

Effect of kaolin on tensile strength and humidity resistance of a water-soluble potassium carbonate sand core

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Abstract: Water soluble cores (WSCs) have been widely applied in manufacture of complex metal components with hollow configurations or internal channels. However, the WSCs without any additions have low tensile strength and low humidity resistance. The purpose of this study is to prepare a water-soluble potassium carbonate sand core with addition of kaolin by the hot-tempering method. The effects of kaolin on tensile strength, humidity resistance, fracture mechanism, as well as the gas evolution and collapsibility of WSCs were investigated. Results show that both the crystal morphology and the fracture mechanism of the inorganic salt are changed under the participation of kaolin, contributing to the increase of the tensile strength and the humidity resistance of the core. With the addition of 3wt.% kaolin, the tensile strength could be increased by a factor of 2, reached 1.50 MPa and the hygroscopic rate could be decreased by 14%, achieved 0.559% (after stored for 8 h), respectively. As the addition amount of kaolin increases from 0wt.% to 3wt.%, the main fracture mechanism changes from a adhesive to a cohesive fracture mechanism. The water-soluble potassium carbonate core obtained has the low gas evolution and excellent collapsibility, which makes it suitable for casting low melting metal with complex cavities and crooked channels.

Key words: water-soluble core; kaolin; tensile strength; humidity resistance; strengthening mechanism

CLC numbers: TG221.1

Document code: A

Article ID: 1672-6421(2016)01-015-07

Due to their excellent collapsibility and low gas evolution, water soluble cores (WSCs) are widely applied in the automotive and aerospace industries for manufacturing complex castings^[1-3]. A wide range of WSC materials have been developed utilizing different methods. According to the proportion of the water-soluble material in the core, WSCs can be classified as follows: (I) cores entirely made from water-soluble material; (II) cores mainly consisting of water-soluble material and other material uniformly dispersed inside the water-soluble material; (III) cores mainly prepared from refractory materials, with the water-soluble material used as binder. For instance, Yaokawa^[4] investigated the strength of four binary systems, i.e., NaCl-Na₂CO₃, KCl-K₂CO₃, KCl-NaCl and K₂CO₃-Na₂CO₃, and the strength of the NaCl-Na₂CO₃ cores was over 30 MPa, which belongs to category I; Zhang^[5] prepared cores from

molten sodium carbonate and a plurality of ceramic particulates such as magnesium oxide, and the cores were used in various industries including production of automobiles, aircraft and spacecraft; and Wan^[6] enhanced the core strength by adding ceramic whiskers to molten sodium chloride, which both fall into the second category. Jia^[7] prepared WSCs with the strength of 1.2 MPa, using zircon sand and fused alumina powder as main components and sodium chloride as binder material, which can be classified as the third category. Although the above cores are different concerning the proportion of the water-soluble material, both the cores of category I and II, and partly cores of category III are formed by fusion casting process or press sintering process, which all require a high forming temperature. Moreover, inorganic salts are added in the form of powder, which requires a series of complex preparing process such as filtration, crystallization, and desiccation. Therefore, considering the consumption of energy and the complex preparing process of inorganic salts, the application potential of the cores prepared via fusion casting or press sintering is limited. While the third type of WSCs prepared by hot-tempering method^[8] offers several advantages, in which the core sand mixture

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Received: 2015-07-06;

Accepted: 2015-11-20

is pressed and heated in a preheated mold; and due to the lower forming temperature and the addition method of inorganic salts (in the form of solution), the hot-tempering method leads to a lower energy consumption and a simpler reclamation process. However, the strength and the humidity resistance of cores prepared via the hot-tempering method are low when only water-soluble salts and refractory materials are used for the preparation of the cores [9]. So, it is essential to enhance the tensile strength and improve the humidity resistance of this kind of cores. Recently, it was mentioned that kaolin could enhance the strength of WSCs [10], but the strengthening and humidity resistance mechanism has not been investigated. In the present study, the WSCs for castings of low melting point metals and alloys were prepared by using potassium carbonate as binder and applying hot-tempering method. The effect of kaolin on the tensile strength and humidity resistance of WSCs was investigated, and the strengthening mechanism was analyzed in detail.

