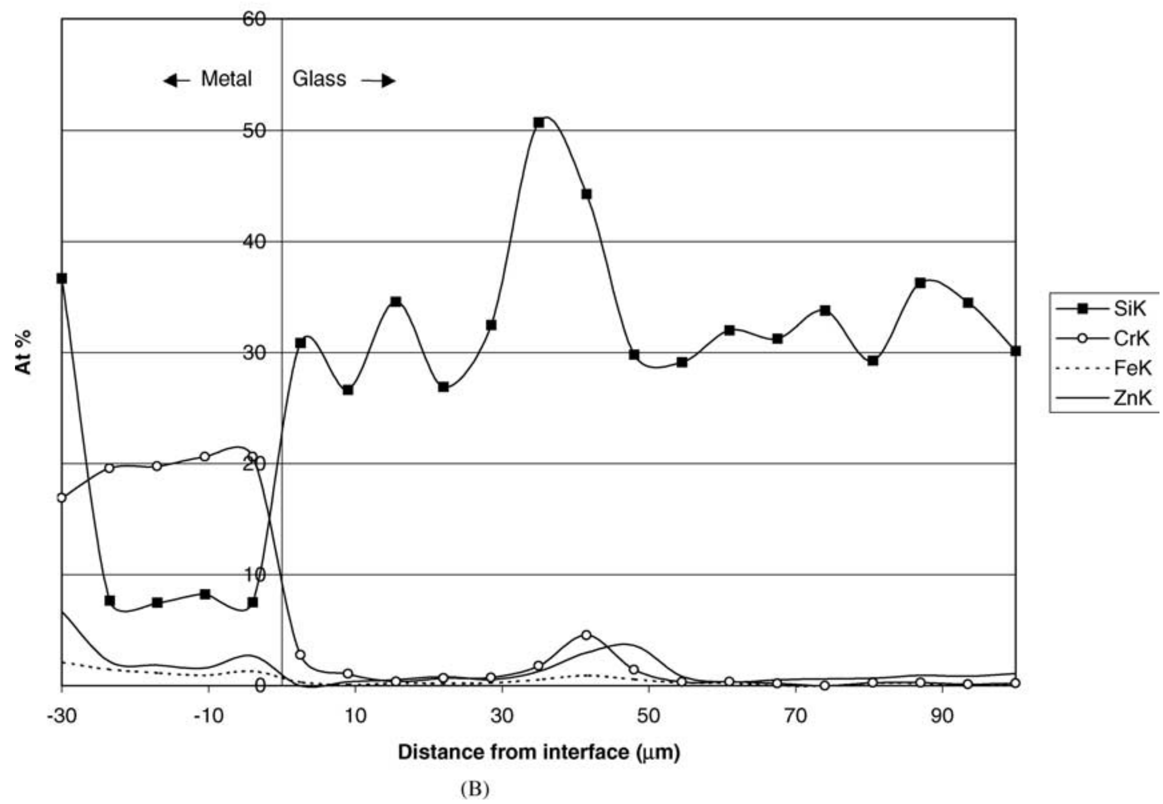

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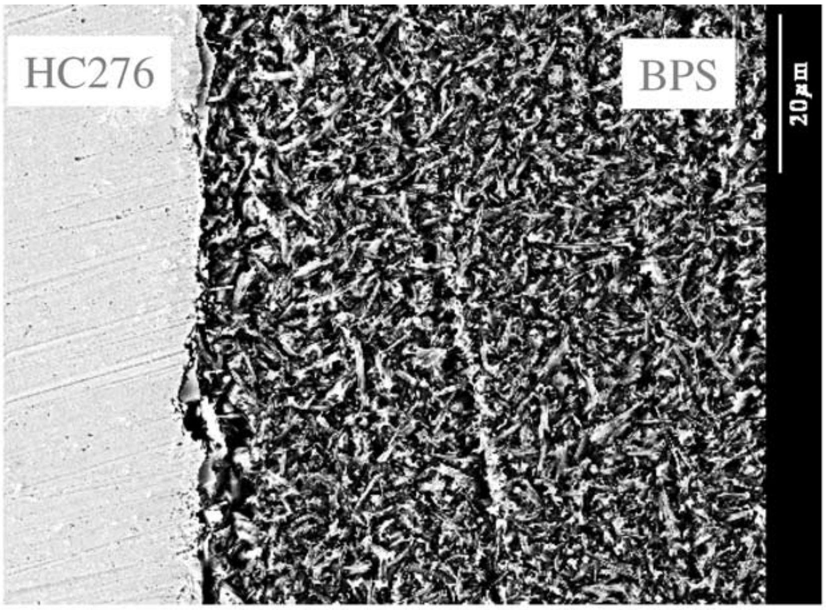
Figure 4 (A) SEM micrographs of as-sealed H230-BPS reaction assembly and (B) EDS line profile showing Si, Cr, Fe, and Zn concentration throughout the seal.



