Bulletin of Materials Science & Metallurgy

Periodical Scientific Journal of UCTEA Chamber of Metallurgical and Materials Engineers

Volume 1, Issue 3, 2024, Pages: 20-24 Received: 07 November 2024 Accepted: 26 December 2024

https://doi.org/10.70342/LCHL4063

Research Article

Effects of Alkali Ratios on Alkali Barium Glasses for Compression Sealing

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Abstract

Alkali barium glasses of the system SiO_2, Al_2O_3, LiO_2, K_2O, Na_2O, and BaO were produced using high-purity powders by the melt-quench technique to evaluate the suitability of these glasses for hermetic sealing. Six different glasses with varying Na_2O and K_2O content were produced. Although both Na and K are alkali elements, their different ionic radii and densities result in different effects on the glass network structure. As a result, they have caused changes in the properties of the glass, leading to alterations in the glass-metal interface as well. Although the total $Na_2O + K_2O$ content of the glasses was maintained at 15 wt%, the Na_2O/K_2O ratio was varied to see the effect of compositional variation on the properties of the glasses produced. In this study, it was observed that as the Na_2O/K_2O ratio increases, properties such as density, Tg, and chemical durability of the alkali barium glass decrease, while CTE increases. Glass pellets, prepared from the glass powders, were used for sealing with 304 stainless steels at different sealing profiles under argon gas. The results revealed that the sealing profile and the alkali ratios (Na_2O/K_2O) of the glass have a profound effect in the microstructure and the interface characteristics of the compression sealing developed between the alkali barium glass and 304 stainless steels.

Keywords

Alkali Barium Glass, Hermetic, Compressive Sealing

1. Introduction

Glass-to-metal (GTM) seals have played critical roles in hermetic packaging technologies for over fifty years. Among the various hermetic sealing methods, compression sealing, characterized by metallic holders with higher coefficient of thermal expansion (CTE) than glasses, stands out [1,2]. For a common example of compression sealings, 304 stainless steel (304 SS) as metallic holder with a CTE of 17.8 x 10-6/°C [3] is sealed with alkali barium glasses (e.g., Corning 9013) exhibiting CTE values in the range of 8.8-9.3 x 10^{-6}/°C, and Alloy 52® as pin material with a CTE of 9.5-9.8 x 10^{-6}/°C. This sealing imparts enhanced strength through compression [4]. One of the common categorizations of sealing glass is "Soft" and "Hard" glasses. Soft glass seals utilize glasses with a working range of approximately 1000 °C and a CTE in the order of 9 x 10-6/ °C [1,3,5].

For effective glass seals, the glass must exhibit wetting behaviour on the metallic holder, creating adhesion between the materials [6,7]. Beyond the sealing profile, effective glasses for GTM sealing must possess key properties, including thermal expansion compatibility with metal components, good adhesion on metal pieces, high chemical durability [8,9]. Another important parameter for a good sealing with strong bonds, either chemically or mechanically are glass composition and sealing treatment [10].

This study aims to optimize the sealing properties of alkali barium glasses, specifically enhancing the CTE, Tg, density, and sealing interface characteristics, while also improving their chemical durability. Glasses with varying Na_2O/K_2O ratios were produced, and the effects of these ratios on the properties of alkali barium glasses, as well as the differences in the glass-metal adhesion interfaces, were investigated. In particular, the influence of the Na_2O/K_2O ratio on the properties of the glasses was thoroughly examined, revealing the structural-property relationship in these glasses.

2. Materials and Methods

The glasses were produced using the melt-quench technique, which offers several benefits, including the production of homogeneous glass with reduced internal stresses, resulting in stronger and more durable materials. Additionally, this method allows for the production of different compositions, easily. Alkali barium glasses, produced with SiO_2, Al_2O_3 LiO_2, K_2O, Na_2O and BaO. SiO_2 and Al_2O_3 were used in their pure powder forms other powders were sourced from lithium carbonate (Li_2CO_3), potassium hydroxide (KOH), sodium hydroxide (NaOH), and barium carbonate ($BaCO_3$) powders, respectively.

The powders were meticulously mixed and subjected to melting at 1550 °C for 30 min in a platinum crucible under ambient conditions. Quenching of the molten glass was achieved by dipping the bottom of the platinum crucible into a container filled with water. To ensure the homogeneity of the glass, this melting process was repeated three times. Following the third melting cycle, the molten glass was cast into a molybdenum mold. The glass compositions produced are presented in Table 1.