1 Experimental procedure

The silica sand (Dalin sand, 40/140 meshes), potassium carbonate solution (Tianjin Dengfeng Chemical Reagent Factory, analytical grade) and calcined kaolin (Shanghai Xincheng Fine Chemical Corporation, 400 mesh) were used to prepare core specimens. The preparation process and parameters were as follows: First, 500 g of silica sand and kaolin respectively at a weight percentage of 0, 1, 3, 5 and 7 wt.% were dry-mixed in an SHY resin sand mixer for 1 min. Then, the K_2CO_3 solution, whose concentration and amount are 50% and 16% by dry weight of the sand, respectively, was added and the resulting mixture was further mixed for 3 min. The specimen preparation temperature was set to 180 °C at the SAR- II intelligent temperature-control of a pre-coated sand sampling machine, and the heating time was 3 min. Prior to the tensile strength tests, the samples were cooled down to room temperature in a drying vessel. Afterwards, the tensile strength was measured according to the Chinese standard JB8583-2008 using a SWY universal hydraulic strength testing machine. The sand mixer, the sampling machine and the strength testing machine were manufactured by Wuxi Sanfeng Equipment Co., Ltd., China. The humidity resistance was assessed by comparing the hygroscopic rate of the specimens, i.e., the higher the hygroscopic rate, the lower the humidity resistance. The hygroscopic rate of the core was calculated using the following equation:

$$H = (W_t - W_0) / W_0 \times 100\%$$

where H represents the hygroscopic rate of the WSCs, W_t is the mass of the specimen exposed to air for t hours, and W_0 is the initial mass of the specimen. The gas evolution was measured using a GET-II intelligent gas evolution tester, also according to the Chinese standard JB8583-2008. The temperature was controlled at $700 \pm 5^\circ\text{C}$, because the core was only applied to castings of low melting metals and their

alloys. Scanning electron microscopy (SEM, FEI Co., Ltd., Netherlands) was used to observe the microstructure, fracture morphology and analyze the elemental composition of the sand specimens.

2 Results

2.1 Effect of kaolin on tensile strength of WSCs

The tensile strength of WSCs with kaolin (respectively at 0, 1, 3, 5 and 7 wt.%) was investigated. As shown in Fig. 1, the relationship between the kaolin content and the tensile strength measured after being exposed in air for 0, 4, and 8 h could basically be described using downward parabola. For a kaolin weight percentage between 0 and 3%, the initial tensile strength of the core gradually increases from 0.50 to 0.91 MPa and further to 1.46 MPa. When the kaolin weight percentage was increased from 3 to 5wt.%, the initial tensile strength of the core does not change significantly, with the measured values at 1.46 and 1.50 MPa, respectively. However, the initial tensile strength of the core gradually decreases from 1.5 to 1.0 MPa when the kaolin weight percentage is increased from 5 to 7 wt.%. As compared with the core fabricated without kaolin, the initial tensile strength could be increased by a factor of 2 by adding up to 5 wt.% kaolin. The stored strength was also investigated. As shown in Fig. 1, when the cores are stored for 4 h, the ratios of the strength loss are all over 50%, and when the cores are stored for 8 h, the ratios of the strength loss are all close to 100%.

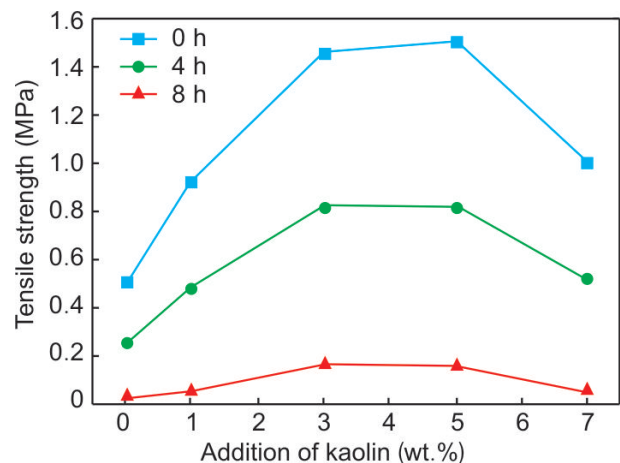


Fig. 1: Effect of kaolin on tensile strength of WSCs (temp. 20–25 °C, relative humidity 75%–85%)

2.2 Effect of kaolin on hygroscopic rate of WSCs

Cores with different amounts of kaolin were used to study the effect of kaolin on the hygroscopic rate. As shown in Fig. 2, with increasing kaolin weight percentage, the hygroscopic rate measured after 4, 8 and 12 h all decreases first and then increases. When the kaolin weight percentage is changed from 0 to 3wt.%, the hygroscopic rate of the core gradually decreases.