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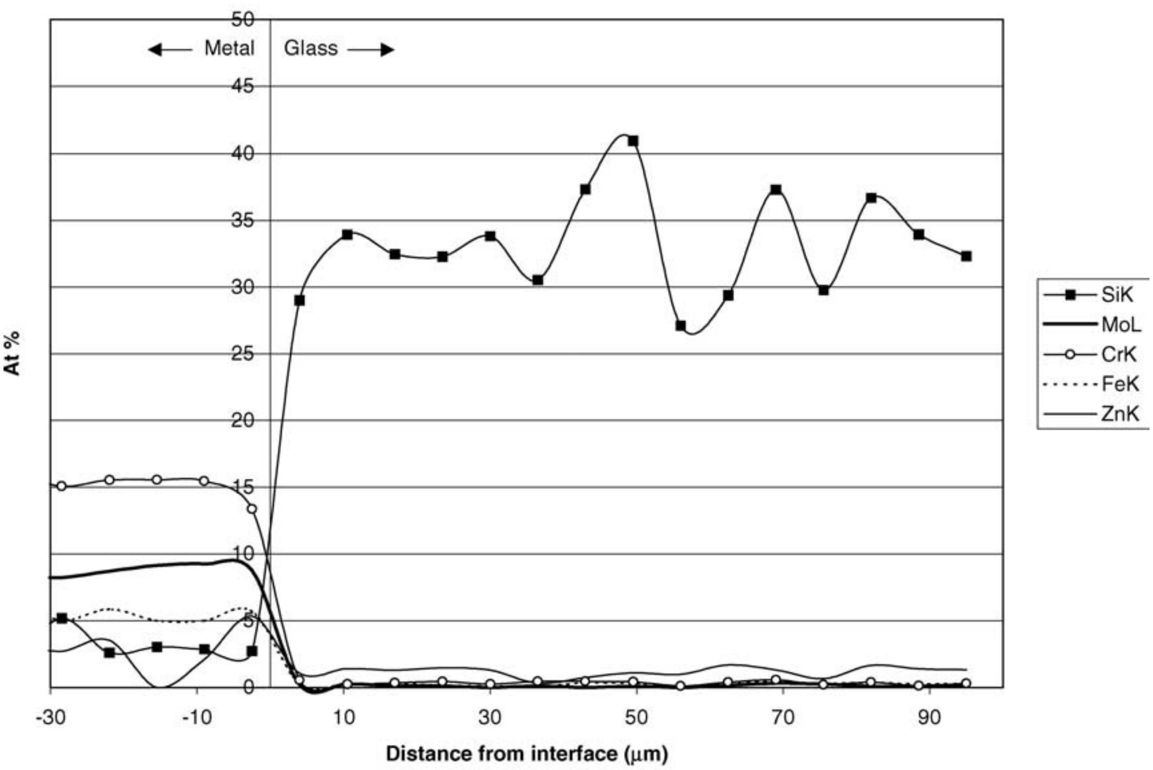
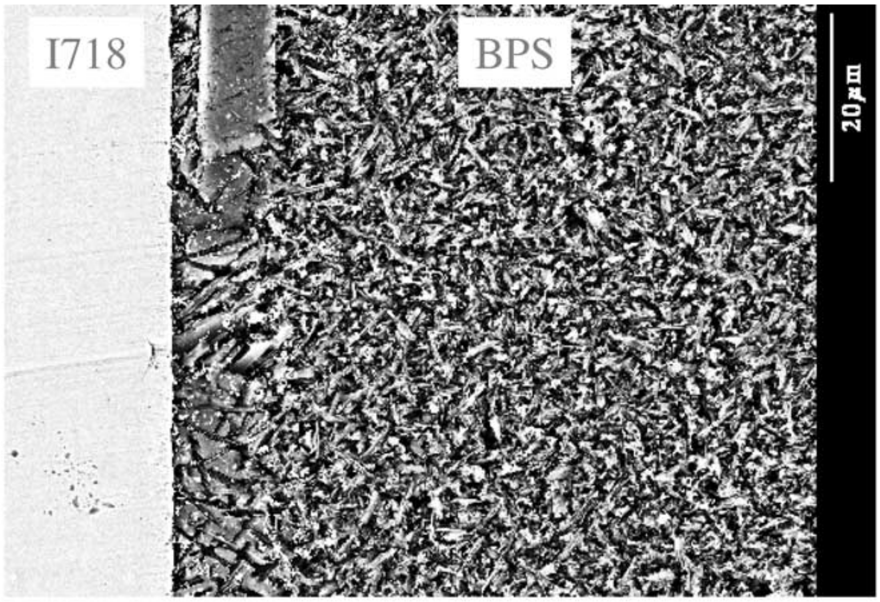


(B)

Figure 5 (A) SEM micrographs of as-sealed HC276-BPS reaction assembly and (B) EDS line profile showing Si, Cr, Fe, Mo, and Zn concentration throughout the seal.

of Zn. The smoother interface in I600/BPS couples can be attributed to the continuous interface layer, which acts as a diffusion barrier, preventing the diffusion of Cr.

Figs 4–6 show the microstructures and corresponding EDS line scans of BPS to H230, HC276, and I718 seals, respectively. One feature that sets these seals apart from I600/BPS seals is the absence of a continuous intermediate layer. Unlike the seals with I600, the zone in the glass side adjacent to the interface has a coarsened microstructure in the case of I718/BPS and limited coarsening is observed in the case of H230/BPS and HC276/BPS seals. The chemical composition of I718 differs from the other superalloys by the presence of ∼5 wt% Nb and a higher amount of Fe (∼18 wt%). Evidence for some Nb and Cr diffusion as far as 50 μm into the glass side is seen (Fig. 6B). Similarly, diffusion of Cr to a distance of 40 μm from the interface is observed in the case of the H230/BPS seal (Fig. 4B). The effect of Cr on Li_3PO_4 nucleating agents is well documented [2]. For example, it was shown that Cr from I718 reacts at the 1000°C sealing temperature with



