Strength of Salt Core Composed of Alkali Carbonate and Alkali Chloride Mixtures Made by Casting Technique*

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The strength of four binary systems NaCl–Na₂CO₃, KCl–K₂CO₃, KCl–NaCl and K₂CO₃–Na₂CO₃ was investigated in order to develop expendable salt core for high pressure die casting processes. Four point bending test was conducted to determine the strength of specimens made from molten salts by using the permanent mold casting technique. The strength of the system NaCl–Na₂CO₃ was over 20 MPa at the Na₂CO₃ composition between 20 mol% and 30 mol%, and between 50 mol% and 70 mol%. The highest strength was about 30 MPa at the composition of NaCl–70 mol% Na₂CO₃. This strength was 5 times as high as that of commonly used sand cores. The system KCl–K₂CO₃ also showed 20 MPa in strength. It was observed that there were the primary particles surrounded by the eutectic structure in the solidification structure of the systems NaCl–Na₂CO₃ and KCl–K₂CO₃ at the composition where the peak strength was obtained. The presence of the primary particles played an important role to strengthen the structure because the primary particles can prevent or deflect the crack propagation. In contrast to these binary systems, the systems KCl–NaCl and K₂CO₃–Na₂CO₃ were very brittle due to the phase decomposition or other solid–solid phase transformation of the solid solution phase. The strength of these systems was under 6 MPa. [doi:10.2320/matertrans.48.1034]

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1. Introduction

A high pressure die casting (HPDC) process is a well-known near-net-shape manufacturing technology that can provide geometrically complicated shaped products of aluminum alloys and other low melting point alloys at a low cost. Recently, there is an increasing need for fabricating undercut shaped components by this process in order to improve mechanical properties, to increase productivity, to save cost and so on. However, it is very difficult to manufacture these components by the HPDC process, because quite severe casting conditions in this process restrict the use of expendable cores. The cores are indispensable to form undercut shaped parts in the products. In the HPDC process, the high flow velocity (more than 30 m/s at gates) and high hydrostatic pressure (more than 60 MPa) of molten metals are commonly used. These casting conditions cause very high mechanical loading on molds and cores. Therefore, the expendable cores must have enough high strength to withstand such high loading. However, the increase of the core strength usually reduces its collapsibility and thus needs more core removal time. In general, the more increase in the core strength, the more decrease in its collapsibility that causes longer core removal time. Accordingly, total processing cost must increase. To solve these problems, many types of expendable cores for the HPDC process have been developed such as sand cores,¹,² metallic cores,³ organic material cores,⁴ and salt cores.⁵ However, no expendable cores have been used in the HPDC process with full satisfaction of the strength and the removability.

Water soluble salt cores fabricated by casting techniques⁶–¹¹ are attractive candidates for the new expendable core, because of its high removability. Moreover, the use of casting techniques enable to fabricate complex shaped salt cores. Recently, it has been reported that the strength of alkali halides reinforced with aluminum borate whiskers made by the permanent mold casting method is very high enough to use in the HPDC processing.¹²,¹³ These studies, however, showed that the addition of the ceramic reinforcements reduces the fluidity property of the molten salts. Furthermore, the use of the ceramic reinforcement increases material costs and requires extra recycle processes. In many patents,⁶–¹¹ it have also been reported that salt cores composed of salt mixtures without any reinforcements have good castability and high removability. Hence, the use of the salt mixtures is more desirable to fabricate the salt core for the HPDC process. However, few studies about the strength of these salt mixtures have been reported, in which the effects of salt the mixture composition on the strength were investigated systematically.

The aim of this study is to investigate the strength of four binary systems, sodium chloride–sodium carbonate, potassium chloride–potassium carbonate, potassium chloride–sodium chloride and potassium carbonate–sodium carbonate. These binary systems are parts of the quaternary system of sodium chloride, sodium carbonate, potassium chloride and potassium carbonate, whose liquidus temperature is adequate to be used in the HPDC processing on aluminum alloys.¹⁴ Four point bending tests were carried out on the specimens fabricated from molten salt mixtures by a permanent mold casting method. The effect of compositions and solidification structures on the strength was discussed based on the fractography and knowledge of phase diagrams. The results showed that very high strength can be realized in the mixtures of the systems, sodium chloride–sodium carbonate and potassium chloride–potassium carbonate.