Table 1. Compositions of the glasses produced.

Glasses	Composition (wt%)					
	SiO_2	Al_2O_3	Li_2O	BaO	Na_2O	K_2O
A-1	65	5	3	12	3	12
A-2	65	5	3	12	6	9
A-3	65	5	3	12	9	6
A-4	65	5	3	12	12	3
A-5	65	5	3	12	15	-
A-6	65	5	3	12	-	15

For the sealing treatments, glass pellets were prepared with glass powders which were obtained from third melting procedure of glass. Following crushing, the glass powders were sieved to particle size less than 25 µm. The next step involved the dry pressing of the glass powders utilizing a uniaxial hydraulic press operating at 38 MPa. This method was employed to compact the glass powders efficiently.

To verify the amorphous nature of the samples, XRD analysis was systematically conducted on all specimens using Rigaku-Miniflex 600 X-ray diffraction analyzer. Compositional analysis of all glasses was obtained using an Energy-Dispersive X-ray Spectroscopy (EDS) system integrated with a Scanning Electron Microscope (SEM) using the Hitachi-FlexSem instrument. The density of the glasses was determined using Archimedes' technique. CTE for the glasses was determined utilizing the Linseis-L75 Vertical Bench Top Model dilatometer. Measurements were conducted over the temperature range of 25 to 500 °C with a controlled heating rate of 4 °C/min. Before the measurements, all glasses were annealed, at 600 °C for 1 h.

A-4 glass was selected for sealing treatments. Sealing profile was carried out first at temperatures of 920, 950, and 980 °C than at second temperatures of 450 and 480 °C. The holding period at the first temperature was 20 min, while it was 1 h at the second temperature. The heating and cooling rates were maintained at 5 °C/min. The examination of the sealing interface between glass and metal was conducted through SEM under high vacuum conditions.

3. Results and Discussion

The XRD patterns for all the glasses (A-1, A-2, A-3, A-4, A-5, and A-6) exhibited no crystalline peaks as shown in Figure 1. No matches with crystalline peaks were evident in the XRD software analysis, confirming their amorphous nature.

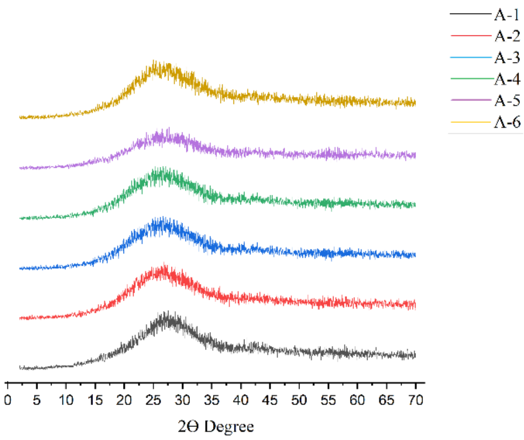

Figure 1. XRD patterns for all glasses.

Chemical composition as determined by EDS for all glasses are presented in Table 2. According to the EDS results, Na_2O and K_2O contents are nearly the same with intended compositions. However, SiO_2 and BaO contents can show different results from intended compositions. This is attributed to incapability of EDS in detecting Li_2O.

Table 2. EDS results for all glasses.

Glasses	Composition (wt%)				
	SiO_2	Al_2O_3	BaO	Na_2O	K_2O
A-1	65.30	6.32	12.29	2.57	11.52
A-2	64.53	7.62	13.41	6.60	7.94
A-3	64.34	7.79	14.18	8.60	5.09
A-4	63.93	6.96	13.77	12.30	3.04
A-5	66.68	6.90	11.30	14.93	-
A-6	69.85	6.94	11.12	-	13.08

The variation of CTE with temperature for all glasses are shown in Figure 2. Two critical results obtained from this CTE values. First one is CTE values exhibit an increasing trend with rising temperature, emphasizing the crucial role of temperature in influencing CTE of glass [11,12]. The second one is that CTE varies with composition. An increase in Na_2O content led to higher CTE values.

