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Zn对Al_2O_3–Al–C滑板中温性能和显微结构的影响

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摘 要：以板状刚玉、氧化铝微粉、金属铝粉、金属锌粉为主要原料，以酚醛树脂为结合剂，制备Al_2O_3–Al–C滑板样品。研究了金属锌粉的引入对Al_2O_3–Al–C滑板显微结构和性能的影响。结果表明：在450～1050 ℃热处理温度条件下，锌粉的引入改变了滑板中金属铝粉的反应进程，金属锌粉氧化后形成的氧化锌沉积在金属铝粉表面，改变了金属铝粉熔化、扩散和反应的进程，有利于材料在较低温度下形成金属结合，提高中温(600~1100 ℃)性能。锌粉的引入对材料显微结构有较大影响，900 ℃热处理3 h后材料内部形成大量颗粒状、柱状和针状氮氧化物，1 050 ℃热处理3 h后材料内部形成大量碳化铝纤维，有利于材料性能的提高。

关键词：金属锌；氧化铝–铝–碳滑板；中温性能；显微结构
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EFFECT OF ADDING ZINC ON INTERMEDIATE-TEMPERATURE PROPERTIES AND MICROSTRUCTURE OF Al_2O_3–Al–C SLIDE GATE PLATE

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Abstract: Al_2O_3–Al–C slide gate plate samples were prepared using tabular alumina, alumina powder, aluminum powder, zinc powder as main starting materials and phenolic resin as a binder. The effects of zinc content on property and microstructure of Al_2O_3–Al–C slide gate plate heat treated at 450 to 1 050 ℃ were investigated. The results show that the addition of zinc changes the reaction process of aluminum. Zinc reacts with oxygen to form zinc oxide, then deposits on the surface of aluminum, which can change the melting, diffusion and reaction rate of aluminum. This process is beneficial to Al_2O_3–Al–C slide gate plate forming a metal bond at a low temperature and increasing the property at intermediate temperature (600 to 1 100 ℃). Zinc has a great impact on the microstructure of the materials. A large number of granular, columnar, needle-like nitride-oxides formed at 900 ℃ for 3 h, and many fibrous aluminum carbides formed at 1 050 ℃ for 3 h, which is favorable for the improvement of material performance.

Key words: zinc; alumina–aluminum–carbon slide gate plate; intermediate-temperature property; microstructure

Slide gate plate is a functional refractory material used in continuous casting of steelmaking industry due to the specific switch function on controlling liquid steel flow.[1] Its service life is closely correlated to the efficiency of steelmaking. As a component controlling liquid steel flow, slide gate plate is primarily affected by washing out of liquid steel, corrosion of slag, thermal stress caused by temperature gradient, high-temperature abrasion during sliding process,[2–5] and so on. Therefore, it is necessary to investigate the performance of slide gate plate and the enhancement of the service life.

Considerable efforts have been made to develop and improve the performance of slide gate plate. It is always attractive for refractories to introduce metal element into slide gate plate. In the conventional slide gate plate, metal, such as aluminum, magnesium, silicon and manganese, is usually introduced as an antioxidant to prevent carbon oxidation.[6–8] Recently, however, the metal is

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reported to improve the hot mechanical properties of slide gate plate.[9–11] As reported, aluminum and magnesium-aluminum alloy are introduced into slide gate plate to form an effective metal bonded phase at an appropriate temperature for the improvement of the hot mechanical properties.

The metal bonded slide gate plate has superior properties, such as the good thermal shock resistance, excellent corrosion resistance and spalling resistance.[12–13] In the literatures, metal disperses in the matrix and presents a liquid phase, which is favorable to release the thermal stress, reduce the abrasion during sliding process, and improve the oxidation resistance.

Some works reported the high-temperature properties of the metal bonded slide gate plate. Itoh, *et al.*[14–15] investigated the influence of chromium and molybdenum on high-temperature properties of metal-bonded slide gate plate. They summarized that chromium and molybdenum could improve the strength and oxidation resistance of slide gate plate. Bo, *et al.*[16] studied the influence of aluminum on high-temperature properties of metal-bonded slide gate plate. Their results showed that aluminum could improve the thermal shock resistance. Leitzel, *et al.*[17] discussed the effect of metal type, content, heating temperature on the mechanical properties of slide gate plate.

However, only a few studies on intermediate-temperature properties of slide gate plate have been reported. Tian, *et al.*[18] analyzed the intermediate-temperature properties of aluminum-bonded Al_2O_3–Al–C slide gate plate. As reported, this slide gate plate has a low bonding strength at a specific intermediate temperature that is caused by the melting of aluminum and the decomposition of phenolic resin. This could not favor the performance of the slide gate plate in intermediate-temperature range. Thus, it is necessary to improve the bonding strength in the intermediate-temperature range.

