TECHNICAL REPORT

Additive effect in salt bath for glass strengthening

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We introduce the additives effect in the molten salts such as commercially pure KNO₃ and polluted KNO₃. The results showed that in case of the commercial purity KNO₃, only KOH improved the compressive stress (CS) of ion-exchanged glasses up to ~50 MPa, and the others additives did not make the CS improvement. Rather than the CS was diminished by additive contamination. In case of the contaminated KNO₃, the additives K₃PO₄, K₂CO₃, and K₂SO₄ successfully removed the impurities, Na⁺, Ca²⁺, Mg²⁺, by precipitating chemical compounds in molten bath and recovered the CS up to ~97 %. X-ray diffraction (XRD) results proved how the harmful ions in molten salt was removed by adding additives.

Key-words : Chemical strengthening, Ion-exchange, Molten salt, KNO₃, Additives

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1. Introduction

In general, glasses do not withstand much of applied tension due to the surface flaws generated during the finishing process by manufacturer as well as the handling by user. Such a brittle nature makes the use of glass limited to nonstructural applications.¹,² To make high-strength glass, chemical strengthening is commonly used as a most promising method for glass strengthening.³ In chemical strengthening, an alkali-containing glass is immersed in bath containing a molten nitrate salt at temperatures below the glass annealing point.

In the past decade, chemical strengthening method had received a great deal of attentions since display industry adopted the cover glass to protect portable devices. Until now a lot of studies have been carrying out to get a high compressive stress (CS) and a deep ion exchange layer by designing the glass compositions as well as optimizing various factors such as exchange time, temperature, salt composition, and process conditions.⁴,⁵

The impurity types and their concentrations in molten salt bath are critical factors to decide the CS and the depth of layer (DOL) in strengthened glasses. When a large ion in molten salt is substituted by a small ion in glass, the concentration of released small ion from glass increase and then it prevents to generate high CS on glass surface by resubstituted into glass. Other impurities, Ca²⁺ & Mg²⁺ released from glass or attended as salt impurities are hindering the K⁺ ion diffusion resulting into the low CS and the shallow DOL.⁶

In this work the additive effect, i.e. KOH, K₂CO₃, K₃PO₄, K₂SO₄, Al₂(SO₄)₃ in nitrate molten bath was mainly studied, which have commercially pure and contaminated KNO₃ salts with various impurity ions, i.e. Na⁺, Ca²⁺, Mg²⁺.

2. Experimental procedure

The glass used in this study is a commercial alkali-aluminosilicate (Asahi Dragontrail-PRO Glass, Chiyoda-ku, Tokyo) especially designed for ion exchange up to a great CS and electrical applications. The original pieces were manually cut into 50 mm × 50 mm square plates, and the edges were carefully ground and polished using SiC abrasive paper; care was also used to avoid any damage especially to the surface of the samples. Commercial potassium nitrate produced by EunJin chemicals (Korea, technical grade ≥99 %) was used for chemical strengthening and the impurity ions analyzed by inductively coupled plasma–optical emission spectroscopy (ICP–OES; Spectro-Ciros, Kleve, Germany) were summarized in Table 2.

To make a contaminated salt bath, NaNO₃ (Sodium Nitrate >99 %, SAMCHUN Chemicals), Mg(NO₃)₂ (Magnesium Nitrate >98 % SAMCHUN Chemicals), Ca(NO₃)₂ (Calcium Nitrate >98.5 %, SAMCHUN Chemicals) were added into molten salt bath. In order to remove those impurity ions in molten salt, various additives, KOH (Potassium Hydroxide, pellets 85 %, SAMCHUN), K₂CO₃ (Potassium Carbonate 99.5 %, SAMCHUN) K₃PO₄ (Potassium Phosphate, Extra Pure, DUKSAN), K₂SO₄ (Potassium Sulfate 98.5 %, SAMCHUN), Al₂(SO₄)₃ (Aluminum Sulfate, Extra Pure, DUKSAN), were introduced into a polluted molten salt bath.

To characterize the strengthened glasses, the CS and the DOL were measured using a surface stress meter (FSM-6000LE; Orihara, Toshiba, Japan) on both sides of the glass. About 2–3 measurements were made at each sample
and the results were addressed in this study based on statistical data. In order to evaluate the precipitated compound materials in the polluted salts, the molten salts after adding additive had one-day reaction at furnace and then cool down. The salts after being ground into fine pieces using a mortar and pestle were examined by X-ray diffraction (XRD, Bruker, AXS Model D5005).