2. Experimental

The materials used in this work were four pure salts, potassium chloride (KCl), sodium chloride (NaCl), potassi-
um carbonate (K$_2$CO$_3$) and sodium carbonate (Na$_2$CO$_3$). Their purity was 99.5 mass%. By mixing these salts, four binary systems NaCl–Na$_2$CO$_3$, KCl–K$_2$CO$_3$, KCl–NaCl and K$_2$CO$_3$–Na$_2$CO$_3$ were prepared. The chemical compositions and their liquidus temperature of the salt mixtures used in this study are listed in Table 1. Salt mixture specimens were fabricated by the permanent mold casting method, using a JIS-SCM440 steel mold in which two large risers were set to feed solidification shrinkage as shown in Fig. 1. Cross section shape of the specimen was trapezoid since a little draft was needed to eject the specimens from the mold smoothly. The salt mixtures were melted in an alumina crucible with an electric resistance heater. Then the molten salt mixtures superheated at 10 K were poured into the permanent mold. The preheating temperature of the permanent molds was 373 K. Sixty seconds after the pouring, solidified specimens were ejected and cooled to the ambient temperature.

The four point bending tests were carried out to determine the strength of as-cast salt mixture specimens. The bending test conditions were as follows. The distances of upper and lower bending bars were 50 mm and 10 mm, respectively. The diameter of the bending bars was 4 mm. The bending rate (the cross head moving rate) was $1 \text{ mm/s}$. The center of the specimens (A–A' line in Fig. 1) was positioned between upper two bending bars. In the bending test, the bending force was recorded automatically. Then the bending strength $\sigma [\text{Pa}]$ was calculated from the obtained maximum bending force $P [\text{N}]$ by the following equation.

$$\sigma = \frac{3LP}{BH^2}$$

where $H = 20 \text{ mm}$ and $B = 18 \text{ mm}$ were the height and width of the cross section area of specimens. $L = 20 \text{ mm}$ was the vertical distance between the upper bar and the lower bar.

After the bending test, specimens were cut and polished with the grade #1000 SiC water proof papers for Vickers hardness measurements. The specimens were polished more carefully with the grade #4000 SiC water proof papers for microstructure observation. A little water was used for the etching. Then a carbon coating was applied on the polished surface to observe the solidified structure with the scanning electron microscope (SEM). The energy dispersive X-ray microanalysis (EDX) was used to determine a local chemical composition in the solidified structure. The crystallized phases existing in the solidification structure were identified with the X-ray diffraction (XRD). Fracture surfaces of the specimens were observed and analyzed with the SEM-EDX system. The commercial software package, ThermoCalc$^{(15)}$ was used to generate phase diagrams.

### 3. Results

#### 3.1 Casting defects

Figure 2 shows a cross section of a cast specimen with the composition of KCl–80 mol%K$_2$CO$_3$, in which two typical casting defects were found. One of the defects was unevenness formed on the casting skin. The unevenness was observed in all specimens in this study because the permanent mold casting technique was used for making them. It is reported that this defect is due to thermal deformation caused by the temperature differences between inside and outside of the initially solidified shell. The thermal deformation occurs immediately after the pouring$^{12,13}$ According to the previous investigations$^{13,16}$ low heat conductivity of the solid salts increases the temperature difference and causes the thermal deformation. Therefore, it was very difficult to prevent the unevenness formation in the permanent casting method. In the commercial process, the
HPDC technique can be used to fabricate salt cores in order to decrease the formation of unevenness.

Another defect was the internal shrinkage which appeared along the center line of the specimens. This defect was observed in almost all specimens although two large risers were set in the permanent mold as shown in Fig. 1. Usually, the internal shrinkage is caused by the solidification shrinkage and by the thermal contraction of salts. The solidification shrinkage ratio of the salt mixtures used in this work is commonly over 15 percent. This value is quite higher than that of metals, e.g., 6 percent for pure aluminum. Hence, the internal shrinkage easily formed in cast specimens. In this study, the four point bending tests were conducted to these specimens that contain casting defects. Therefore, the influence of these defects on the strength was not taken into account in calculating the bending strength by eq. (1). The detail of the bending strength is given in the following sections.

