

Original Research Article

Performance of water-soluble composite sulfate sand core for magnesium alloy castings



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ABSTRACT

A novel water-soluble sand core hardened by twice microwave heating was fabricated using composite solution of magnesium sulfate and sodium sulfate as a binder. The tensile strength, water absorption rate, gas evolution and water-soluble rate of the water-soluble composite sulfate sand core (WCSSC) were studied. The micro-morphology of WCSSC was observed by scanning electron microscope (SEM). The results show that tensile strength of WCSSC is 1.2 MPa, and the 4 h storage tensile strength exceeds 1 MPa, and also the water-soluble rate is about 42.65 kg/(min m²), which indicates that WCSSC possesses good moisture resistance and water-soluble collapsibility. The microscopic analysis demonstrates that there are some micro-cracks or holes in the bonding bridge that decreases the strength of WCSSC after being put in humidistat for several hours.

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1. Introduction

A lot of high-strength and low-density magnesium [1] or aluminum [2] alloys are applied in the new generation aviation castings [3], and the structures of casting parts are developed toward to integration, hollow thin wall and complication [4], therefore it makes the casting parts and the foundry sand cores become very complex, and the intracavity pores of casting parts are difficult to be clean [5]. Most of complex thinwalled magnesium alloy castings often possess complex cavities or thin, curved, long pore structures [6], which makes the foundry sand core very complicated, and even an integral sand core is usually composed of several sand cores [7]. But magnesium alloy possesses a low pouring temperature (700–760 $^{\circ}$ C) and small hot-melt content, and so the sand core is difficult to be collapsed by solidification latent heat, which

increases cleaning work after casting, and thereby reduces the production efficiency of the castings [8]. The water-soluble sand core can solve the above problem with outstanding casting collapsibility, high strength, low gas evolution and green environmental protection [9,10]. The water-soluble sand core can greatly improve the production efficiency of complex castings, and has greater prospects in forming magnesium alloy castings with complex cavity structures [11,12]. In the previous research papers, there were many binders used to form the water-soluble sand core, such as sodium hydrogen phosphate [13], potassium carbonate [9,14], plaster [12], magnesium sulfate [15] and so on. Generally, the curing process heated in industrial furnace or hot box was used to form the water-soluble sand core because the aqueous solution of salt used as binder [9]. However, the above conventional heating curing process has some shortcoming, such as low efficiency, high energy consumption, easy

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stratified and so on [7]. Recently, microwave heating process has been successfully used in food, automobile, rubber and other processing industries [16]. Microwave heating is a volumetric heating mode with advantages of uniform heating, high efficiency and environmentally friendly [17], and it can fully develop inorganic binder bonding potential and reduce the binder content [18,19]. Therefore, the water-soluble sand core hardened by microwave heating process has an important application prospect, and it can greatly improve the production efficiency of thin-walled complex magnesium alloy castings [20].

In the paper, the water-soluble composite sulfate sand core was prepared by twice microwave heating process. The tensile strength, water absorption rate, gas evolution and watersoluble rate of the sand core were investigated. ESEM was used to investigate the micro-morphology of WCSSC.

2. Experimental

2.1. Materials and equipment

The raw sand was Dalin scrubbed silica sand with 50/100 meshes. The binder consists of industrial magnesium sulfate (MgSO₄·7H₂O), analytical pure sodium sulfate (Na₂SO₄·10H₂O) and water. The microwave heating device was the type DWIM-2F microwave oven with the power level 1400 W. The sand mixer was the type SHY blade-type sand mixer. The sand samples were fabricated manually using a standard "8" font wood mold with the dimension of 22.36 mm \times 22.36 mm \times 66 mm and a cylindrical wood mold with the dimension of Φ 30 mm \times 30 mm. Other test equipment included the type SWG lever-type universal strength testing machine, the type JA5003N electronic balance with the accuracy of 0.001 g, the type GET-III intelligent gas evolution tester, the rotating-screen surface performance tester and Quanta 200 environmental scanning electron microscope (ESEM).