Zinc has a lower melting point (419℃), compared to aluminum (660 ℃).[19] It melts before aluminum during the heat treatment process. Therefore, it is possible to form a metal bonding phase before aluminum melting, which will be supposed to improve the intermediate-temperature bonding strength of slide gate plate.

This paper mainly investigated the effects of adding zinc on the properties and microstructure of Al_2O_3–Al–C slide gate plate.

1 Experimental procedure

1.1 Fabrication

Tabular corundum (99.50%, in mass, the same below, 0–2 mm in particle size), alumina powder, (99.50%, 44 μm in average particle size), aluminum (99.50%, 44 μm in average particle size), thermosetting phenolic resin (carbon yield >40%) and zinc (95.50%, 44 μm in average particle size) were used as the starting materials.

Table 1 shows the composition of starting materials for Al_2O_3–Al–C slide gate plate. The mixtures were pressed into the bricks with a size of 230 mm × 115 mm × 65 mm by friction brick pressing under 240 MPa, then, dried at 200 ℃ for 24 h. Finally, the bricks were cut and ground into the smaller samples with a size of 25 mm × 25 mm × 130 mm.

Various samples were then placed in a refractory block covered with carbon powder to prevent the surface oxidation. The samples were heat treated from room temperature to a higher temperature (450, 600, 750, 900 ℃ and 1 050 ℃) for 3 h.

Table 1 Composition of starting materials for Al_2O_3–Al–C slide gate plate *w*/%

Samples	Tabular corundum (particles)	Tabular corundum (powder)	Alumina powder	Aluminum	Phenolic resin	Zinc
A1	60	24	10	6	5	0
A2	60	23.4	10	6	5	0.6
A3	60	22.8	10	6	5	1.2
A4	60	22.2	10	6	5	1.8
A5	60	21.5	10	6	5	2.5

1.2 Characterization

The apparent porosity (AP) and bulk density (BD) were examined by Archimedes method according to the GB/T 2997—2000. The cold crushing strength (CCS) and the modulus of rupture (MOR) were determined by electro-hydraulic pressure testing machine (model YAW, Shanghai, China) and hydraulic universal testing machine (model WE–50B, Changchun, China) according to the GB/T 5072—2008 and the GB/T 3001—2007, and the hot modulus of rupture (HMOR, at 700 ℃) were measured by the high-temperature bending testing machine (model HMOR–03A, Luoyang, China) according to the GB/T 3002—2004. The microstructure of the samples was characterized by a scanning electron microscope (SEM, model JSM6360, Japan) with an energy dispersive X-ray spectroscope (EDS, model EX250, Japan).

2 Results and discussion

2.1 Effect of zinc content on AP and BD

Figure 1 shows the AP and the BD of the samples heat treated at different temperatures for 3 h. The AP of