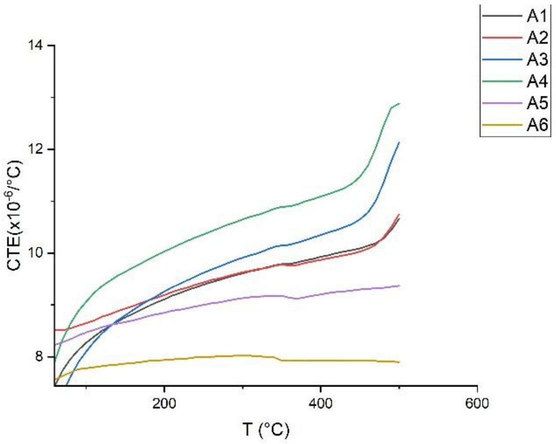

Figure 2. CTE results graphs for all glasses.

In sealing experiments, A-4 was selected as the test sample across all sealing profiles. This choice was motivated by two primary factors. Firstly, A-4 illustrated the lowest Tg, it was more affected by the second sealing temperature than the other glasses. Secondly, with the highest CTE, A-4 demonstrates superior spreading on surfaces, providing a clear illustration of the bonds between glass and metal.

3.1 Sealing Results for A-4 Glass

The images taken from a sealing profile for A-4 glass and 304 SS at temperatures of 920 and 450 °C is shown in Figure 3. In Figure 3 clear interface is observed between GTM. EDS line (yellow line) indicates the region analysed for elemental composition. EDS reveals dendritic Fe structures inside the glass. Dendritic Fe structures contribute to strong mechanical bonds, also the Fe ion saturated the glass gives strong chemical bonds between GTM [12].

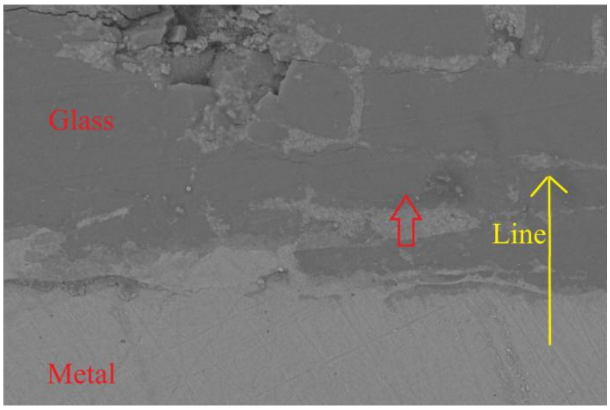

Figure 3. GTM interface for A-4 glass with a sealing profile at temperatures of 920 and 450 °C at X5000.

The second sealing profile for A-4 is at temperatures of 920 and 480 °C. When it is examined, it is clearly observed that, interface is not saturated with Fe ions. This can be as a result of weak Van der Waals bonds. The presence of cracks in glass may be due to differences in CTE between 304 SS and glass.

Figure 4 depicts the sealing interface for A-4 at the sealing profile at temperatures of 950 and 450 °C. Figure 4 shows the bonds between glass and metal, resembling a dendritic structure. EDS analysis detects these Fe ions, which appear dendritic inside the glass. The saturation of the glass with Fe ions suggests the presence of strong chemical bonds between them [12].

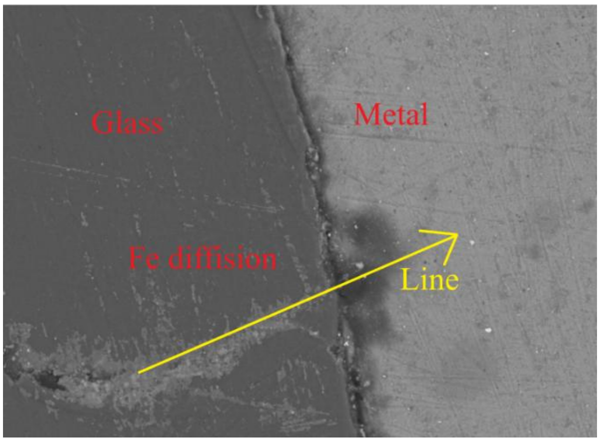

Figure 1. GTM interface for A-4 glass with a sealing profile at temperatures of 950 and 450 °C at X5000.

Figure 5 shows the EDS analysis results taken along the yellow line in Figure 4. The EDS analysis was performed along the line to examine all temperature profiles. As seen in this figure, Fe ions are present inside the glass.