2.2. Preparation

2.2.1. Composite binder preparation

Firstly, a certain mass fraction of magnesium sulfate aqueous solution was prepared. Secondly, 0.3–1% sodium sulfate crystals (Na_2SO_4 ·10H₂O) were added. Finally, the solid–liquid mixture was heated to about 70 °C, meanwhile stirring the mixture until a transparent solution obtained, then the composite binder was prepared.

2.2.2. The sand samples preparation

The raw sand and the composite binder were mixed uniformly with a certain proportion in the sand mixer about 90 s, and then the mixed sand was poured into the wood mold, finally, the sand samples were hardened by twice microwave heating process.

2.2.3. Twice microwave heating process

The power level of microwave oven was 1400 W. First, the sand samples and wood mold were heated in the microwave oven for 60 s to obtain the stripping strength of the sand samples. Next, the two parts were taken out from the microwave oven, and the sand samples were demoulded from the wood pattern. Then, in order to obtain the final strength, the sand samples without the wood mold were heated for a certain time for the second time. At last, the hardened sand samples were obtained.

2.3. Properties test

Room temperature strength (σ_b) is the tensile strength of the samples cooled to the room temperature after microwave heating. Storage strength (σ_s) is the tensile strength of the samples after being put into a humidistat (relative humidity at 98–100%) for a certain period of time. Gas evolution (G) is tested by the type GET-III intelligent gas evolution tester. Water absorption rate (Ψ) can be calculated by the equation of Ψ = $(M_1 - M_0)/M_0$, where M_0 is the original weight (the sample cooled to the room temperature was measured) of a sand sample, M₁ is the weight of the sample after being put into a humidistat for a certain period of time. Surface stability (φ) is tested as follows: the original weight (M) was measured after a sample was cooled to the room temperature, the final weight (M₂) was measured after the sample was put into the rotatingscreen surface performance tester for 1 min, then the surface stability was obtained by $\varphi = M_2/M \times 100\%$. Water-soluble rate (K) can be calculated by the equation of $K = m/(S \times t)$ [10], where *m* is the weight of a sample, S is the surface area of the sample, t is the dissolution time of the sample (at 750 °C for 10 min, then cooled to the room temperature) in water. Each result was the average value of five measurements. Microwave heating time is represented by t_m.

3. Results and discussion

3.1. Performance comparison of two simple substance sulfate water-soluble sand cores

Fig. 1 shows the performance comparison of the water-soluble $MgSO_4$ sand core and the water-soluble Na_2SO_4 sand core when the mass fraction and addition amount of the simple substance sulfate binder are 30% and 5% (by weight of the raw sand, the same as below), respectively. The storage strength, water absorption rate, gas evolution and other performances are tested with the maximum room temperature strength of the same samples, the same as below.

Fig. 1(a) reveals that when the microwave heating time prolongs, the room temperature strength of the sand samples firstly increases and then decreases, the room temperature strength of water-soluble MgSO₄ sand core reaches maximum 0.7 MPa with the heating time of 90 s, while the water-soluble Na₂SO₄ sand core reaches maximum 0.11 MPa with the heating time of 100 s. The strength of the sand samples is determined by binder quantity and bonding strength of different bonding between grains of sand, and sulfate hydrates by crystallization forms bonding bridges. As the microwave heating time increases, the heating temperature of the samples rises, and sulfate hydrates firstly crystallizes and precipitates, and then gradually dehydrates, and finally the tensile strength of the samples reaches peak value when



Fig. 1 – Performance comparison of water-soluble MgSO₄ sand core and water-soluble Na₂SO₄ sand core. (a) Room temperature strength, (b) storage strength, (c) water absorption rate and (d) gas evolution.

sulfate hydrates possess the highest bonding strength. If the heating temperature continues to rise, then sulfate hydrates continues to dehydrate, finally the bonding bridge with higher bonding strength will emerge hole defects and be destroyed, which decreases the strength of the samples. Because the bonding bridge formed by $MgSO_4$ hydrate has the higher bonding strength compared with Na_2SO_4 hydrate, the watersoluble $MgSO_4$ sand core has the higher room temperature strength.