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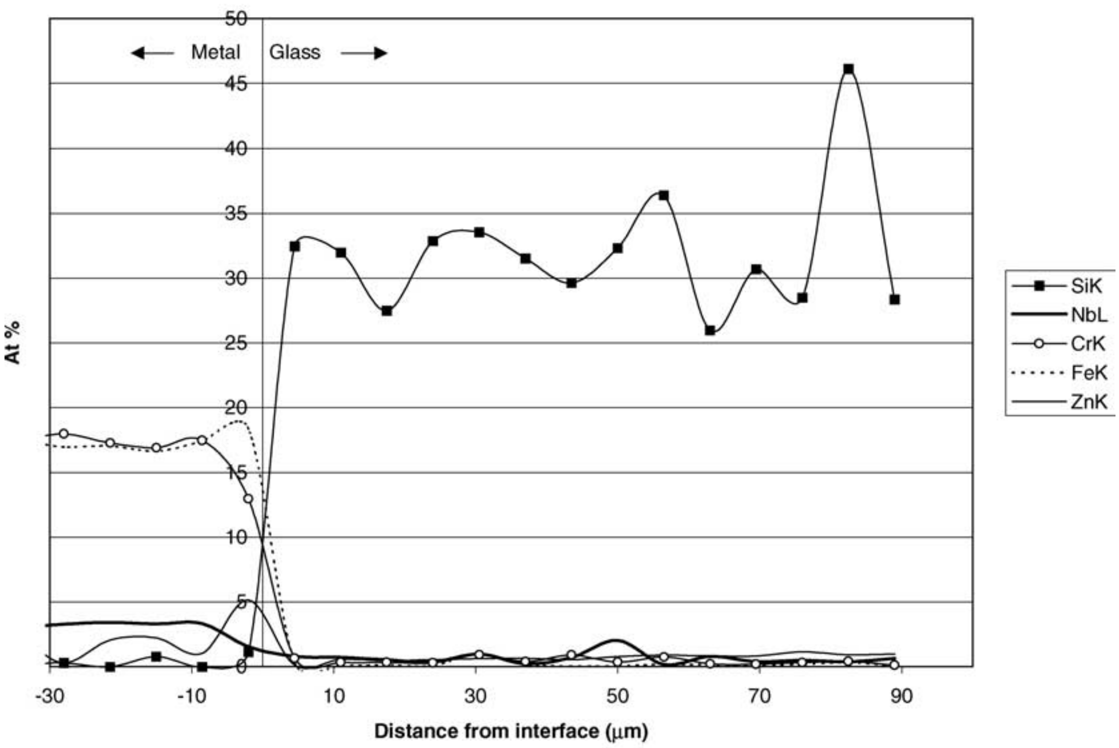


(B)

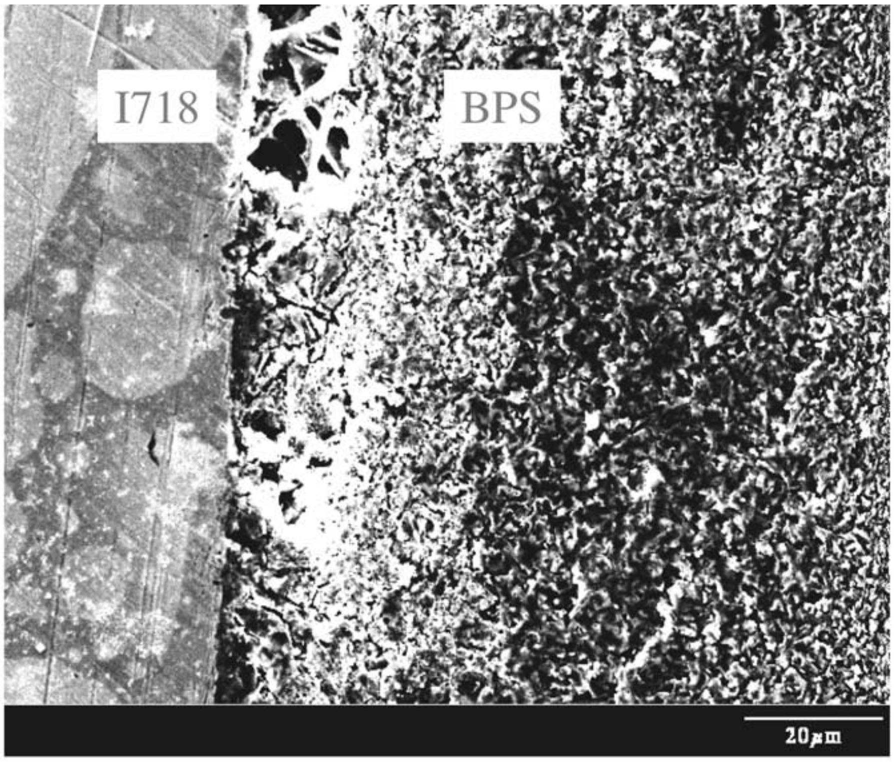
Figure 6 (A) SEM micrographs of as-sealed I718-BPS reaction assembly and (B) EDS line profile showing Si, Cr, Fe, Mo, and Zn concentration throughout the seal.

Li_3PO_4 crystallites and destroys them, thus altering the distribution of crystals at the interface. However when the sealing temperature is 950°C, as used in the present case and a previous study using a similar material system [3], XRD analysis does not reveal any transition metal phosphide phases in the interfacial zone. The coarsening at the interface of I718/BPS can be attributed to the interaction of Cr and Nb with the nucleation and growth of lithium disilicate crystals within the BPS glass. The amount of Cr increases significantly with post-seal heat treatments at 700°C for 100 h, further coarsening the microstructure (Fig. 7).

3.2. Effect of firing at 700–900°C in air

Each glass-ceramic/metal couple that formed a strong initial bond also survived a subsequent 100 h exposure at 700°C in air. However, only I600-S and I600-BPS couples remained bonded after 100 h at 800°C and no sample remained bonded after 100 h at 900°C.