3.2 Strength of the system KCl–NaCl and system K$_2$CO$_3$–Na$_2$CO$_3$

Figure 3 shows two cast specimens used for the four point bending test. A lot of cracks are observed parallel and perpendicular to the center line of the KCl–30 mol%NaCl specimen as shown in Fig. 3(a). These cracks appeared during a cooling process owing to thermal stress generated in the specimen. In all specimens composed of the system KCl–NaCl, similar cracks were observed. Usually, the specimens with the cracks were broken at the cracks in the four point bending test. The strength of specimens composed of the system K$_2$CO$_3$–Na$_2$CO$_3$ was very low. Figure 3(b) shows the specimen of K$_2$CO$_3$–50 mol%Na$_2$CO$_3$. Similar to this sample, many specimens of the system K$_2$CO$_3$–Na$_2$CO$_3$ were brittle.

Figure 4 shows the phase diagrams and the bending strength of the systems KCl–NaCl and K$_2$CO$_3$–Na$_2$CO$_3$, respectively. As shown in Fig. 4(a), the minimum liquidus point of the system KCl–NaCl is 932 K at the composition of KCl–49 mol%NaCl. The solid phase under the solidus temperature is a continuous series of solid solution that will decompose into KCl phase and NaCl phase below the two-phase separation temperature. The decomposition makes the salt mixture very brittle, and thus the cracks in the specimens were initiated and propagated easily by the thermal stress as shown in Fig. 3(a). Figure 4(b) shows the strength of this binary system. The highest strength was up to 5 MPa and was smaller than that of the commonly used resin bonded sand core (6 MPa). Some of the strength was about zero MPa. Such a low strength was due to the two-phase separation and the cracks.

Similar to this, the solid phase under the solidus temperature is a continuous series of solid solution in the system K$_2$CO$_3$–Na$_2$CO$_3$ as shown in Fig. 4(c). The solid solution phase changes to other solid phases by cooling although this solid–solid phase transition in this system can not be shown in this Fig. 4(c). However the phase equilibria of solid phases has not been well understood, yet. The minimum liquidus temperature is 986 K at the composition of K$_2$CO$_3$–59 mol% Na$_2$CO$_3$. Figure 4(d) shows the strength of this system. The strength was under 6 MPa in the whole composition. Low strength especially was obtained in the Na$_2$CO$_3$ composition between 30 mol% and 70 mol%, where the specimens showed very brittle behavior as shown in Fig. 3(b). This was due to the solid–solid phase transition.

3.3 Strength of the system NaCl–Na$_2$CO$_3$ and system KCl–K$_2$CO$_3$

Figure 5(a) shows the phase diagram of the system NaCl–Na$_2$CO$_3$. This binary system has the simple eutectic phase diagram. The lowest liquidus temperature is 905 K at the eutectic composition of NaCl–45 mol%Na$_2$CO$_3$. Figure 5(b) shows the strength of this binary system. Generally speaking, the strength was low at the composition near the eutectic and near the unary while it was high at the intermediate composition between the unary and the eutectic. The strength exceeded 20 MPa in the Na$_2$CO$_3$ composition between 20 mol% and 30 mol%, and between 50 mol% and 70 mol%. The highest strength was over 30 MPa at the composition of NaCl–70 mol%Na$_2$CO$_3$. This value is about 5 times as high as the strength of the sand core.

Almost the same relationship between the phase diagram and strength was obtained in the system KCl–K$_2$CO$_3$. Figure 5(c) shows the phase diagram of this binary system. The system KCl–K$_2$CO$_3$ has the eutectic phase diagram. The lowest liquidus point is 897 K at the eutectic composition of KCl–38 mol%K$_2$CO$_3$. The strength of this system is shown in Fig. 5(d). The lowest strength was obtained near the eutectic composition. The strength was about 5 MPa at KCl–40 mol%K$_2$CO$_3$. The strength of the pure KCl and pure K$_2$CO$_3$ was under 5 MPa. In contrast to these, the strengths at the K$_2$CO$_3$ composition of 20 mol%, and in the K$_2$CO$_3$ composition between 50 mol% and 80 mol% were over 10 MPa. The highest strength was 25 MPa at the K$_2$CO$_3$ compositions of 50 mol% and 60 mol%. By comparing the strength of these
Fig. 4  Strength and phase diagrams\(^{(15)}\) of KCl–NaCl and K\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\) binary systems.