Fig. 1(b) and (c) show that when the storage time prolongs, the water absorption rate of the samples increases and the storage strength decreases, and the reason is that sulfate binder absorbs water which breaks bonding bridges and then decreases the strength of the samples. Compared to the watersoluble MgSO₄ sand core, the water-soluble Na₂SO₄ sand core has a lower water absorption rate during the early storage time, but a stronger capable of absorbing moisture.

Fig. 1(d) shows that the gas evolution of the water-soluble $MgSO_4$ sand core is higher than the water-soluble Na_2SO_4 sand core. The heating temperature of the samples during being tested is 850 °C, and sulfate hydrates playing a function of bonding can dehydrate gradually until it becomes anhydrous sulfate, and then the steam formed by sulfate crystal water is the main source of gas. After the samples hardened by

microwave heating, the number of crystal water carried by Na_2SO_4 is less than MgSO₄, and so the water-soluble MgSO₄ sand core has a high gas evolution.

The different performances of the two water-soluble sand cores are compared comprehensively, including room temperature strength, storage strength, water absorption rate and gas evolution, the water-soluble MgSO₄ sand core has the higher strength while the water-soluble Na₂SO₄ sand core has the lower water absorption rate and gas evolution, but sodium sulfate has a stronger capable of absorbing moisture. Thus, single MgSO₄ or Na₂SO₄ used as binder cannot prepare the excellent comprehensive properties of the water-soluble sand core. Therefore, the water-soluble composite sulfate sand core is investigated using MgSO₄ as major ingredient and Na₂SO₄ as auxiliary ingredient.

3.2. Effect of the composite sulfate binder on the performance of WCSSC

3.2.1. Effect of the mass fraction of magnesium sulfate solution

Fig. 2 shows the effect of different mass fraction (20%, 25%, 30%) of magnesium sulfate solution on the performances of WCSSC, when the addition amount of magnesium sulfate



Fig. 2 – Effects of MgSO₄ solution mass fraction on the performance of WCSSC. (a) Room temperature strength, (b) storage strength, (c) water absorption rate and (d) gas evolution.

solution and sodium sulfate decahydrate crystals are 5% and 0.5%, respectively. The symbol of Max in the figures is the maximum value of the room temperature strength, the same as below.

Fig. 2(a) reveals that when the microwave heating time prolongs, the room temperature strength of the sand samples firstly increases and then decreases. As the mass fraction of magnesium sulfate solution increases, the maximum of the room temperature strength of the sand samples increases, and the reason is that when the addition amount of composite binder keeps constant, the larger mass fraction, and the more MgSO₄ in unit volume, then the more bonding bridge formed by crystallization, finally the greater strength of the samples.

Fig. 2(b) shows that the storage strength of the samples dramatically reduces as the storage time prolongs. When the storage time is constant, the larger mass fraction of magnesium sulfate solution, and the greater storage strength of the samples. This is because the water-soluble sand core can absorb water, but the larger mass fraction, the more bonding bridge preserved well in unit volume.

Fig. 2(c) shows that the mass fraction of magnesium sulfate solution has little effect on the water absorption rate. Fig. 2(d)

shows that the larger mass fraction, and the greater gas evolution of the samples, which is caused by the increasing $MgSO_4$ hydrate in composite binder.