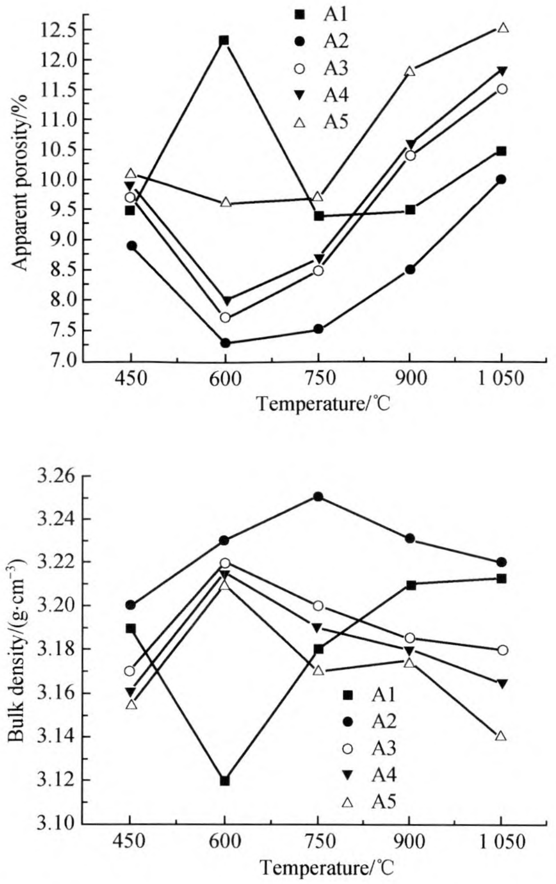

Fig.1　The AP and BD of samples at different heat treatment temperatures for 3 h

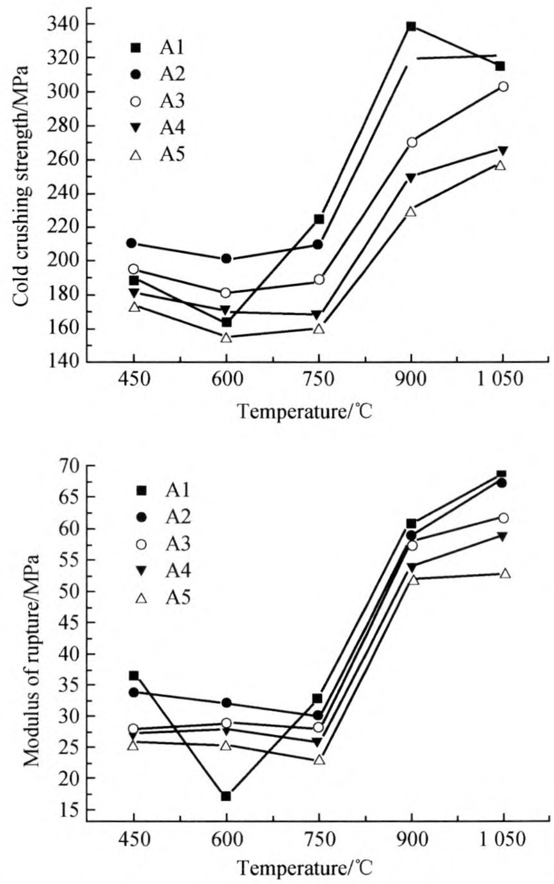

Fig.2　The CCS and MOR of samples with various zinc content at different heat treatment temperatures for 3 h

zinc-free sample A1 heat treated at 600 ℃ is higher and the BD is lower than other samples at the same temperature. Its AP reduces from 12.34% to 7.28% and the BD improved from 3.12 g/cm^3 to 3.23 g/cm^3. From 750 ℃ to 1050 ℃, the AP of samples A3, A4 and A5 increases while their BD decreases with increasing of the zinc content. Especially, the AP of sample A5 with 2.5% (in mass, the same below) of zinc is the highest and the BD is the lowest in the five samples at the heat treatment temperature range. Meanwhile, in each specific temperature tested, the AP of sample A2 with 0.6% of zinc is the lowest and the BD is the highest among the five samples. This means that the addition of an appropriate amount of zinc can improve the densification. However, the excessive addition of zinc impairs the densification of slide gate plate sample.

2.2 Effect of zinc content on CCS and MOR

Figure 2 shows the CCS and MOR of the samples with various zinc content at different heat treatment temperatures for 3 h. At 600 ℃, the MOR of the sample A1 appears a minimum value, and the CCS is relatively low. However, the sample A2 appears a superior performance, of which the CCS is increased by 22.4% and the MOR is increased by 26.5%, compared to those for the sample A1. This indicates that zinc addition of 0.6% can significantly improve the strength of Al_2O_3–Al–C slide gate plate at 600 ℃. From 750 ℃ to 1 050 ℃, the CCS and the MOR of the five samples increase with increasing the temperature (except for the sample A1 heat treated at 1 050 ℃), but decrease with increasing zinc content in the specific temperature tested. Thus, it can be seen that the strength would decrease when excessive amount of zinc was added in the materials. This could be correlated to the low boiling point (906 ℃)[19] and the gasification of zinc. The vapor pressure of zinc is low at the melting point (419 ℃), but it increases rapidly with the temperature increasing. It is suggested that there would be more and more zinc vapor in the system as the temperature increases, which in turn leads to the more and more pores within the material after cooling. The porous structure is disadvantageous to the properties of the material. Thus, the appropriate addition of zinc in the material should be considered.

2.3 Effect of zinc content on HMOR at 700 ℃

Figure 3 shows the HMOR of the samples heat treated at 700 ℃. It can be seen that the HMOR of sample A2 with 0.6% of zinc is the highest among the five samples. Meanwhile, the HMOR of other samples decreases with