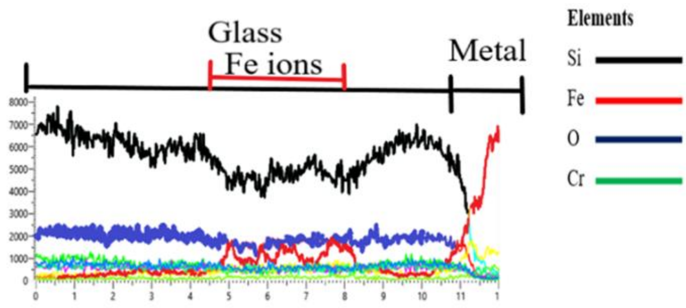

Figure 5. GTM interface EDS analysis for A-4 glass with a sealing profile at temperatures of 950 and 450 °C.

Even though the Fe ions inside the glass are clearly visible, is not any dendric structure like the one seen in the sealing profile at temperatures of 950 and 450 °C. This sealing profile shows weak Van der Waals bonds. However, Fe ions are detected inside the glass in sealing profile at temperatures of 980 and 480 °C, shown in Figure 6 so, it has strong chemical bonds.

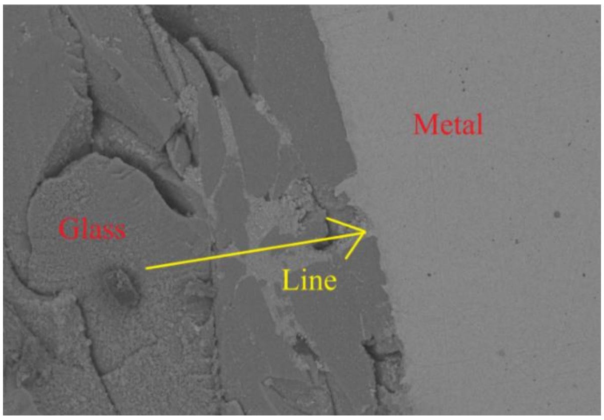

Figure 6. Glass metal interface for A-4 glass with a sealing profile at temperatures of 980 and 480 °C at X3000.

Even though other sealing profiles can be used for sealing of A-4 glass, sealing profile at temperatures of 950 and 450°C offer the best features for A-4 glass. This sealing profile demonstrates a mechanical bond, supported by Fe diffusional areas and chemical bonds supported with saturated Fe ions at the GTM interface.

3.2 Sealing Results for A-1, A-2, A-3 Glasses

Although A-4 glass demonstrated the best microstructural features compared to the other glasses, A-1, A-2, and A-3 glasses were sealed with 304 SS using a sealing profile at temperatures of 980 and 480 °C. This profile selection was based on the Tg of the glasses. The Tg of A-1 glass is higher than 450 °C. Therefore, 480 °C was selected as the second temperature for sealing, for all glasses.

Figure 7 depicts the sealing interface for A-1 at the sealing profile at temperatures of 980 and 480 °C. The diffusion of Fe ions into the A-1 glass, particularly within the interface region enriched with Fe ions. Hence, A-1 glass, and 304 SS has mechanical bonds. Throughout the interface between them, there are some diffusional regions. For A-1 glass, this sealing profile is sufficient. Thanks to that interface is saturated by Fe.

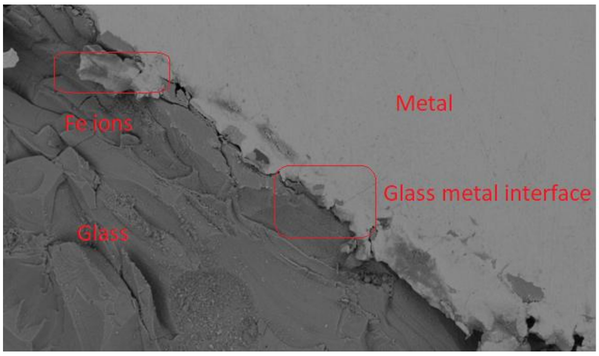

Figure 7. GTM interface for A-1 glass with a sealing profile at temperatures of 980 and 480 °C at X1000.

Figure 8 shows the A-2 sealing interface and EDS results. According to the line EDS analysis indicates nearly sharp elemental changes. However, there is no evidence of Fe diffusion through the A-1 glass. Thus, strong bonds could not be detected due to the non-presence of Fe in the A-2 glass.