From Fig. 1 with Fig. 2, it can be seen that compared to the water-soluble MgSO₄ sand core, WCSSC (the mass fraction of magnesium sulfate solution is 30%) has a better comprehensive performance. There is a significant increase from 0.7 MPa to 1.22 MPa at the room temperature strength, and the reason is that the bonding bridge, which is formed by composite binder crystallization, contains complex salt composition, $Na_2Mg(SO_4)_2 \cdot 4H_2O$ [21], and the complex salt can obviously enhance the bonding strength of the MgSO₄ bonding bridge. Meanwhile, Na₂SO₄ added to composite binder also increases the number of bonding bridge. The storage strength of composite sulfate sand core has been greatly increased, on the one hand, because the room temperature strength increases greatly; on the other hand, Na₂SO₄ has a strong capable of absorbing moisture, which can slow down the water absorption of MgSO₄, thus WCSSC still has a greater strength in a long period of time. Water absorption rate of WCSSC changes little. Due to the increased number of crystal water with Na₂SO₄ adding to the composite binder, gas evolution of WCSSC increases.

The larger mass fraction of magnesium sulfate solution, and the greater room temperature strength and storage strength of the water-soluble composite sulfate sand core, but water absorption rate and gas evolution of the sand core have little change. Therefore, the mass fraction of magnesium sulfate solution of 30% in the composite sulfate binder should be selected for the future experiment.

3.2.2. Effect of the addition amount of magnesium sulfate solution

Fig. 3 shows the effect of the different addition amount (4%, 5%, 6%) of magnesium sulfate solution on the performances of WCSSC, when the mass fraction of magnesium sulfate solution and the addition amount of sodium sulfate decahydrate crystals are 30% and 0.5%, respectively.

Fig. 3(a) reveals that when the microwave heating time prolongs, the room temperature strength of the sand samples firstly increases and then decreases. As the addition amount of magnesium sulfate solution increases, the maximum of the room temperature strength of the sand samples increases firstly increases and then decreases, and the addition amount of 5% has the greatest strength. The more water content in the composite binder solution, then the longer microwave heating time to harden sand samples and the higher heating temperature of sand samples, so when the addition amount is

5%, high strength of bonding bridge can be formed at the heating temperature of the hardened sand samples. If the addition amount continues to increase, the heating temperature is too high when the samples are hardened, and sulfate hydrates are dehydrated excessively, then high strength of the bonding bridges are destroyed, which reduces the strength of the samples.

Fig. 3(b) shows that when the storage time is constant, the larger addition amount of magnesium sulfate solution, and the greater storage strength of the samples, and the reason is that bonding bridges are destroyed during stored in air due to water absorption, but the larger addition amount, and the more bonding bridge preserved well, and then the greater strength of the samples. Compared to the room temperature strength, the 2 h storage strength of the samples are heated by microwave oven, there will be part of sulfate hydrate which contain little crystal water leading to the low bonding strength of bonding bridges forming, but a period of storage time later, the part of sulfate hydrate by water absorption will become high bonding strength of bonding bridges are shown and then the strength of samples increases as well.

Fig. 3(c) shows that the addition amount of magnesium sulfate solution has little effect on the water absorption rate. Fig. 3(d) shows that the larger addition amount, and the greater



Fig. 3 – Effects of MgSO₄ solution addition amount on the performance of WCSSC. (a) Room temperature strength, (b) storage strength, (c) water absorption rate and (d) gas evolution.

gas evolution of the samples, due to the increased ${\rm MgSO_4}$ hydrate in composite binder.

The larger addition amount of magnesium sulfate solution, and the greater storage strength and gas evolution of the water-soluble composite sulfate sand core, but water absorption rate of the sand core has little change, and the samples have the greatest room temperature strength with the addition amount of 5%. Therefore, the addition amount of magnesium sulfate solution of 5% in the composite sulfate binder should be selected.

3.2.3. Effect of the addition amount of sodium sulfate decahydrate crystals

Fig. 4 shows the effect of the different addition amount (0.3%, 0.5%, 1.0%) of sodium sulfate decahydrate crystals on the performances of WCSSC when the mass fraction and addition amount of magnesium sulfate solution are 30% and 5%, respectively.