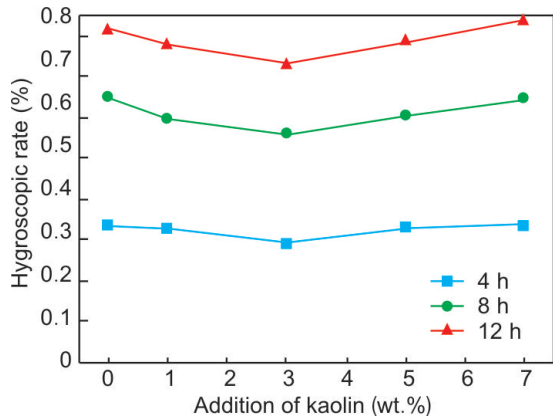


Fig. 2: Effect of kaolin on hygroscopic rate of WSCs (temp. 10±1 °C, relative humidity 98%±1%)

When the kaolin weight percentage is increased from 3wt.% to 7wt.%, the hygroscopic rate of the core gradually increases. For example, the hygroscopic rate of the core without kaolin was 0.652% after 8 h, and that of the core with 3wt.% kaolin was 0.559% after 8 h, corresponding to a decrease by 14%. Thus, cores with 3wt.% can be expected to have a better humidity resistance.

2.3 Effect of kaolin on fracture morphology

Figure 3 shows the fracture morphology of the core with 0wt.% kaolin. A large number of bonding bridges and caves between the sand grains can be seen in Fig. 3(a). Figure 3(b) shows the transition areas between the sand grains, and the fracture morphology features smooth lamellar structures and bare sand grains. In Fig. 3(c), there are massive and acicular structures with smooth boundaries covering the sand grains. In Fig. 3(d), there exist a comparatively large number of lamellar and acicular structures.

Figure 4 displays representative SEM micrographs of the fracture morphology of the core with 1wt.% kaolin. As shown in Fig. 4(a), the fracture morphology again features a large number of bonding bridges and caves between the sand grains. Fig. 4(b) also shows bare sand grains on the fracture surface, but the fracture surface is less smooth and there are more dimples compared to Fig. 3(b). Figure 4(c) reveals a compact coating with small lamellar structures and tiny pores covering the sand grain, and Fig. 4(d) shows a crack that occurs on a bonding bridge between sand grains with an arc transition.

Figure 5 shows representative SEM micrographs of the fracture morphology of the core with 3wt.% kaolin. Once more, the