The thickness of the interfacial second phase layer in the I600/BPS couple is reduced upon firing at 700 and 800°C for 100 h (Figs 8A and 9A). In a previous study, dissolution of a CrO interfacial layer was observed [11]. A similar dissolution effect seems to occur



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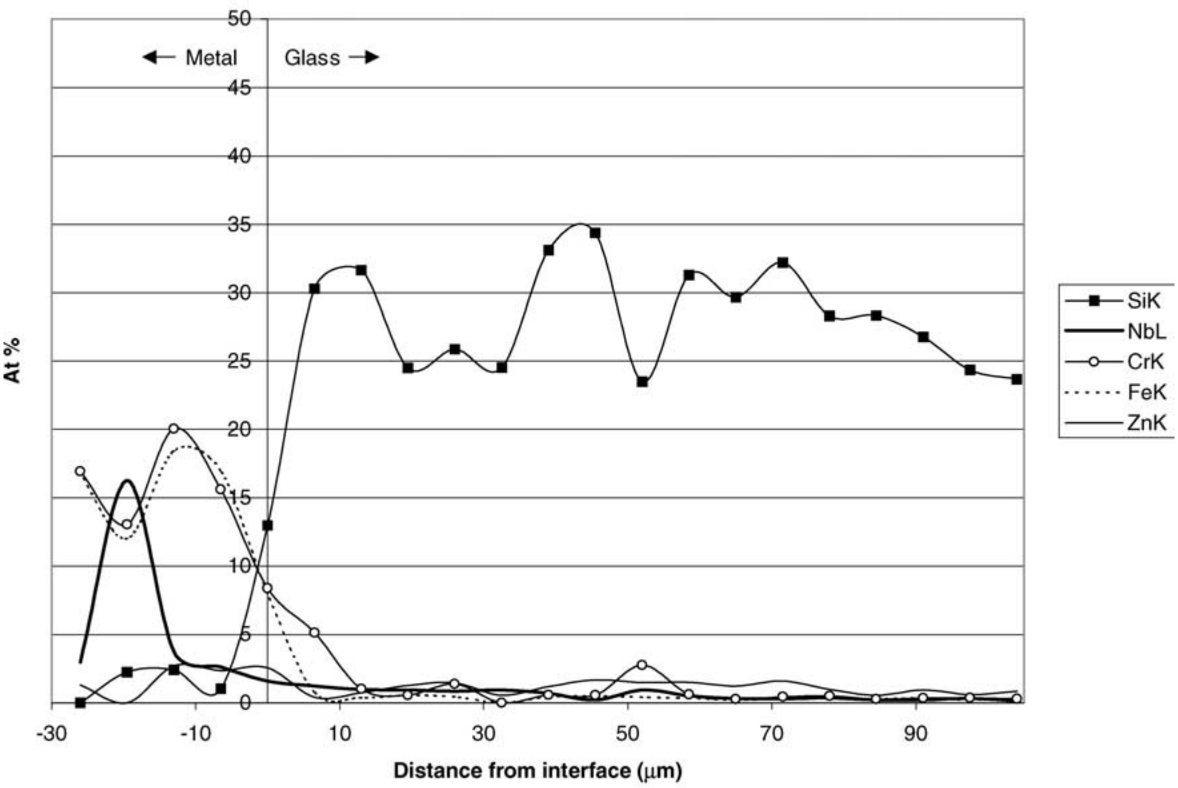
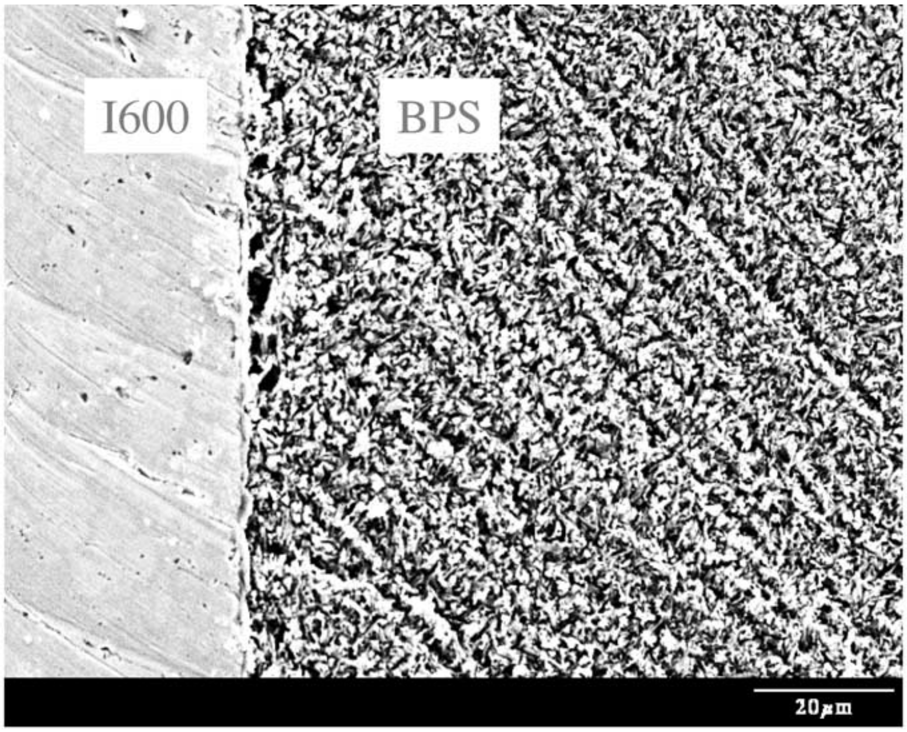


(B)

Figure 7 (A) SEM micrograph of I718-BPS reaction assembly sealed and fired at 700°C for 100 h and (B) EDS line profile showing Si, Cr, Fe, Nb, and Zn concentration throughout the seal.

in the present study, although the interface chemistry is different according to EDS and XRD results (Figs 2B, 8B, and 9B). EDS spot analysis from the interface region indicates that the Cr concentration increased from 8.6 wt% in the as-sealed I600/BPS reaction assembly to 24.4 wt% and 29.9 wt% upon heat treatment at 700 and 800°C, respectively. However the mechanism of dissolution and the role of Cr in this phenomenon is not clear.