Fig. 4(a) indicates that when the microwave heating time prolongs, the room temperature strength of the sand samples firstly increases and then decreases. As the addition amount of sodium sulfate decahydrate crystals increases, the maximum of the room temperature strength of the sand samples increases, but the strength changes slightly in the late. This is because Na_2SO_4 being added to the composite binder increases, complex salt $Na_2Mg(SO)_2$ ·4H₂O formed by crystallization increases, thereby the bonding strength of bonding bridges is enhanced.

Fig. 4(b) shows that when the storage time is constant, as the addition amount of sodium sulfate decahydrate crystals increases, the storage strength generally increases firstly, and then keeps constant. The reason is that too much Na_2SO_4 can increase the water absorption of the sand samples, which results in the strength decreasing excessively.

Fig. 4(c) shows that when the storage time is constant, as the addition amount of sodium sulfate decahydrate crystals increases, the water absorption rate of sand samples increases slightly. Fig. 4(d) shows that the addition amount of sodium sulfate decahydrate crystals has little effect on the gas evolution of the samples.

The addition amount of sodium sulfate decahydrate crystals has little effect on the water absorption rate and gas evolution of the samples, and excessive addition amount do not greatly increase the room temperature strength and storage strength of the samples either. Therefore, the addition amount of sodium sulfate decahydrate crystals of 0.5% in the composite sulfate binder should be selected.



Fig. 4 – Effects of Na₂SO₄·10H₂O crystals addition amount on the performance of WCSSC. (a) Room temperature strength, (b) storage strength, (c) water absorption rate and (d) gas evolution.

Table 1 – Performance comparison of different water-soluble sulfate sand core.					
Sand core species	t _m /s	K/kg min $^{-1}$ m $^{-2}$	φ /%	$\sigma_{ m b}/{ m MPa}$	$\sigma_{ m s(4~h)}/ m MPa$
Water-soluble MgSO ₄ sand core	90	57.99	97.12	0.68	0.60
Water-soluble Na ₂ SO ₄ sand core	100	-	-	0.11	0
Water-soluble composite sulfate sand core	90	42.65	96.73	1.22	1.08

3.3. Surface stability and water-soluble rate of the watersoluble sulfate sand core

Surface stability can be used to characterize the surface strength of water-soluble sand core, and water-soluble rate can be used to characterize the solubility in water of water-soluble sand core. Table 1 illustrates the surface stability, water-soluble rate and tensile strength of different water-soluble sulfate sand core, including the water-soluble MgSO₄ sand core (the mass fraction and addition amount of solution are 30% and 5%, respectively, microwave heating time is 90 s), the water-soluble Na₂SO₄ sand core (the mass fraction and addition amount of solution are 30% and 5%, respectively, microwave heating time is 100 s) and WCSSC (the mass fraction and addition amount of MgSO₄ solution are 30% and 5%, respectively, addition amount of Na₂SO₄·10H₂O crystals is 0.5%, microwave heating time is 90 s).

Table 1 lists that the water-soluble sulfate sand core has a good surface stability with around 97%. After holding at 750 °C for 10 min, these sand cores can rapidly dissolve in still water. The water-soluble rate of WCSSC can reach 42.65 kg/(min m²), which proves that the water-soluble sand cores have outstanding water-soluble collapsibility.

Fig. 5 shows the water-soluble phenomenon of WCSSC in still water, it can be seen that WCSSC can completely dissolve. The principle of WCSSC dissolution in water is that the sulfate can be soluble, which leads to the bonding bridges dissolved in water.

The research shows that WCSSC possesses more excellent comprehensive performance, and it is also easy to be clean after casting. Therefore, it is suitable to form magnesium alloy castings with complex cavity structures, which can greatly reduce the time for cleaning up magnesium alloy castings after casting and improve the production efficiency of magnesium alloy castings with complicated cavities.