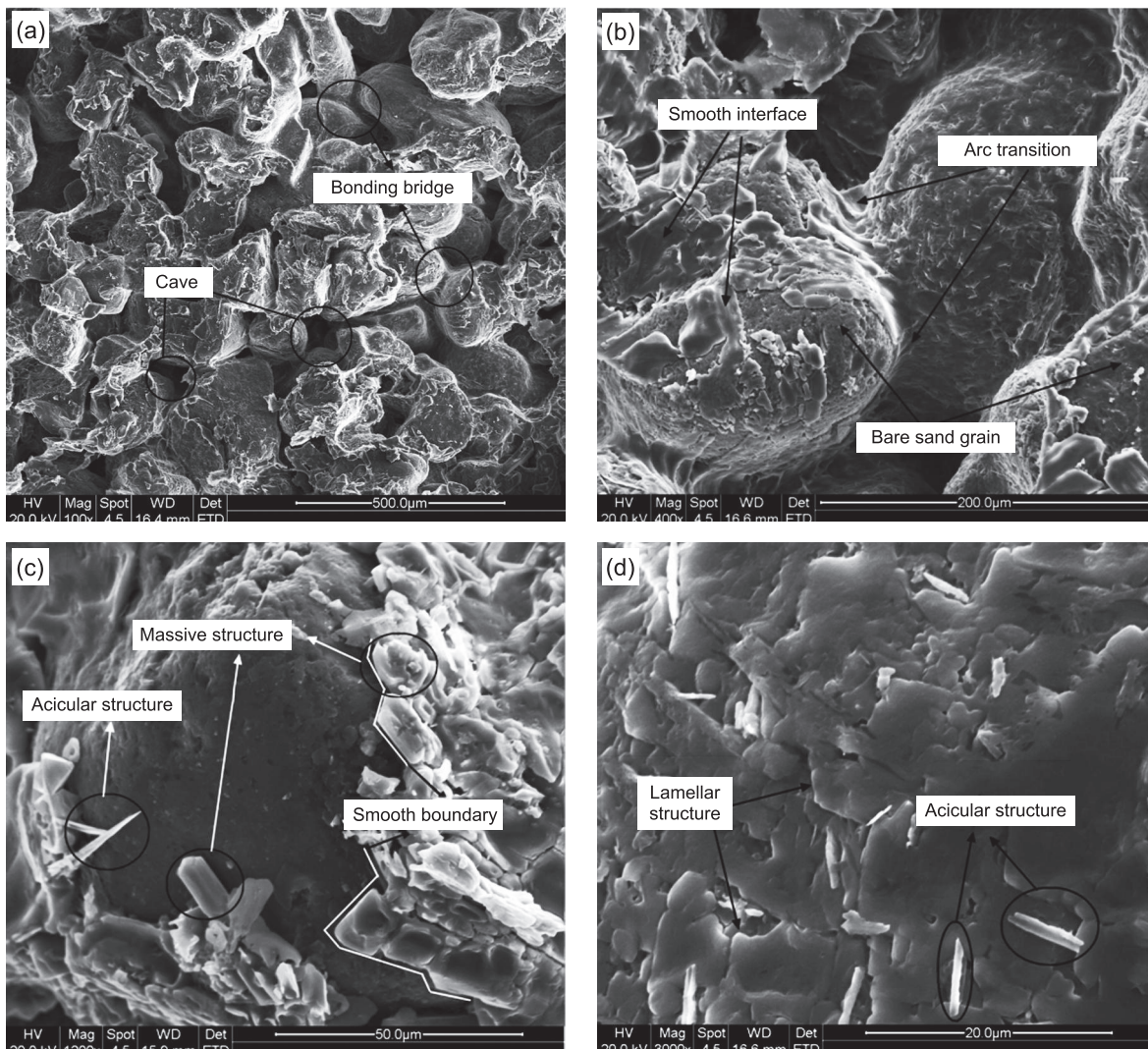


Fig. 3: Fracture morphology of core with 0wt.% kaolin

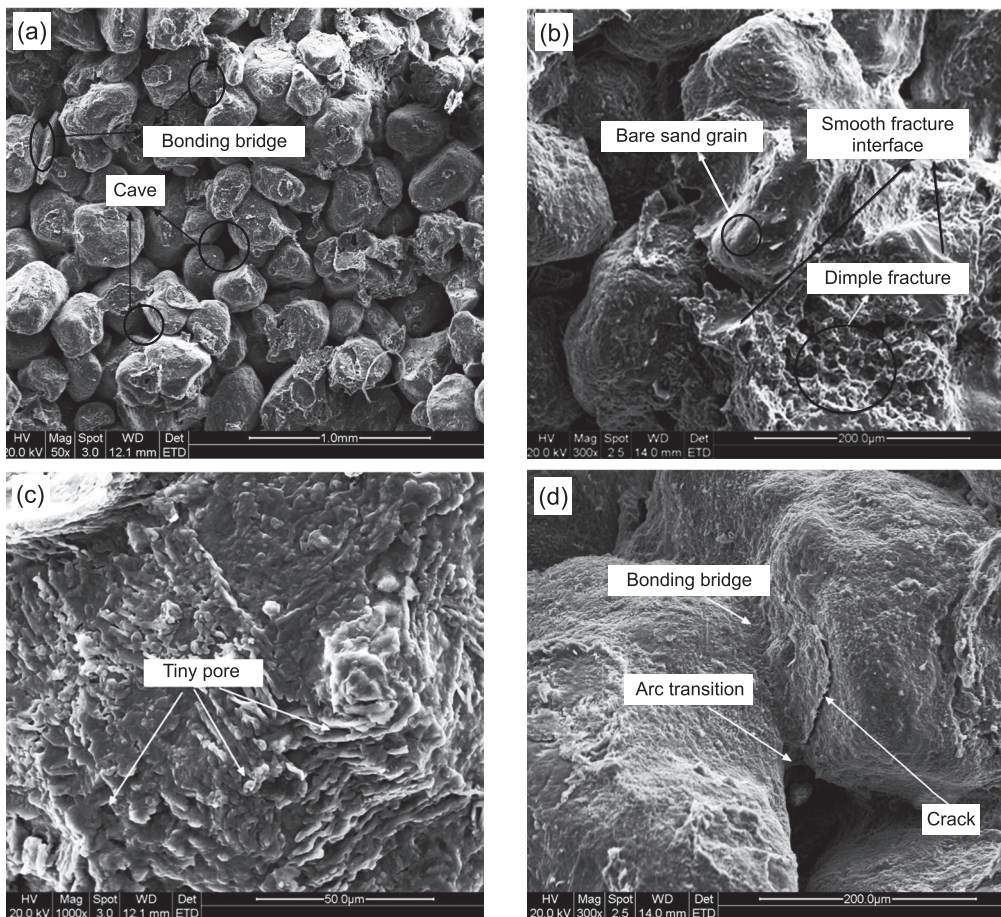


Fig. 4: Fracture morphology of core with 1wt.% kaolin

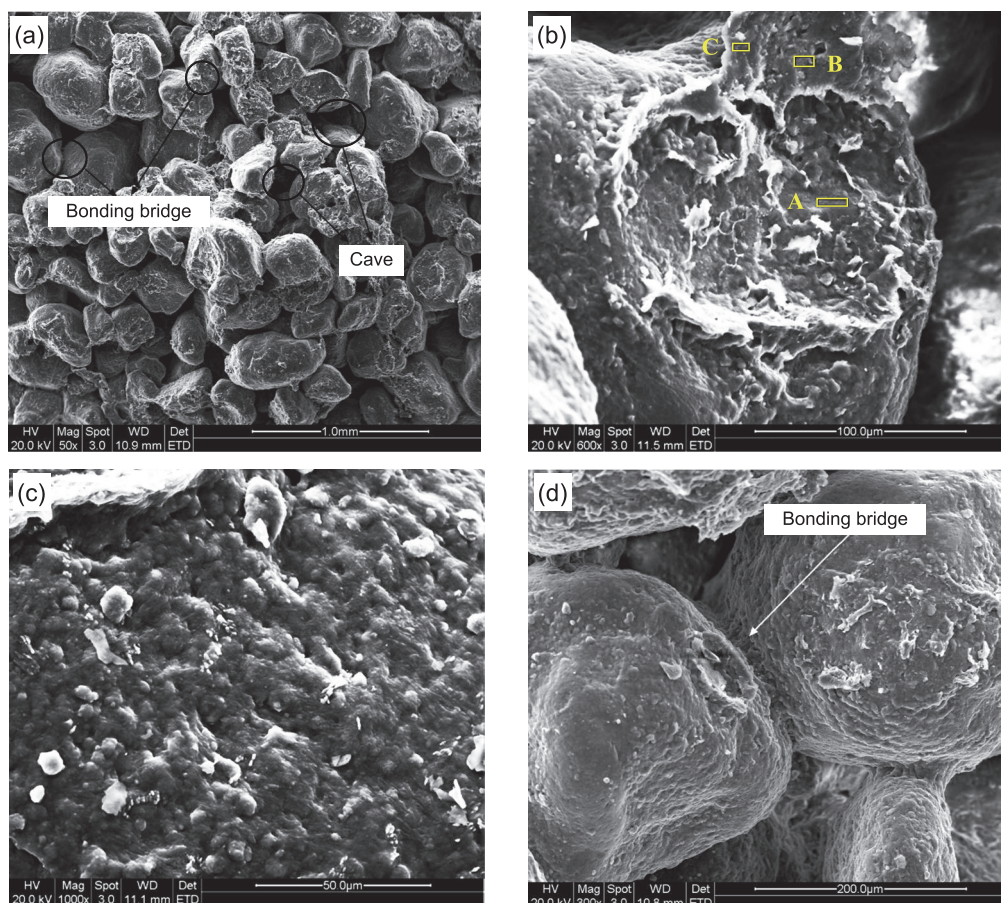


Fig. 5: Fracture morphology of core with 3wt.% kaolin

fracture morphology features a large number of bonding bridges and caves in Fig. 5(a). Figure 5(b) shows fracture phenomena with the shape of a trumpet, and a necking phenomenon that occurs on the binder covering the sand grain. Figure 5(c) reveals the microstructure of the binder. Its surface is smooth and compact and does not feature tiny pores. Figure 5(d) displays a bonding bridge between sand grains with an arc transition.