The fine microstructure adjacent to the interface in I600/BPS remained unchanged as seen in Figs 8A and 9A. Similarly, the interface region of H230/BPS and HC276/BPS did not coarsen after 100 h at 700°C



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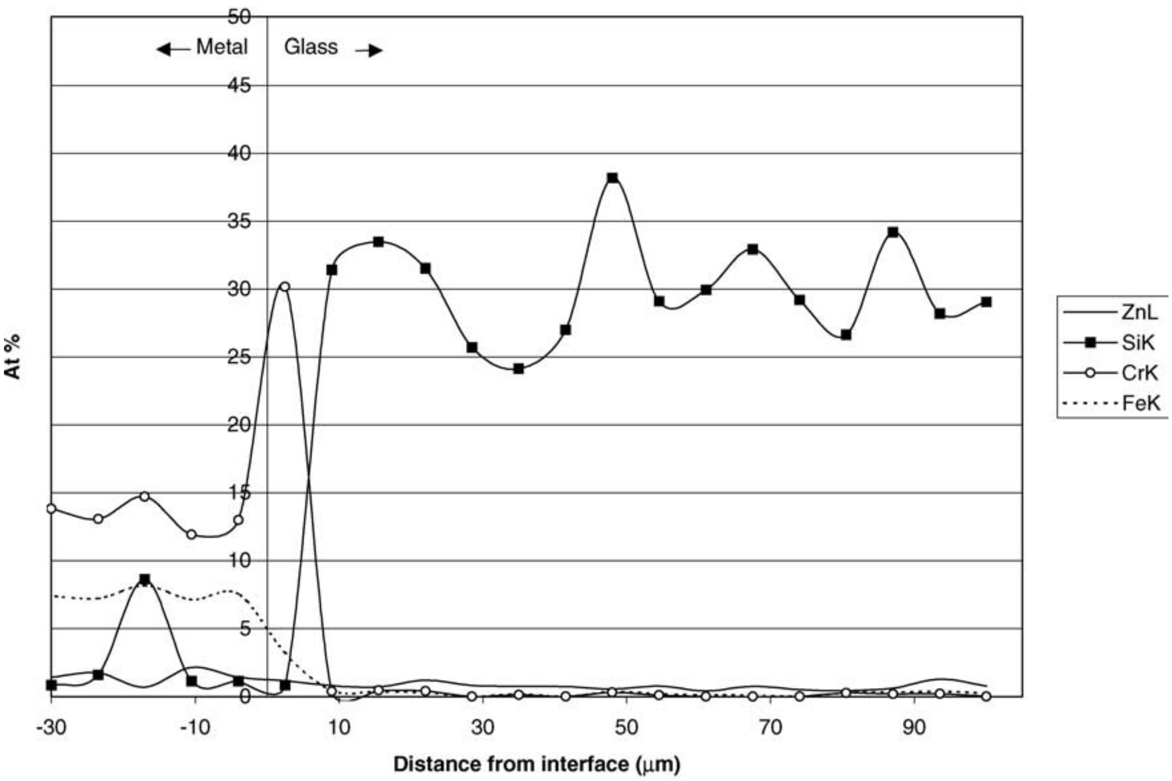


(B)

Figure 8 (A) SEM micrograph of I600-BPS reaction assembly sealed and fired at 700°C for 100 h and (B) EDS line profile showing Si, Cr, Fe, and Zn concentration throughout the seal.

(Fig. 10A and B). On the other hand, the coarse zone at the I718/BPS interface became thicker after 100 h at 700°C (Fig. 7A). The Cr concentration at the glass side of the interface increased upon firing at 700°C for 100 h (Fig. 7B). According to these results, the reason for the coarsened microstructure in I718/BPS could be attributed to the reaction of the inward diffusing Cr with the glass.

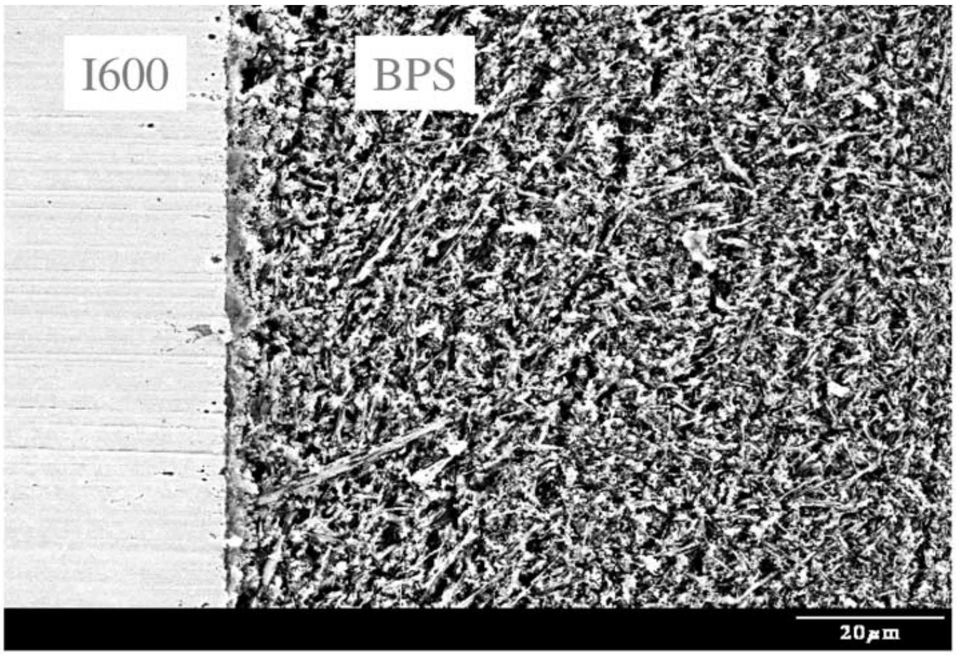
One interesting feature seen in all of the couples fired at 800°C is the formation of precipitates with spherical or square shape (Fig. 11A, arrow). EDS analysis of these particles indicated a phase containing Si and O (as expected from the glass composition) as well as K and Zn (Fig. 11B).

