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In-situ Formation of $MgAl_2O_4$: A Method of Tailoring Microstructure and Properties for Development of High-performance Refractories

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Abstract

The *in-situ* formation mechanism of $MgAl_2O_4$ was introduced, focusing on the formation process by solid phase reaction and gas phase reaction as well as the phenomenon of secondary spinelization. The influencing factors of the *in-situ* $MgAl_2O_4$ formation and its effect on the microstructure and the properties of materials were systematically summarized for the Al_2O_3–MgO–$MgAl_2O_4$ system and the carbon–containing refractories systems. It was pointed out that the *in-situ* formation of $MgAl_2O_4$, including secondary spinelization, can regulate the microstructure and the service performance of materials. Its expansion effect can not only offset the shrinkage caused by sintering to improve the corrosion resistance of refractories, but also seriously restrict the reliability of functional refractories. The composition, the particle size, the atmosphere, and the temperature are important factors affecting the *in-situ* formation of $MgAl_2O_4$. In the carbon-containing materials systems, the solid–solid reaction and the gas–solid reaction coexist to produce $MgAl_2O_4$, which provides an effective way to further regulate the microstructure and the properties of materials through the reaction process.

Key words: $MgAl_2O_4$; *in-situ*; spinalization; gas phase; secondary spinalization; high temperature

1 Introduction

$MgAl_2O_4$ is the only binary compound in the MgO–Al_2O_3 system with cubic crystal system structure, which is widely used as refractories because of its high melting point (2 135 °C), stable chemical properties, low thermal expansion coefficient, low thermal conductivity, good thermal shock resistance and good slag corrosion resistance, such as MgO–Al_2O_3 bricks, MgO spinel bricks, Al_2O_3–MgO castables, MgO–Al_2O_3–C bricks, and $MgAl_2O_4$–C stoppers[1–3]. In addition to its inherent properties, the *in-situ* formation of $MgAl_2O_4$ from MgO and Al_2O_3 during service can regulate the microstructure and the service performance of materials[3]. The spinelization at the composite interfaces of MgO–C materials and Al_2O_3–C materials also affects the quality stability of functional products for continuous casting during service[4]. In this paper, the *in-situ* formation mechanism of $MgAl_2O_4$ was introduced first, and then the influencing factors of *in-situ* formation and its influence on the microstructure and the properties of materials were analyzed based on the Al_2O_3–MgO–$MgAl_2O_4$ system and carbon-containing refractories system.

2 *In-situ* Formation Mechanism of $MgAl_2O_4$

2.1 Solid Phase Reaction

In general, $MgAl_2O_4$ is mainly *in-situ* formed by the solid phase reaction of Al_2O_3 and MgO[5–6]. According to the Wargner

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mechanism, as shown in Fig. 1. A $MgAl_2O_4$ layer is first formed in the region where Al_2O_3 and MgO contact, and then Al^{3+} and Mg^{2+} diffuse through the layer to the MgO–$MgAl_2O_4$ interface and Al_2O_3–$MgAl_2O_4$ interface, respectively. To maintain the electrovalent equilibrium, two Al^{3+} ions diffuse to the MgO–$MgAl_2O_4$ interface and three Mg^{2+} ions diffuse to the Al_2O_3–$MgAl_2O_4$ interface, forming one and three $MgAl_2O_4$ mdecules at the two interfaces. Thereby, as the reaction proceeds, $MgAl_2O_4$ is gradually generated at the sites of Al_2O_3 and MgO. However, due to the inconsistent diffusion rate of the two kinds of ions, a certain number of pores form (Kirkendall effect). The density of $MgAl_2O_4$ differs from that of Al_2O_3 and MgO, leading to a volume expansion of 8.1% and 16.7% or even 56% (calculated by different models) [6–7], which can increase the porosity, reduce the strength, deteriorate the corrosion resistance and affect the