Figure 6 is the energy spectra recorded for different areas of the fracture surface shown in Fig. 5(b), which was obtained for the core with 3wt.% kaolin. As shown in Fig. 6, significant differences in the elemental composition were found for the different areas. For area A, silicon and oxygen are the main elements, with an atomic percentage of 31.45at.% and 47.31at.%, respectively. Carbon (19.22at.%) and other trace elements were found as well. Compared with area A, a lower amount of silicon and oxygen was detected for area B, with

atomic percentages of 13.07at.% and 36.00at.%, respectively, whereas the amount of potassium is significantly higher (23.89at.%). At the same time, the amounts of carbon, aluminum, magnesium and iron are slightly higher as well. Compared with area A and area B, the concentrations of silicon (7.71at.%) and oxygen (29.62at.%) in area C are lower, while those of potassium (26.56 at%) and carbon (32.08 at%) are slightly higher. The contents of aluminum, magnesium and iron are lower compared with area B, and higher compared with area A.

2.4 Gas evolution and collapsibility of WSCs

Figure 7 shows the influence of kaolin on the gas evolution. The gas evolution of the cores is relatively low and increases generally with the addition of kaolin. Specifically, the gas evolution of the core with 3wt.% kaolin is $9.5 \text{ mL}\cdot\text{g}^{-1}$, indicating that the core is qualified for casting process.