3. Results and discussion

(1) Additive effect in pure KNO₃ bath

Various additives were added into a pure molten salt bath and then glasses were strengthened at 420 °C for 2–4 hr. Table 1 shows the CS measured with samples. An obvious effect in the CS was not observed in additives [K₂CO₃, K₃PO₄, K₂SO₄, Al₂(SO₄)₃] and rather than the CS was diminished by additive contamination. However, the KOH increased slightly the CS from 838 to 883 Mpa. Lyu et al. and Tang et al. reported that the OH⁻ anion makes glass network depolymerized and increased the diffusion rate of alkali ions for ion-exchange. According to A. K. Varshneya et al., the CS is built and relaxed during ion exchange strengthening. The linear network dilation coefficient based on volume change is a critical factor to decide the CS. The more ion diffusion, therefore, the higher CS will be expected.⁷,⁸ Thereby the chemical strengthening process of Na₂O⁻Al₂O₃⁻SiO₂ glass materials is improved.⁹,¹⁰

\[ \text{Si-O-Si} + \text{OH}⁻ \rightarrow \text{Si-O-} + \text{HO-Si} \]

As a such reaction, however, some haze on glass surface was observed depending on the KOH concentration in molten salt and it represents the loose glass network induced by OH⁻ anion was still harmful to the chemical durability as well as the mechanical properties of the glass.

Likewise the KOH, the K₃PO₄ and K₂CO₃ made the molten salt alkalinity. Minor corrosion on glass surface was observed at inspection with light emitting diode (LED) lamp but there was no CS increase made by accelerating the diffusion rate of K⁺ ion.

(2) Additive effect in contaminated KNO₃ bath

To analyze the impurities in used salt bath, the molten salt was analyzed every 10 days by using inductivity coupled plasma optical emission spectrometer (ICP-OES) and the result was summarized in Table 2. The pure salt is containing a various and a small amount of impurities below 15 ppm. Interesting point is that only Na⁺ ion increased with time rapidly meanwhile the impurities such as Al³⁺, Mg²⁺, Ca²⁺, Fe³⁺ are steady state. It is expected that the Na⁺ ion produced by ion-exchanged process decreased the CS by diffusion to glass.

In order to prove the additive effect on contaminated salt, the Ca(NO₃)₂, Mg(NO₃)₂ and NaNO₃ were added in molten salt bath separately. As soon as adding the impurity ions into salt bath, the CS decreased as shown in Table 3. It can be explained by the “blocking effect” caused by the presence of Ca²⁺ in the KNO₃ bath. A little Ca²⁺ in salt decreases the rate of K⁺–Na⁺ exchange as well as the strength. In terms of Mg²⁺, it is clear that the blocking effect made by Mg³⁺ is much weaker than that of Ca²⁺. The CS reduction behavior made by Na⁺ is relatively an easy slope compared to Ca²⁺ or Mg²⁺. The interesting point is that the CS was recovered soon after adding additives as shown in Table 3. K₂PO₄ increased the CS of Ca²⁺ containing salt up to ~97% and Mg²⁺ containing salt was recovered ~97% after adding K₂CO₃ in case of NaNO₃ containing salt, K₂PO₄ is the most effective than K₂CO₃ or K₂SO₄. The CS was recovered up to ~83% without haze. So far, we do not know the reason why the haze sample has high CS value but it will be considered in future.

The salt is analytically pure and contains only small amount of Ca²⁺, Mg²⁺ and Na⁺ ions shown in Table 2. Thus the impurity Ca²⁺ ion was introduced into nitrate to control impurity concentration and the additive K₂PO₄ was also introduced into nitrate to remove the Ca²⁺ ion in molten salt. The molten nitrate was rapidly cooled down and the salt was analyzed by using XRD. Figure 1 shows the XRD patterns measured with salts collected from top and bottom of beaker. It is interesting that the XRD pattern of the top part of salt are exactly same with KNO₃. However, new peaks indicating K₃CaPO₄ crystal was observed on the salt collected from bottom of beaker.

Table 1. Anion additive effect in pure KNO₃ bath

| Impurity | Oxide | Pure KNO₃ | KNO₃⁻⁺ Anion Additive |
|----------|-------|-----------|----------------------|
| SO₄²⁻    | 1000  | K₂SO₄     | 842                  | 843                  |
| PO₄³⁻    | 15000 | K₃PO₄     | 840                  | 850                  |
| OH⁻      | 6000  | KOH       | 838                  | 883                  |
| CO₃²⁻    | 60000 | K₂CO₃     | 841                  | 836                  |

¹Haze under LED Lamp, ²Haze with naked Eye.

Table 2. Daily analysis of impurity ions in molten salt using ICP-OES

| Impurity Ions (ppm) | 0 Day | 10 Day | 20 Day | 30 Day | 40 Day |
|---------------------|-------|--------|--------|--------|--------|
| Al                  | 14.9  | 14.5   | 14.9   | 14.8   | 15.2   |
| Na                  | 87    | 1520   | 3672   | 4971   | 6359   |
| Mg                  | 14.8  | 14.2   | 14.1   | 14.2   | 14.3   |
| Ca                  | 9.3   | 9.2    | 8.7    | 8.7    | 8.6    |
| Fe                  | 8.8   | 8.7    | 9.1    | 8.6    | 8.8    |
| Compressive Stress [MPa] | 850   | 800    | 740    | 680    | 630    |