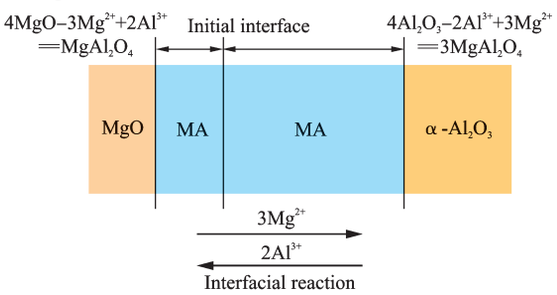

Fig. 1 Formation mechanism diagram of $MgAl_2O_4$ by solid phase reaction

stability of materials. Nevertheless, the expansion of refractories can integrate the refractory lining of high-temperature devices such as ladles into a whole, reducing the possibility of penetration and corrosion by molten steel/slag through the brick joints[8–10].

2.2 Gas Phase Reaction

In carbon-containing refractories, carbon hinders the contact between MgO and Al_2O_3 and limits the *in-situ* formation of $MgAl_2O_4$ by the Wargner mechanism. However, the partial pressure of Mg gas phase in the non-oxidizing atmosphere is high, which provides an alternative pathway for the *in-situ* production of $MgAl_2O_4$[11]. Firstly, MgO decomposes to generate Mg gas, and then it undergoes gas–solid reaction with Al_2O_3 or gas–gas reaction with aluminum-containing gas phase to produce $MgAl_2O_4$, as shown in equations 1–3. When both gas–gas and gas–solid reactions exist, more $MgAl_2O_4$ forms[12]. In addition, $MgAl_2O_4$ can also *in-situ* form in the gas phase in MgO–C materials added with metallic Al[13]. Yamaguchi[14] suggested that $MgAl_2O_4$ *in-situ* formed from Al gas, CO and MgO. Zhu, *et al.*[15] analyzed the formation process of hollow $MgAl_2O_4$ whiskers, as shown in Fig. 2, and concluded that Mg gas phase played an important role in the formation of hollow $MgAl_2O_4$ whiskers.

$$MgO(s)+C(s)=Mg(g)+CO(g) \quad (1)$$

$$Mg(g)+Al_2O_3(s)+CO(g)=MgAl_2O_4(s)+C(s) \quad (2)$$

$$Al_2O(g)+Mg(g)+3CO(g)=MgAl_2O_4(s)+3C(s) \quad (3)$$

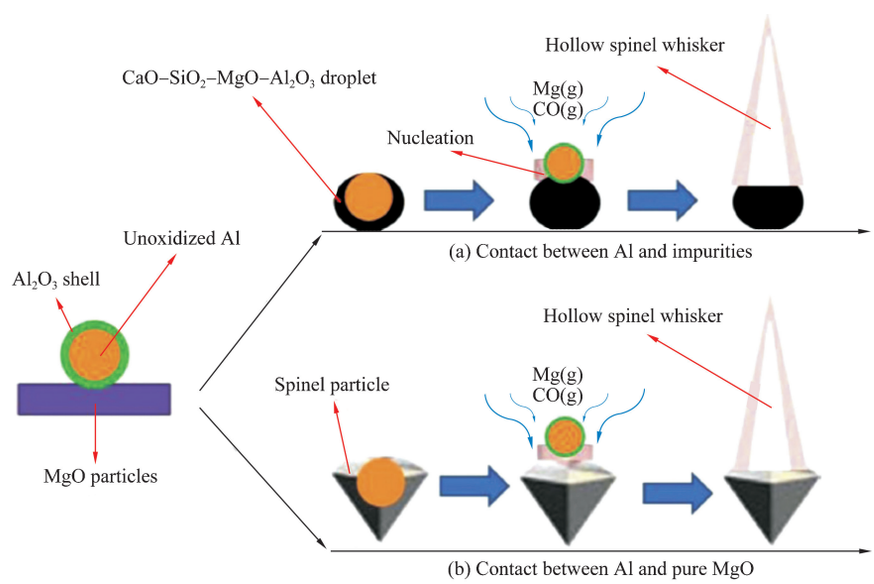

Fig. 2 Formation mechanism diagram of hollow $MgAl_2O_4$ whiskers [15]