Fig. 5  Strength and phase diagrams\(^{(10)}\) of NaCl–Na\(_2\)CO\(_3\) and KCl–K\(_2\)CO\(_3\) binary systems.
systems, it was found that the strength of the system NaCl–Na$_2$CO$_3$ was commonly higher than that of the system KCl–K$_2$CO$_3$.

### 3.4 Hardness of the system NaCl–Na$_2$CO$_3$ and system KCl–K$_2$CO$_3$

Figure 6 shows the Vickers hardness of the systems NaCl–Na$_2$CO$_3$ and KCl–K$_2$CO$_3$. The hardness more than 5 points for each specimen was measured. In Fig. 6, the average hardness values of each composition for both binary systems were connected by the dotted line or the solid line, respectively. According to this figure, the hardness of the system NaCl–Na$_2$CO$_3$ was higher than that of the system KCl–K$_2$CO$_3$ in the whole composition range. The hardness value of the pure NaCl was a little higher than that of pure KCl. The hardness of the pure Na$_2$CO$_3$ was higher than that of pure K$_2$CO$_3$. For both systems, the higher hardness value was obtained in the hyper eutectic composition rather than in the hypo eutectic composition. In particular, more than 70HV in the hardness value was obtained in the Na$_2$CO$_3$ composition range between 50 mol% and 90 mol% for the system NaCl–Na$_2$CO$_3$.

### 3.5 Microstructure of the system NaCl–Na$_2$CO$_3$

As the microstructure of materials strongly relates to the fracture mechanism and to their strength,

the solidification structures of the cast specimens in the system NaCl–Na$_2$CO$_3$ that showed high strength were analyzed by using the phase diagram, the SEM–EDX and the XRD qualitatively.

Considering the sequence of the solidification, the solidification structure can be decided by the phase diagram of the system NaCl–Na$_2$CO$_3$ shown in Fig. 5(c). In the hypo eutectic composition, the primary phase is pure NaCl. The eutectic structure should appear at the eutectic temperature after the solidification of the primary phase. Therefore, the solidification structure should be composed of the primary NaCl particles surrounded by the eutectic structure. In contrast, the primary phase is Na$_2$CO$_3$ in the hyper eutectic composition. The solidification structure should be composed of the primary Na$_2$CO$_3$ particles surrounded by the eutectic structure.

Figures 7(a) and (b) show the solidification structure of NaCl–10 mol%Na$_2$CO$_3$, in which a lot of dendrites and the eutectic structure were observed. The EDX analysis showed
that the compositions of these dendrites were pure NaCl. It was found that the binary eutectic structure was composed of Na$_2$CO$_3$ and NaCl. These results matched with the solidification structure predicted by the phase diagram of this system. Figures 7(c) and (d) show the solidification structure of NaCl–70 mol%Na$_2$CO$_3$. The primary particles with about 50 μm in diameter are shown in the eutectic structure. The EDX analysis showed that the composition of the primary particles was Na$_2$CO$_3$. The XRD quantitative analysis was also conducted to identify very fine eutectic structure. Figure 8 shows the XRD pattern of the NaCl–70 mol%Na$_2$CO$_3$ specimen. This and the EDX analysis showed that the eutectic structure was composed of pure NaCl and pure Na$_2$CO$_3$. These results exactly matched with the phase diagram of this binary system. From the microstructure observation, it can be said that there were the primary particles surrounded by the eutectic structure in the solidification structure at the composition where the high strength was obtained.