3.4. Micro-morphology analysis of the water-soluble composite sulfate sand core

Fig. 6 shows the micro-morphology of bonding bridge of the water-soluble composite sulfate sand core, and Fig. 7 shows the fracture morphology of bonding bridge.

It can be seen from Fig. 6(a) that the bonding bridge between grains of sand before moisture absorption is smooth, compact and without defects. Therefore, bonding strength of the bonding bridge is great, and then the tensile strength of sand samples is also high. Fig. 6(b) shows that after moisture absorption (put in the humidistat for 4 h), micro-holes or micro-cracks appear on the bonding bridge. This is because that the composite binder absorbs water, and then the crystal water of sulfate hydrate increases even sulfate hydrate dissolves, which can lead to the bonding strength of bonding bridge decreasing or holes and cracks appearing due to partially dissolving. Therefore, bonding strength of the bonding bridge decreases, and then the tensile strength of sand samples also declines.

It can be seen from Fig. 7 that before moisture absorption, the surface of bonging bridge is smooth and compact, and there are small cracks within the bonding bridge, which is caused by the binder crystal and dehydration. After moisture absorption, small holes appear within the bonding bridge, and small cracks extend to the surface and its number increase as well. Therefore, the binder absorbing water is the main reason for breaking the bonding bridge, and decreases the strength.

3.5. Practical casting test

The magnesium alloy practical casting test was carried out for the further study on the water-soluble collapsibility of WCSSC after casting. WCSSC (the mass fraction and addition amount of MgSO₄ solution are 30% and 5%, respectively, the addition



Fig. 5 – The water-soluble phenomenon of WCSSC (a) 0 s, (b) 5 s and (c) 10 s in water.



Fig. 6 - The morphology of bonding bridge of WCSSC (a) before (b) after moisture absorption.



Fig. 7 - The morphology of fracture of WCSSC (a) before (b) after moisture absorption.



Fig. 8 – The water-soluble cleaning effect pictures of the magnesium alloy castings after casting. (a) Before and (b) after water-soluble cleaning.

amount of Na₂SO₄·10H₂O crystals is 0.5%) were prepared by twice microwave heating process with the heating time of 90 s. The magnesium alloy is AZ91D, and the pouring temperature is 730 °C. Fig. 8 shows the water-soluble cleaning effect of magnesium alloy castings after casting.

The test results reveal that after pouring completed, the sand cores still maintain the original shape, which indicates that the sand cores can sustain the impact of alloy liquid and can be used for casting forming of castings with intracavity. When the magnesium alloy castings with sand cores were put into stationary water, the sand cores could be self-collapsing water-soluble within 15 s. The intracavity surface of magnesium alloy castings after water-soluble cleaning is smooth, and there is no obvious metal penetration, chemical scab and other defects. Therefore, WCSSC has an excellent watersoluble collapsibility, and also does not react with the magnesium alloy melt during casting forming.

4. Conclusion

 The water-soluble composite sulfate sand core prepared by twice microwave heating technology possesses a better comprehensive performance with room temperature strength of 1.2 MPa, 4 h storage strength above 1 MPa. In addition, the sand core possesses a lower water absorption rate and gas evolution while it has a high surface stability at around 97%.

- (2) The water-soluble composite sulfate sand core prepared by twice microwave heating technology possesses outstanding water-soluble collapsibility after casting. The watersoluble sand core can rapidly dissolve in still water, and its water-soluble rate can reach 42.65 kg/(min m²), which greatly reduces the difficulty of cleaning work of castings after casting and improve the production efficiency of complex castings.
- (3) The microscopic analysis indicates that the composite sulfate binder absorbs water and then causes that bonding bridges appear holes or cracks that decreases the strength of water-soluble composite sulfate sand core.
- (4) The magnesium alloy castings with intracavity formed by WCSSC can be cleaned rapidly by water-soluble after casting. The intracavity surface of castings is smooth, and there are no obvious surface defects as well.

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