2.3 Secondary Spinelization

There is a wide solid solution range for $MgAl_2O_4$ in the Al_2O_3–MgO system, and the solid solution amount of Al_2O_3 or MgO in $MgAl_2O_4$ gradually increases with the increase of the temperature. Therefore, solid solution occurs between $MgAl_2O_4$ with the theoretical composition and Al_2O_3 or MgO at high temperatures, which is known as secondary spinelization[16]. The solid solution of periclase in $MgAl_2O_4$ starts at 1 500 °C, reaching the maximum amount of 10 *mass*% at 1 995 °C. As the temperature decreases, the solid solution degree decreases, resulting in the complete desolution of MgO from $MgAl_2O_4$ at below 1 500 °C. The solid solution amount of Al_2O_3 in $MgAl_2O_4$ can be more than 20 *mass*%, which is more than that of MgO in $MgAl_2O_4$. After solid solution of Al_2O_3, $MgAl_2O_4$ has cationic lattice defects, which increase with the increase of the solid solution degree of Al_2O_3, thus affecting the activity and the reaction with slag. In addition, as Al_2O_3-rich spinel is thermodynamically unstable, corundum phase precipitates again after high temperature calcination, whose amount gradually increases with the number of

treatments[17–19], until it reaches the equilibrium state described in the phase diagram.

3 Al_2O_3–MgO–$MgAl_2O_4$ System

With two or three components of Al_2O_3, MgO or $MgAl_2O_4$, spinelization or secondary spinelization occurs at high temperatures, thus affecting the microstructure and the performance of refractories. With Al_2O_3 as the main component and an appropriate amount of MgO, Al_2O_3–MgO castables produce volume expansion during service, offsetting the shrinkage caused by sintering and other factors, which improves the slag penetration resistance of castables. The studies on the *in-situ* formation of $MgAl_2O_4$ in Al_2O_3–MgO castables showed that in addition to the temperature, the particle size, the purity, the crystalline morphology, and the Al_2O_3/MgO mass ratio are all important factors[8, 20–22] affecting the microstructure and the properties of materials. The smaller the particle size of MgO, the higher the reactivity of MgO and the more the *in-situ* formed $MgAl_2O_4$[9]. Coarse MgO brings cracks and large pores, which is beneficial to the thermal shock resistance, but not conducive to the improvement of the slag resistance. With different morphologies of Al_2O_3 and MgO, the spinalization degree of the fused MgO–tabular Al_2O_3 is the lightest, producing the smallest expansion; the spinalization degree of the sintered MgO–sintered Al_2O_3 is the most serious, producing the largest expansion[10]; and sintered MgO presents better effect than $MgCO_3$. The binders and the additives of Al_2O_3–MgO castables also affect the *in-situ* formation of $MgAl_2O_4$. For example, the addition of silica powder or the composites of silica powder and TiO_2 can balance the expansion[23] and improve the workability of castables. The *in-situ* formation of $MgAl_2O_4$ starts at 1 000–1 300 °C, which is closely related to the above influencing factors.

Generally, it is believed that the formation of $MgAl_2O_4$ is proportional to the square root of time under normal pressure; however, the effect of the pressure on the formation is rarely studied. Watson, *et al.*[24] investigated the growth rate of $MgAl_2O_4$ at the Al_2O_3–MgO interface under the condition of 1 200–2 000 °C and 1.0–4.0 GPa using a solid state piston cylinder apparatus and found that the reaction rate was log-linearly related to the temperature and the pressure. The higher the temperature and the lower the pressure, the higher the reaction rate. So, the external constraint condition imposes a great influence on the performance of Al_2O_3–MgO castables. Compared with those under the condition without external constraint, the number of pores and the permanent linear change of castables produced by spinelization decrease by 21.9% and 70.4%, respectively, and the slag penetration resistance index decreases from 18.2% to 9.2%, with an improvement close to 50%, under the condition with external constraint to simulate the actual service condition[25]. Most laboratory studies were conducted under unconstrained conditions where materials were free to expand and more pores formed due to the Kirkendall effect[6], which deteriorated the key service performance of materials, such as the corrosion resistance. Although the laboratory results of materials were poor, they presented good practical applications. Therefore, a proper evaluation method will yield twice the result with half the effort.