Figure 9(a) shows the broken surfaces of the specimen composed of NaCl–10 mol%Na$_2$CO$_3$ in which many fractured surfaces of the primary NaCl particles were observed. According to Ashby,21) these surfaces are a group of the {100} cleavage planes. This meant that the crack propagating through the eutectic structure deflected its direction along the cleavage planes. This mechanism is called the “crack deflection”,20) which can increase the specimens in strength. Figure 9(b) shows the broken surface of the NaCl–70 mol%Na$_2$CO$_3$. There were a lot of primary particles in the eutectic structure. These primary particles were fine and were well dispersed in the eutectic structure. The edge of the primary particles was so smooth as to decrease the stress concentration. Therefore, it was shown that the existence of these particles prevented the crack propagation by the “crack bowing” strengthening mechanism,20) as well as the deflection mechanism. In the fracture surface of the NaCl–70 mol%Na$_2$CO$_3$ specimen, the crack deflection angle was very small. Hence, the crack bowing mechanism was more important than the deflection mechanism in this specimen whereas the deflection mechanism was observed in the specimen of NaCl–10 mol%Na$_2$CO$_3$.

4. Discussion

4.1 Strengthening mechanism of the system NaCl–Na$_2$CO$_3$ and system KCl–K$_2$CO$_3$

The binary systems of NaCl–Na$_2$CO$_3$ and KCl–K$_2$CO$_3$ showed very high strength. There were two peaks of the strength at the hypo eutectic and the hyper eutectic composition, where the primary particles solidified surrounded by the eutectic structure as shown in Fig. 7. This unique solidification structure attributed the strength to the increase at these compositions. The presence of the primary particles in the eutectic structure prevented and deflected the crack propagation. The former mechanism is called “crack bowing” and latter is “deflection”.20) The schematic drawings of these strengthening mechanisms are shown in Fig. 10. In the crack bowing mechanism, specimens are strengthened by a change in the crack front shape from straight line to the line with some curvature, as shown in Fig. 10(a). In the crack deflection mechanism shown in Fig. 10(b), there are the tilt mode and the twist mode, in which their deflection axes are different. In both modes, the particles in the matrix may cause the deflection of the crack propagation. The effect of the deflection on the strengthening increases with increase of the crack deflection angle. These two strengthening mechanisms are usually observed at the same time.20) The phase diagrams of the systems NaCl–Na$_2$CO$_3$ and KCl–K$_2$CO$_3$ shown in Figs. 4(a) and (c) give the information about the solidification structure. By considering the sequence of solidification, for example Scheil’s equation,22) the amount of the primary phase and eutectic phase in the

Fig. 8 The X-ray diffraction pattern of NaCl–70 mol% Na$_2$CO$_3$.

Fig. 9 The scanning electron microscope (SEM) images of broken surface. (a) : NaCl–10 mol%Na$_2$CO$_3$. (b) : NaCl–70 mol%Na$_2$CO$_3$. 

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solidification structure can be explained. This is schematically drawn in Fig. 11. At the eutectic composition, the fraction of the primary phase is very few. The structure is composed of the eutectic structure fully as shown in Fig. 11(a). Therefore, if a crack initiation occurs at the surface of the eutectic structure like Fig. 11(b), the crack can propagate straightly because there are no particles preventing or deflecting the crack propagation. Hence, the strength was low at the eutectic composition in the systems NaCl–Na$_2$CO$_3$ and KCl–K$_2$CO$_3$. Also, at the composition near the unary, the greater part of the solidification structure is composed of the primary phase as shown in Fig. 11(c). In the single phase structure, the cracks propagate very easily on their cleavage planes of each particle as shown in Fig. 11(d). Thus, the specimens of pure salts showed quite a low strength. In contrast, the primary particles exist among the eutectic structure at the intermediate composition between the eutectic and the unary. This structure is drawn in Fig. 11(e). In this structure, particles or dendrites of the primary phase prevent or deflect the crack propagation by the bowing mechanism or the deflection mechanism as shown in Fig. 11(f). Therefore, high strength was obtained at the composition between the eutectic and the unary of the systems NaCl–Na$_2$CO$_3$ and KCl–K$_2$CO$_3$.