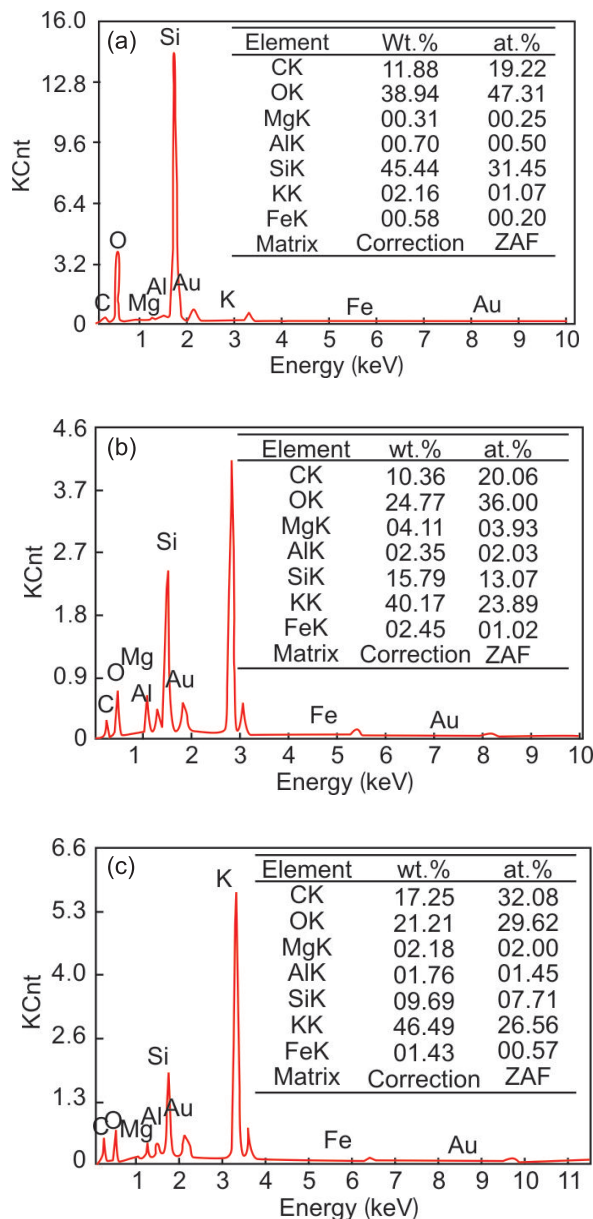


Fig. 6: Energy spectra obtained from different fracture areas of cores with 3wt.% kaolin in Fig. 5(b): (a) area A; (b) area B; (c) area C

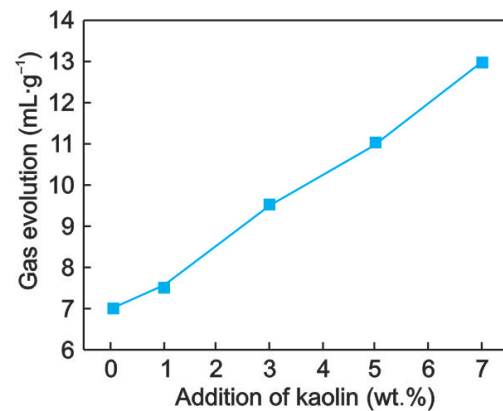


Fig. 7: Effect of kaolin on gas evolution of WSCs

In order to evaluate the collapsibility of the water-soluble cores, specimens ($\phi 50 \text{ mm} \times 50 \text{ mm}$) were prepared with the same compounds and under the same process parameters, and then baked at $700 \pm 5 \text{ }^\circ\text{C}$ for 10 min. After cooling down to about $200 \text{ }^\circ\text{C}$, the baked specimens were put into the water at room temperature. The results show that all the cores collapsed in a minute. It is obvious that the addition of kaolin has no significant effect on collapsibility of water-soluble cores. In conclusion, the water-soluble potassium carbonate sand core has properties of excellent collapsibility and low gas evolution, which makes it suitable for producing castings with complex cavities and crooked channels. However, it is confined to cast low melting metals and their alloys because of the low melting point of the potassium carbonate ($891 \text{ }^\circ\text{C}$).

3 Discussion

When the WSC (fabricated with the inorganic solution used as binder and the silica used as refractory material) was heated during the preparation process, the water in the inorganic salt solution evaporated quickly, and the solution changed to a saturated solution and eventually a supersaturated solution. Meanwhile, the inorganic salt nucleated and the salt crystallites grew quickly. Then, the inorganic salt crystallized from the

solution formed bonding bridges between the sand grains, acting as binder. As shown in Fig. 3, when the kaolin weight percentage was 0wt.%, inorganic salt crystals were found covering the surface of the sand grains, including massive crystals, lamellar crystals and acicular crystals, whose interface bonding strengths were low. When the core broke, cracks formed at the weak interface, resulting in the low tensile strength of the core.

When kaolin was added to the core, the crystal morphology of the inorganic salt and the fracture mechanism of the core were changed. On the one hand, kaolin changed the crystal morphology of the inorganic salt, from the large lamellar, massive crystals and small acicular crystals to the small and compact crystals with a large number of tiny pores, and eventually to the smooth and compact structure without any tiny pores. It is believed that the participation of kaolin leads to a heterogeneous nucleation, which would explain the observed phenomena. Because the main components of kaolin are SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , K_2O and Na_2O , and the main component of silica is SiO_2 , the contents of Al, Mg and Fe can be used to verify the existence of kaolin using the Si content as a reference. Similarly, the contents of C and K can be used to verify the existence of K_2CO_3 , and those of Si and O can be used as a reference to decide whether or not the test point is at the surface of a sand grain. Therefore, it can be concluded that area A is the surface of a sand grain, the components of area B and C are kaolin and potassium carbonate, and the kaolin content in area B is higher than that of C. Because the surface of the sand grains only consists of K_2CO_3 and kaolin, and the kaolin content of the surface layer is low, the concentration of K_2CO_3 in the surface layer must be high. Thus, it can be concluded that kaolin leads to a heterogeneous nucleation process. As a result, the grain size was refined, and the crystal morphology of the inorganic salt changed.