In the Al_2O_3–MgO–$MgAl_2O_4$ system, secondary spinelization also has an important effect on the microstructure and the properties of materials. In the Al_2O_3–$MgAl_2O_4$ system, the expansion caused by the solid solution of Al_2O_3 into $MgAl_2O_4$ at high temperatures can offset the shrinkage caused by sintering. The more the amount of $MgAl_2O_4$[26] and the smaller the particle size[27], the more obvious the spinelization effect. In addition, the solid solution of Al_2O_3 into $MgAl_2O_4$ can enhance the bonding degree of the matrix of Al_2O_3–$MgAl_2O_4$ castables, thus improving the creep resistance[26], the hot strength, the thermal shock resistance, *etc.*[28] In the MgO–$MgAl_2O_4$ system, the solid solution of MgO into $MgAl_2O_4$ at high temperatures is limited and the effect of secondary spinelization on the microstructure and the properties of materials is rarely reported.

4 Carbon-containing Refractories System

Al_2O_3–MgO–C refractories present good corrosion resistance and high mechanical strength, which are commonly used on the side walls and the bottom of ladles. Due to the formation of $MgAl_2O_4$, a continuous slight volume expansion occurs at the working surface of Al_2O_3–MgO–C bricks, counteracting the gaps created at the brick joints because of thermal cycling, which ensures the corrosion resistance of refractories. In addition, the formed $MgAl_2O_4$ has a high refractoriness and good corrosion resistance, which contributes to the corrosion resistance of furnace linings. However, for the refractories on the the sidewalls and at the bottom of ladles, it is proven that the expansion behavior is more important compared with the corrosion resistance. Unstable or excessive expansion can lead to spalling or accelerate corrosion[29].

It is also generally believed that the particle size, the purity, and the crystalline form of raw materials affect the *in-situ* formation of $MgAl_2O_4$ in Al_2O_3–MgO–C materials. Due to its higher sintering activity, sintered Al_2O_3 is more conducive to the *in-situ* formation of $MgAl_2O_4$ than fused Al_2O_3[30], and corundum with uniform impurity distribution is more likely to form $MgAl_2O_4$ than regular brown fused alumina[31]. The smaller the particle size of MgO, the higher the degree of spinelization, the more the amount of $MgAl_2O_4$, and the higher the Al_2O_3-rich degree of $MgAl_2O_4$. However, with a too large particle size, MgO cannot be completely converted into $MgAl_2O_4$ after high temperature heat-treatment[32–33]. For carbon-containing materials, the *in-situ* formation of $MgAl_2O_4$ starts at 950–1 300 °C, showing little difference with Al_2O_3–MgO castables.

The formation of $MgAl_2O_4$ can improve the ceramic bonding of MgO–C materials, increasing their corrosion resistance[14]. The temperature, the atmosphere and the carbon content are important factors affecting the microstructure of *in-situ* formed $MgAl_2O_4$ by gas phase reaction. In MgO–C materials with Al, the $MgAl_2O_4$ morphology is highly dependent on the heat treatment temperature. Octahedral $MgAl_2O_4$ particles form at lower heat treatment temperatures[15, 34], $MgAl_2O_4$ fibers and hollow $MgAl_2O_4$ fibers form at about 1 500 °C, and octahedral $MgAl_2O_4$ particles also form at 1 600 °C. N_2 is more favorable than Ar for the formation of $MgAl_2O_4$ fibers[35].