**4.2 Effect of hardness on strength**

In the deflection mechanism or crack bowing mechanism, the hardness of primary particles plays an important role for preventing the crack propagation and for strengthening the structure, as well as strengthening of the eutectic structure. Figure 6 shows the hardness of the systems NaCl–Na$_2$CO$_3$ and KCl–K$_2$CO$_3$. From this figure, it is found that the hardness value at the eutectic composition or the unary of the system NaCl–Na$_2$CO$_3$ was higher than that of the system KCl–K$_2$CO$_3$. This means that the hardness of both the primary particles and eutectic structure in the system NaCl–Na$_2$CO$_3$ was higher than that for the system KCl–K$_2$CO$_3$. These results corresponded to the strength difference of the system NaCl–Na$_2$CO$_3$ and KCl–K$_2$CO$_3$ shown in Figs. 5(a) and (c). The system NaCl–Na$_2$CO$_3$ showed higher strength than the system KCl–K$_2$CO$_3$ as described in the previous section. Furthermore, the strength of the system KCl–K$_2$CO$_3$ was not so high in the K$_2$CO$_3$ composition between 10 mol% and 30 mol% where the hardness of the primary pure KCl particles was low.

4.3 Brittle behavior of the system KCl–NaCl and the system K$_2$CO$_3$–Na$_2$CO$_3$

The phase diagrams of the systems KCl–NaCl and K$_2$CO$_3$–Na$_2$CO$_3$ are shown in Figs. 4(a) and (c). In these systems, the solid phase is a continuous series of solid solution under the solidus temperature. However, the solid solution phase is unstable at the ambient temperature. Thus, solid–solid phase transitions that make the structure very brittle occur during the cooling process. These solid–solid phase transitions contain the two-phase separation for the system KCl–NaCl$^{23}$ and the eutectoid reaction for the system K$_2$CO$_3$–Na$_2$CO$_3$.$^{18}$ No phase transition boundaries are drawn in Fig. 4(c) because the sub-solidus of the system K$_2$CO$_3$–Na$_2$CO$_3$ has not been understood completely, yet.$^{18,19}$

In the whole composition in these systems, the solidification structure is the single phase structure of solid solution phase under the solidus. This structure is very similar to the fully eutectic structure as schematically shown in Fig. 11(a). In this case, the solidification structure is hardly strengthened by the crack bowing mechanism or the deflection mechanism since there is no particle that can prevent the crack propagation. Additionally to say, there are the solid–solid phase transitions in the systems, KCl–NaCl and K$_2$CO$_3$–Na$_2$CO$_3$ at the low temperature, which make their solidification structure very brittle because the phase transitions cause the lattice misfit. The negative effect of the phase transition on the strength was described in previous investigation.$^{23}$ Therefore, the strength of the systems KCl–
NaCl and K$_2$CO$_3$–Na$_2$CO$_3$ was very low in the whole composition.

5. Conclusion

In this study, the four point bending test was carried out to determine the strength of four binary systems NaCl–Na$_2$CO$_3$, KCl–K$_2$CO$_3$, KCl–NaCl and K$_2$CO$_3$–Na$_2$CO$_3$. The microstructures of the cast specimens were analyzed with the SEM-EDX and the XRD. The result could be summarized as follows.

1. The strength of the system NaCl–Na$_2$CO$_3$ was over 20 MPa in the Na$_2$CO$_3$ composition between 20 mol% and 30 mol%, and between 50 mol% and 70 mol%. The highest strength exceeded 30 MPa at the composition of NaCl–70 mol%Na$_2$CO$_3$.

2. The strength of the system KCl–K$_2$CO$_3$ was over 10 MPa in the K$_2$CO$_3$ composition at 20 mol%, and between 50 mol% and 60 mol%. The highest strength exceeded 25 MPa at the K$_2$CO$_3$ composition of 50 mol% and 60 mol%.

3. The increase in the strength in the systems NaCl–Na$_2$CO$_3$ and KCl–K$_2$CO$_3$ was due to their solidification structure in which the primary particles were present in the eutectic structure because the primary particles were able to prevent or to deflect the crack propagation.

4. The strength of the system NaCl–Na$_2$CO$_3$ was higher than that of the system KCl–K$_2$CO$_3$. This is because the hardness value of the primary particles and the eutectic in the system NaCl–Na$_2$CO$_3$ was higher than that of the system KCl–K$_2$CO$_3$.

5. The strength of the systems KCl–NaCl and K$_2$CO$_3$–Na$_2$CO$_3$ was lower than 6 MPa. Such a low strength was due to their solidification structure and the solid–solid phase transformations.

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