Table 3. Effect of additive on compressive stress and glass surface in contaminated KNO₃ bath

| Impurity | Pure Salt | After Contamination | After Additive Addition |
|----------|-----------|---------------------|------------------------|
| Ca²⁺ | 200       | K₂PO₄               | 850                    | 200 | 825 |
| Mg²⁺ | 300       | K₂CO₃               | 775                    | 825 |
| Na⁺ | 10,000    | K₂PO₄               | 600                    | 828 | (Haze) |
|      |           | K₂CO₃               | 704                    | (Clear) |
|      |           | K₂SO₄               | 697                    | 628 |
Figure 2 shows the XRD results of molten salts containing various impurities and additives. The Na\(^+\) impurity in molten salt was removed by adding K\(_2\)PO\(_4\) and K\(_2\)SO\(_4\), and the Na\(_3\)PO\(_4\) crystal and K\(_2\)Na(SO\(_4\))\(_2\) crystals were precipitated as shown in Fig. 2(a). The Ca\(^{2+}\) impurity in molten salt was removed by adding K\(_3\)PO\(_4\), K\(_2\)CO\(_3\) and K\(_2\)SO\(_4\) to produce KCaPO\(_4\), K\(_2\)Ca(PO\(_4\))(SO\(_4\))\(_3\), and CaCO\(_3\). The Mg\(^{2+}\) impurity was removed by adding K\(_2\)CO\(_3\) and it produced MgCO\(_3\) crystal as seen in Fig. 2(c).

The chemical reactions according to the impurities and the additives were summarized in Table 4. Xu et al. reported that the impurity Ca\(^{2+}\) ion was removed by adding 2PO\(_4^{3-}\) ion by producing a Ca\(_3\)(PO\(_4\))(OH)\(_2\)\(_2\)\(_2\). However, this work proves that KCaPO\(_4\) is easier to precipitate. It should be noted that the K\(_3\)PO\(_4\) additive is very effective to remove Na\(^+\), Ca\(^{2+}\) impurities and the impurity Mg\(^{2+}\) is only removed by adding K\(_2\)CO\(_3\) additive.

### 4. Conclusions

In case of ion-exchange process with pure nitrate salt, KOH additive only improved the CS in strengthening glass.

| Impurity Ions | Additives | Molten Salt Products |
|---------------|-----------|---------------------|
| Na\(^+\)      | K\(_2\)PO\(_4\) | K\(_3\)NO\(_3\) + NaNO\(_3\) + K\(_3\)PO\(_4\) |
|               | K\(_2\)SO\(_4\) | K\(_2\)NO\(_3\) + NaNO\(_3\) + K\(_2\)SO\(_4\) |
|               | K\(_2\)CO\(_3\) | K\(_3\)NO\(_3\) + NaNO\(_3\) + K\(_2\)CO\(_3\) |
| Ca\(^{2+}\)   | K\(_3\)PO\(_4\) | K\(_3\)NO\(_3\) + Ca(NO\(_3\))\(_2\) + K\(_3\)PO\(_4\) |
|               | K\(_2\)SO\(_4\) | K\(_2\)NO\(_3\) + Ca(NO\(_3\))\(_2\) + K\(_2\)SO\(_4\) |
|               | K\(_2\)CO\(_3\) | K\(_3\)NO\(_3\) + Ca(NO\(_3\))\(_2\) + K\(_2\)CO\(_3\) |
| Mg\(^{2+}\)   | K\(_2\)CO\(_3\) | K\(_3\)NO\(_3\) + Mg(NO\(_3\))\(_2\) + K\(_2\)CO\(_3\) |

![Fig. 1. XRD patterns of solidified salts containing impurities and additives; (1) top salt of beaker, (2) bottom salt of beaker.](image1.png)

![Fig. 2. XRD patterns of molten salts containing impurities and additives.](image2.png)
up to \( \sim 50 \text{ MPa} \) and the others additives did not make the CS improvement. Rather than the CS was diminished by additive contamination. In case of strengthening process with contaminated nitrate salt, on other hand, small amount of additives in the composition of nitrate slat bath showed a huge difference by recovering the CS. The additives \( \text{K}_3\text{PO}_4, \text{K}_2\text{CO}_3, \) and \( \text{K}_2\text{SO}_4 \) successfully removed the impurities, \( \text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+} \), by precipitating compounds in molten bath and recovered the CS. FSM analysis showed that the \( \text{K}_3\text{PO}_4 \) recovered the CS of \( \text{Ca}^{2+} \)-containing salt up to \( 97\% \). \( \text{Mg}^{2+} \)-polluted salt was recovered \( \sim 97\% \) after adding \( \text{K}_2\text{CO}_3 \) and the main impurity \( \text{Na}^+ \) was successfully removed by adding \( \text{K}_3\text{PO}_4 \) or \( \text{K}_2\text{CO}_3 \) up to \( \sim 83\% \).

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