Hollow $MgAl_2O_4$ fibers form more easily in lower carbon-containing materials because of the larger contact area of Al and MgO[15].

To satisfy the requirement of clean steel production, low carbon refractories are one of the current hot spots for research[36], but they perform poor thermal shock resistance and slag penetration resistance. In terms of improving the slag resistance of low carbon MgO–C materials, certain attempts have been made based on the perspective of *in-situ* spinelization reaction. A certain amount of fine Al_2O_3 powder was introduced, so that the microstructure and the slag resistance of the materials were improved by the expansion characteristics of *in-situ* spinelization during service[13, 37]. $MgAl_2O_4$ can be *in-situ* formed in carbon-containing refractories not only by solid phase reaction of Al_2O_3 and MgO, but also by gas phase reaction. Changing the path of $MgAl_2O_4$ formation can regulate the microstructure and the properties of materials. Zheng Han[33] and Shang Xinlian[38] prepared carbon-coated Al_2O_3 powders by physical granulation and chemical deposition, and then added the powders into MgO–C materials to control the $MgAl_2O_4$ formation through gas–solid reaction, showing that the carbon-coated Al_2O_3 powder addition increased the formation temperature of $MgAl_2O_4$, reduced the volume expansion effect from spinelization, and effectively improved the bonding of aggregates and matrix, which provided an innovative method for the property and structural modulation of carbon-containing refractories.

Because of their good resistance to CaO corrosion, MgO–C refractories are often used as the key parts of functional refractories for continuous casting to cast calcium-treated steel, such as the head of monoblock stoppers and the wrist of submerged entry nozzles. Due to their poor thermal shock resistance, MgO–C refractories are generally used in combination with Al_2O_3–C refractories. During service, monoblock stoppers or submerged entry nozzles are prone to fracture, thus interrupting casting process and leading to production accidents[36]. Through analyzing the microstructure of the used materials, it is found that Mg near the interface between MgO–C and Al_2O_3–C refractories diffuses to Al_2O_3–C materials *in-situ* forming $MgAl_2O_4$, as shown in Fig. 3. The expansion effect from spinelization weakens the interface bonding, therefore, the functional refractories are easy to fail under the action of external forces[4]. To reduce the spinelization effect, $MgAl_2O_4$ powder was introduced into MgO–C materials, but it did not affect the diffusion of Mg gas phase to Al_2O_3–C materials, which still weakened the interface bonding[4].

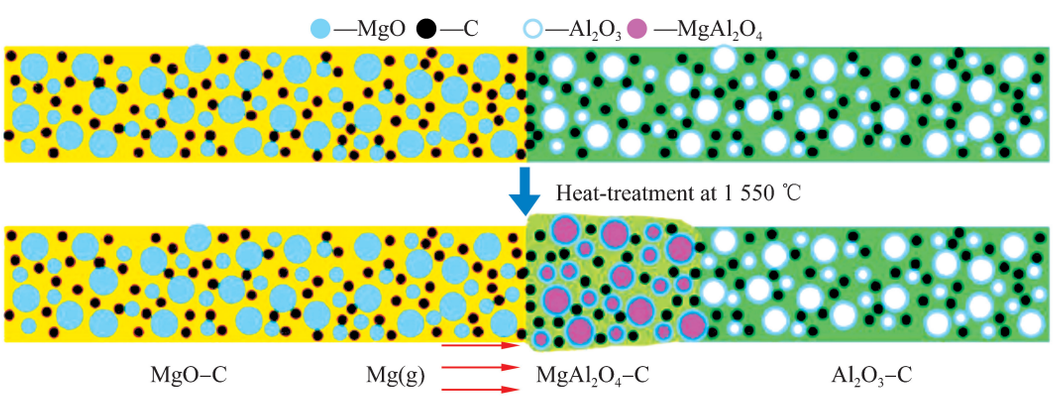

Fig. 3 Mechanism of *in-situ* spinelization at interface between Al_2O_3–C and MgO–C materials[4]