On the other hand, kaolin changed the fracture mechanism of the core. When the core contained 0wt.% kaolin, the core fracture occurred at the interface of the layers, and the cracks grew along the boundary of the massive structure. At the place of fracture, the surface of the sand was exposed, and the necking phenomenon could not be found [Fig. 3(b) and 3(c)], suggesting that adhesive fracture was the main fracture mechanism. For the core with 1wt.% kaolin, the bare sand grain surface and a smooth fracture interface were found at the place of fracture, but a honeycomb-like fracture interface was observed as well, as shown in Fig. 4(b), suggesting that both adhesive and cohesive fractures were the main fracture mechanisms. For the core with 3wt.% kaolin, fracture phenomena with the shape of a trumpet and an evident necking phenomenon were observed, suggesting that only cohesive fracture was the main fracture mechanism.

In conclusion, with increasing kaolin weight percentage, the grains of the inorganic salt crystals were gradually refined, and the fracture mechanism changed from adhesive fracture to cohesive fracture, resulting in an increase in tensile strength. However, as the kaolin content was increased even further, the number of bonding bridges was found to decrease, and therefore, the tensile strength declined.

Potassium carbonate absorbs moisture from the air when the relative humidity of the environment is above the critical value^[11], which leads to the absorption of moisture by the core. For the core without kaolin, potassium carbonate covered the surface of the sand grains, and the moisture absorption occurred from the outside to the inside. The initial contact area of the inorganic salt with air was large, and therefore, the hygroscopic rate of the core was high during the initial phase. With the extension of the exposure time, the humidity absorption rate of the core decreased because of the deliquescence of the inorganic salt on the surface layer and the decrease of the curvature radius of the crystallized layer covering the sand grains. This resulted in a gradual decrease of the hygroscopic rate when the exposure time was increased from 0 to 4 h, 4 to 8 h and 8 to 12 h, respectively. For cores containing kaolin, the core continued to absorb humidity only if the moisture in the environment could bypass the kaolin particles in the inorganic salt. This contributed to the relatively high stored strength and the evident decrease of the hygroscopic rate of the cores after adding a small amount of kaolin. The humidity resistance and the stored strength of the core with 1wt.% kaolin was lower compared to the core with 3wt.% because of the lamellar structure with tiny pores observed for the core with 1wt.% and the smooth and compact structure without tiny pores observed for the core with 3wt.%. As the amount of kaolin was further increased, the incrustation of the crystallized layer covering the sand grains resulted in an increase of the contact area of the inorganic salt with air, which led to an increase of the hygroscopic rate when the kaolin weight percentage exceeded 3wt.%.

4 Conclusions

(1) Kaolin can increase the tensile strength and humidity resistance of the water-soluble potassium carbonate sand core, achieving the values of 1.50 MPa and 0.559% (stored for 8 h), respectively, when 3wt.% kaolin was added. As compared with the core without kaolin, the tensile strength could be increased by a factor of 2, and the hygroscopic rate could be decreased by 14%.

(2) Kaolin changes the crystal morphology of the inorganic salt and the fracture mechanism of the core, which contributes to the increase of the tensile strength and the humidity resistance. Without the participation of kaolin, the sand grains are covered with a lot of large lamellar, massive crystals and small acicular crystals and the adhesive fracture appears to be the main fracture mechanism. When the addition of kaolin increases from 1wt.% to 3wt.%, the coating layer of the sand grains changes from an small lamellar structure with tiny pores to a smooth and compact structure without tiny pores, and the main fracture mechanism changes from a adhesive and cohesive fracture mechanism to a cohesive fracture mechanism.

(3) The water-soluble core has the low gas evolution (9.5 $\text{mL}\cdot\text{g}^{-1}$ with 3wt.% kaolin addition) and excellent collapsibility, which makes it suitable for casting low melting metal with complex cavities and crooked channels.

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This research was financially supported by the National Natural Science Foundation of China (No. 51405002).