The effect of firing at 700 and 800°C on the bond strength was measured by 4-point bend testing of H230 bars butt-sealed by a thin layer of BPS glass. Results of these tests are listed in Table II. The seal strength is significantly lower than the bulk strength of the glass-ceramic as seen in Table II. This is to be expected due to two reasons:

1. Formation of stress-concentration regions or discontinuities at the outer edges of metal/glass seals
2. Introduction of residual stress into the seal region due to thermal expansion mismatch.

TABLE II 4-Point flexural strength of Haynes 230/BPS seals and BPS glass-ceramic

Material and heat treatment	Flexural strength (Mpa)	Standard deviation (Mpa)
H230/BPS/H230 as sealed (960°C, 20 min; 800°C, 90 min)	33.0	8.1
H230/BPS/H230 sealed + 100 h at 700°C	29.6	8.8
H230/BPS/H230 sealed + 100 h at 800°C	33.3	12.6
BPS as heat treated (960°C, 20 min; 800°C, 90 min)	204.9	63.5



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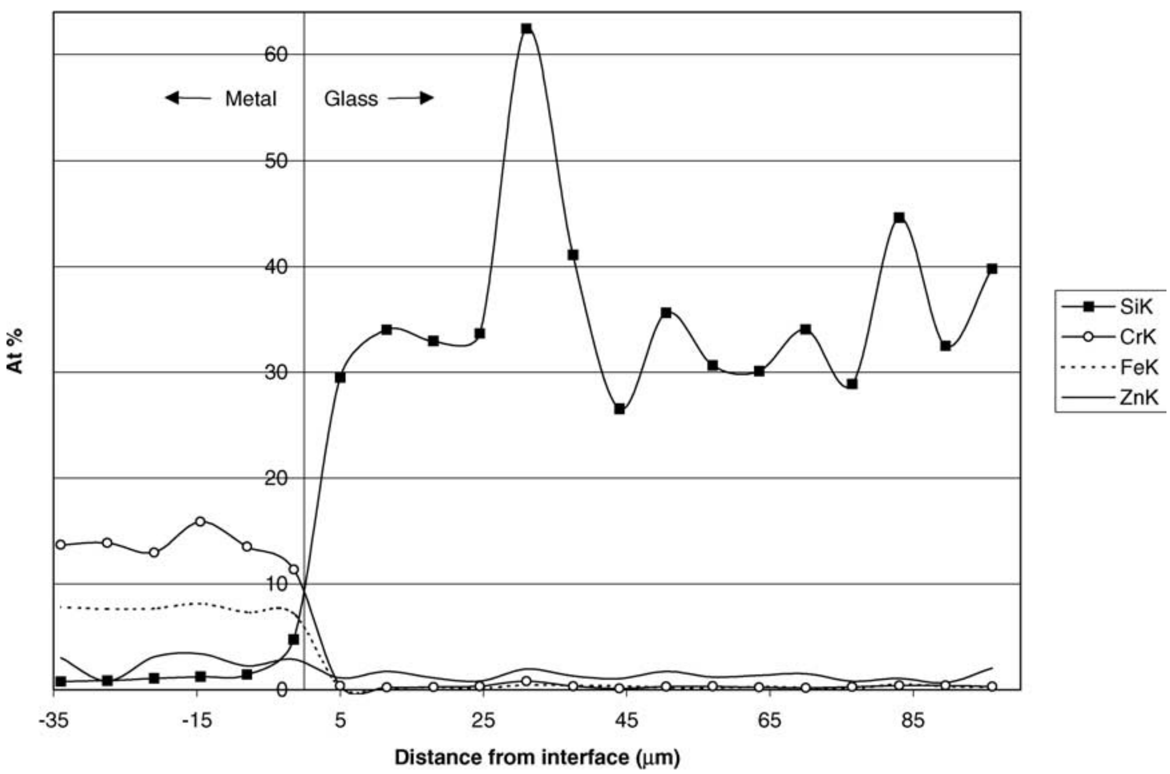
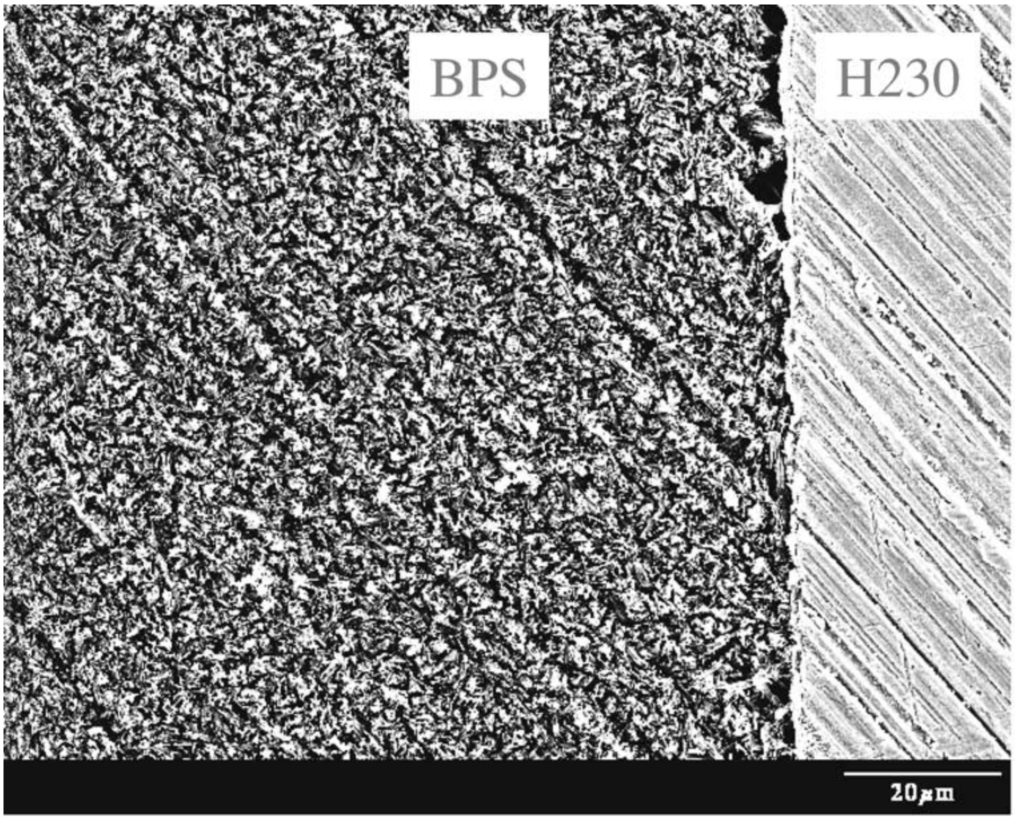