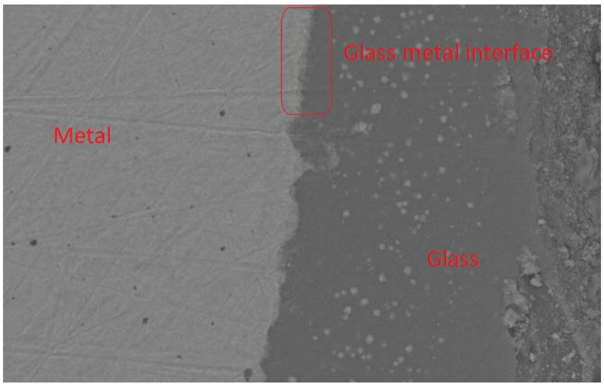

Figure 8. GTM interface for A-2 glass with a sealing profile at temperatures of 980 and 480 °C at X8500.

Figure 9 depicts the A-3 glass sealing interface and EDS results for the sealing profile at temperatures of 980 and 480 °C. According to the microstructure of the interface and EDS results for A-3 glass, it is evident that there are strong mechanical and chemical bonds at the interface.

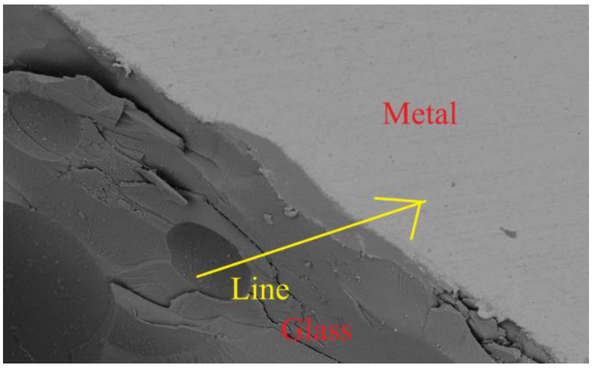

Figure 9. GTM interface for A-3 glass with a sealing profile at temperatures of 980 and 480 °C at X1000

Cr ions diffusional region at the A-3 glass and metal interface is indicated by Figure 10. Other studies have observed Cr and Fe ions at the GTM interface [13,14]. However, in those studies, the metal was subjected to a pre-oxidation process before the sealing procedure, which enabled the adhesion between the glass and metal through the oxide layer. The presence of Cr and Fe at the interface in A-3 glass could be due to an oxide layer formed during the sealing process. Additionally, this oxide layer may contribute to the chemical bonding between the glass and metal [12].

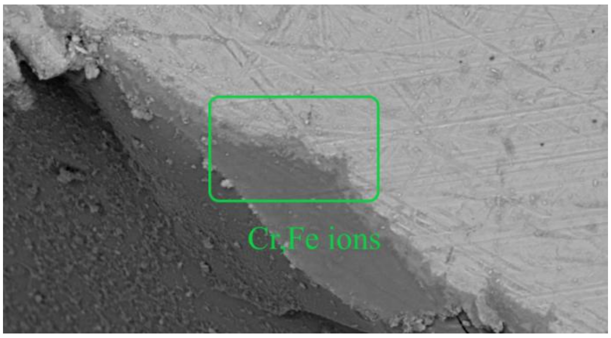

Figure 10. GTM interface with Cr and Fe diffusion for A-3 glass at X6000.

4. Conclusion

To sum up, the changes in the glass's properties, such as density, Tg, chemical durability, and CTE, as influenced by the Na_2O/K_2O ratio of alkali barium glasses. In additionally, the microstructure developed between 304 SS and glass is also affected by both the sealing profiles and the Na_2O/K_2O ratios of the glass.

Even A-3 glasses form strong chemical bonds with the sealing profile at temperatures of 980 and 480 °C, thanks to the presence of Cr. A-4 glasses can seal with 304 SS using different sealing profiles, resulting in strong bonds. A-4 glass exhibits the most favorable sealing interface with a sealing profile at temperatures of 950 °C and 450 °C, which is attributed to the saturated interface formed by Fe and its bonding with the glass region.

Authors' Contributions

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

I would like to thank TÜBİTAK SAGE, who provided financial and technical device support for this research.

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