After spinelization is completed, with the increase of the temperature, Al_2O_3 further solidifies into $MgAl_2O_4$ forming secondary spinalization. Figure 4 shows the XRD patterns of Al_2O_3–C–MgO samples heat-treated at different temperatures and the lattice constant of *in-situ* formed $MgAl_2O_4$. It can be seen that the peak of $MgAl_2O_4$ shifts in the direction of high 2θ value and the lattice constant of $MgAl_2O_4$ decreases. An appropriate addition of Al_2O_3 increases the hot strength of $MgAl_2O_4$–C materials, but excessive alumina deteriorates the hot service performance[32]. For Al_2O_3–C materials added with MgO heat treated at 1 650 °C, the Al_2O_3

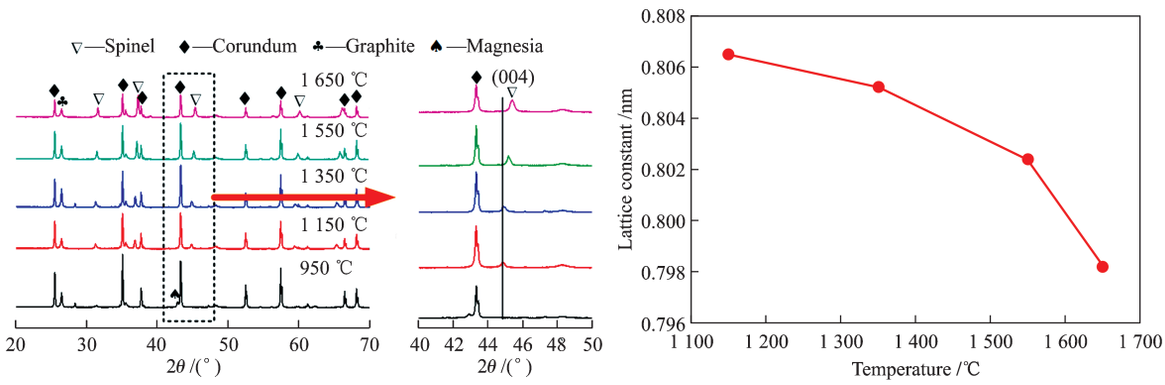

Fig. 4 XRD patterns of Al_2O_3–C–MgO samples heat-treated at different temperatures and lattice constant of *in–situ* formed $MgAl_2O_4$[39]

content in $MgAl_2O_4$ can reach 91 *mass*%, which can enhance the ceramic bonding in the matrix, and improve the strength of materials. Secondary spinelization also creates a certain volume expansion of Al_2O_3–C materials, thus increasing the apparent porosity, decreasing the bulk density, and increasing the permanent linear change, which should be considered for materials design[33].

5 Conclusions

The *in-situ* formation and secondary spinelization of $MgAl_2O_4$ is an important mean of regulating the microstructure and the service performance of refractories. Although the expansion effect can offset the shrinkage produced by sintering and improve the corrosion resistance of furnace lining materials, such as Al_2O_3–MgO castables, low-carbon MgO–C refractories, and Al_2O_3–MgO–C materials, it severely limits the reliability of functional refractories. The composition, the particle size, the atmosphere, and the temperature are important factors affecting the *in-situ* formation of $MgAl_2O_4$, whose morphology and amount have an important effect on the properties of materials. In the carbon-containing materials systems, the solid–solid reaction and the gas–solid reaction coexist to produce $MgAl_2O_4$, which provides an effective way to further regulate the microstructure and the properties of materials through the reaction process.

However, in the current studies, it is difficult to precisely regulate the *in-situ* formation of $MgAl_2O_4$ in carbon-containing materials. At the same time, laboratory studies rarely consider practical applications. In addition, there are few reports on the effects of secondary spinelization on the properties and the microstructure of refractories. Therefore, effectively utilizing the *in-situ* formation of $MgAl_2O_4$ to produce refractories with low pollution, good corrosion resistance and high reliability will be an important way for future research and development.

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