(B)

Figure 9 (A) SEM micrograph of I600-BPS reaction assembly sealed and fired at 800°C for 100 h and (B) EDS line profile showing Si, Cr, Fe, and Zn concentration throughout the seal.



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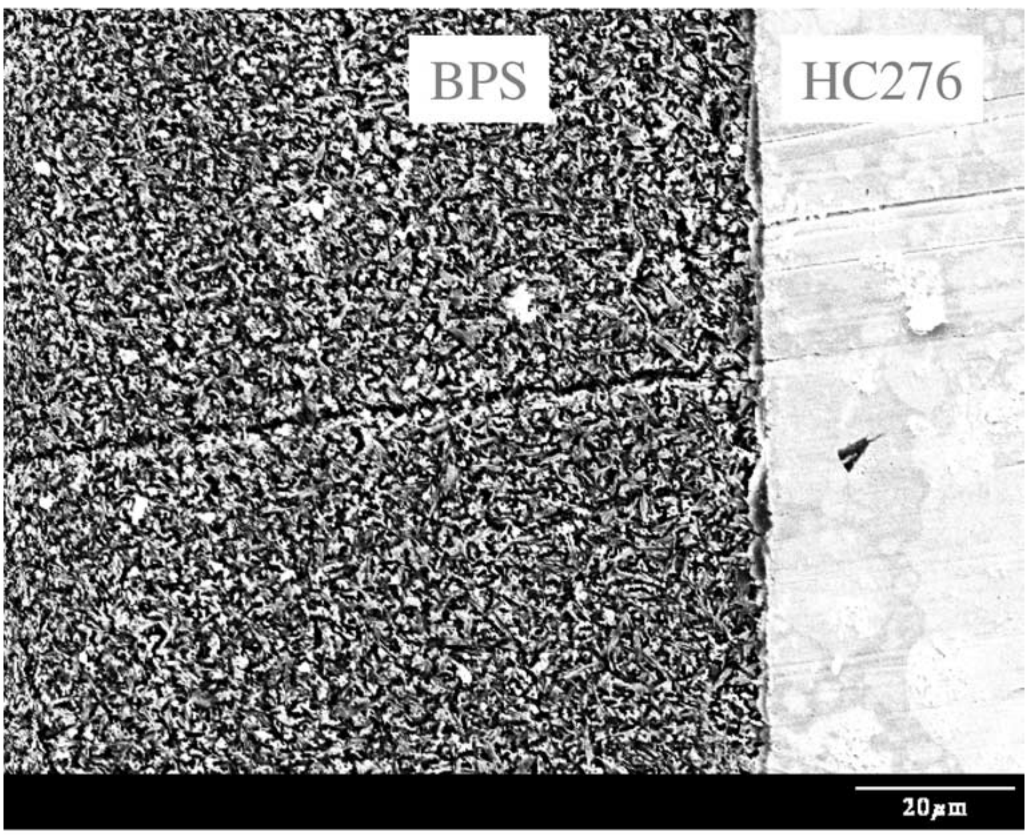
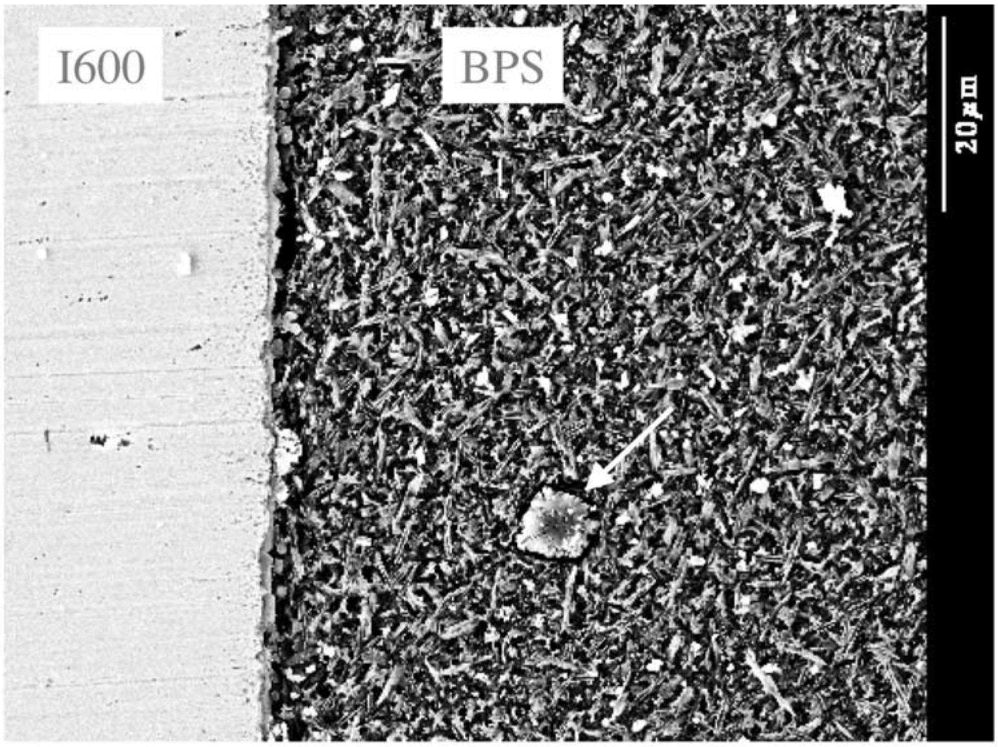


(B)

Figure 10 SEM micrographs of (A) H230-BPS and (B) HC276-BPS reaction assemblies after firing for 100 h at 700°C.

The measured seal strength is sufficient for low stress level or static applications and can further be improved by careful matching of the thermal expansion of the glass-ceramic to the selected superalloy by using a proper heat treatment [12].

In the case of as-sealed samples, all of the failures occurred within the glass-ceramic layer and not at the metal/glass-ceramic interface, although this layer was relatively thin (0.3 to 0.9 mm). The average flexural strength did not decrease after heating to 700°C or



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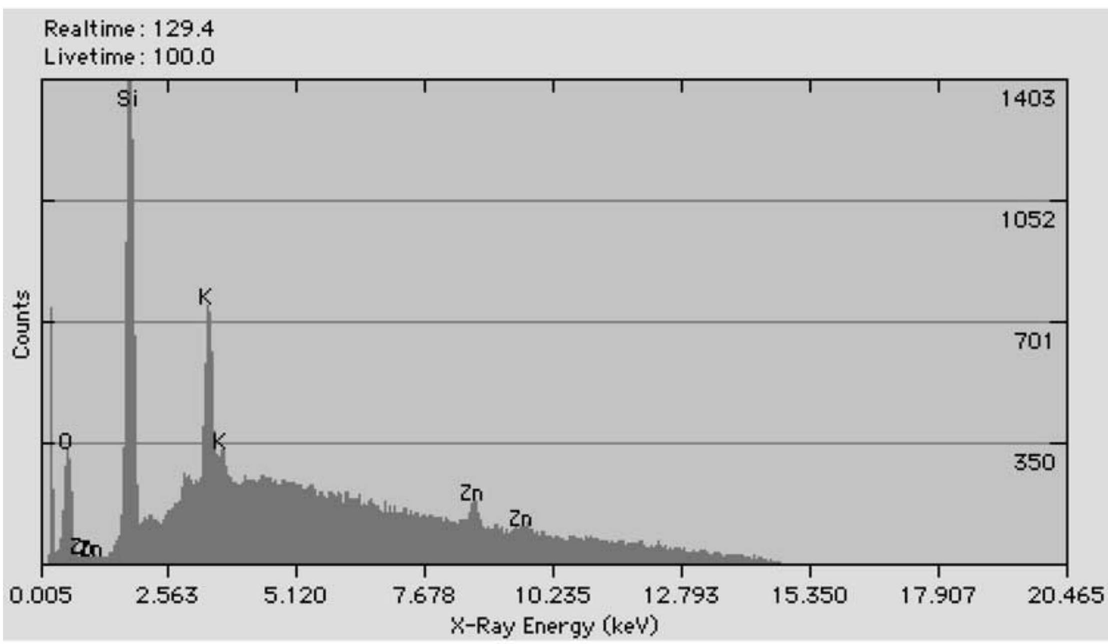

(B)

Figure 11 (A) SEM micrograph of I600-BPS reaction assembly after firing for 100 h at 800°C and (B) EDS spectra from the precipitate indicated by arrow.

800°C. However, one of the eight samples failed at the interface in samples fired at 700°C for 100 h and 3 out of 8 failed at the interface when fired at 800°C. Some dark colored oxidation products were visible on the metal side after separation. At 900°C, all the seals failed spontaneously, probably due to excessive oxidation of the metals. These results indicate that a relatively strong seal is obtained with these materials with a thin BPS layer that can be used to temperatures up to 800°C. Based on our observations, thick (>1.5 mm) glass layers are not suitable for such applications because they result in weaker bonds and cracking.

4. Conclusions

The wide range of materials involved in this study made it possible to determine some factors that are important in developing an optimized and reliable seal between Ni-based superalloys and Li-silicate glass-ceramics. A comparison of the four superalloys investigated indicates that I718 is the most and I600 is the least reactive with the molten glass during sealing, which makes I600 preferable for a fine and fully developed interfacial glass-ceramic microstructure. Interfacial analyses indicate that the presence of Nb (5 wt%) is not desirable for optimized microstructures. There is strong evidence indicating that among the two glass compositions analyzed, a small amount (2 wt%) of ZnO plays a beneficial role in creating a controlled interfacial microstructure and a reliable, stronger seal. Except for I718/BPS, the microstructure of the seals did not change significantly. The bond strength of H230/BPS seals prepared using a similar heat treatment remained practically unchanged with post-seal heat-treatments up to 800°C for 100 h in air.

These results demonstrate the feasibility of I600, H230, and HC276 superalloys to BPS seals for applications up to 800°C in air. This could open up the way for new sealing and coating applications aimed for elevated temperatures and oxidizing conditions in which Ni-based superalloys have superior performance.

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