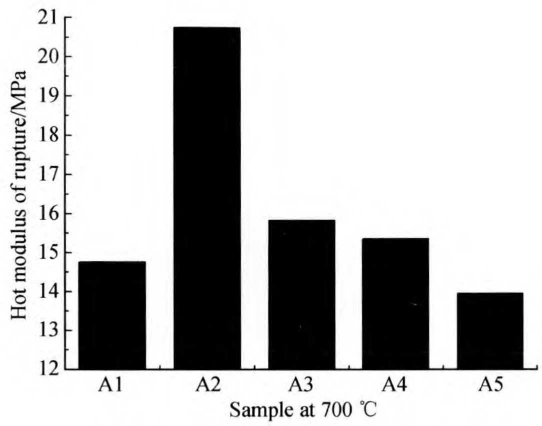

Fig.3 HMOR of the samples at 700 ℃

the increasing of the zinc content. It can be seen that the HMOR of sample A2 is increased by 39.4%, compared to zinc-free sample A1. This indicates that the addition of 0.6% zinc could favor the improvement of the HMOR. The excessive addition of zinc is inappropriate. The following main reactions that may take place during heating the samples involved (1) the melting–oxidation of zinc and aluminum, and (2) the formation of zinc oxide and alumium oxide. According to Ref. [19], the melting of zinc and aluminum occurs at 419 ℃ and 660 ℃, respectively. The formation of zinc oxide and alumium oxide usually occurs in a large temperature range. Therefore, the metal bond could be formed by the melting of zinc and aluminum in the materials, and then the ceramic bond would be formed due to the formation of zinc oxide and alumium oxide. Both the metal bond and ceramic bond are favorable to enhance the mechanical property, which is weakened by the oxidation and decomposition of phenolic resin. There may be much zinc vapor in the system when the zinc content is too high, because the vapor pressure of zinc is higher at 700 ℃. This could lead to a large number of pores in the material, which is unfavorable to the HMOR. In this work, the appropriate content of zinc is 0.6%.

2.4 Effect of zinc on microstructure

Figure 4 shows the SEM photographs of the samples with 0.6% of zinc heat treated at different temperatures. It can be seen that the shape of zinc in the structure changes remarkably.

In Figs.4(a) and 4(b), some pores formed in the materials, and some white substances appear on aluminum surface such as "1" and "2". According to the EDS results, these white substances are zinc oxide, which mainly come from the oxidation of zinc. It is easy for zinc to react with oxygen to form zinc oxide. The generated zinc oxide deposits on the aluminum surface, and then reacts with aluminum. Finally, zinc generates again. This cycle can cause the consummation of oxygen promote the

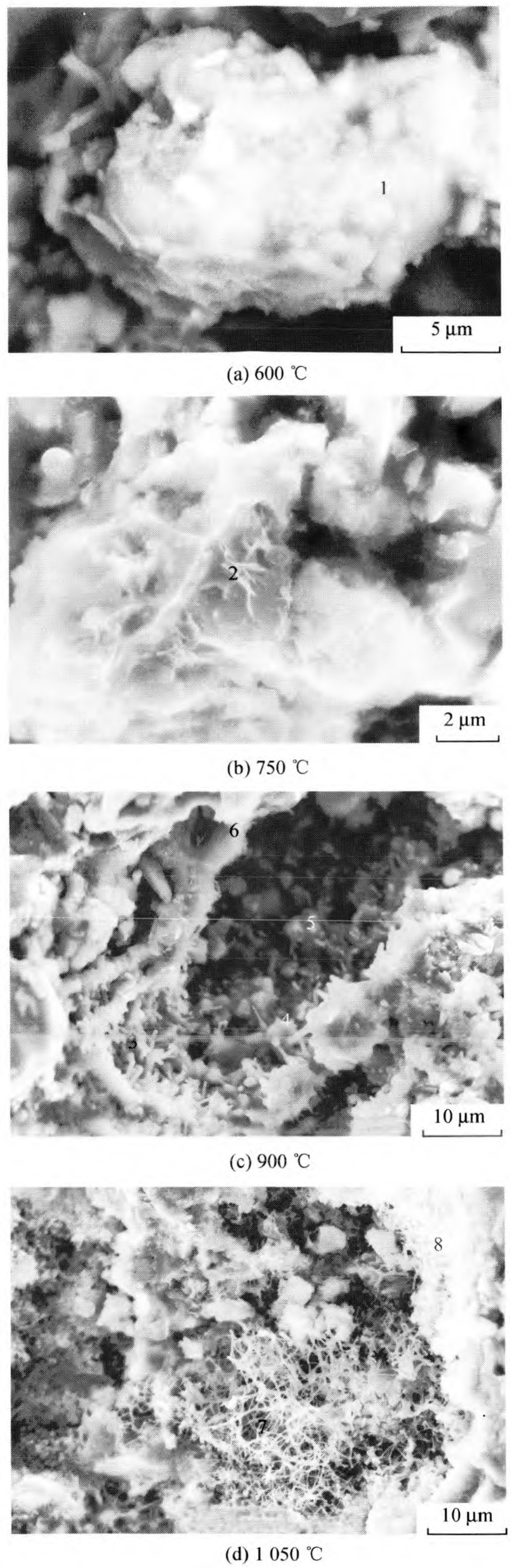

Fig.4 SEM photographs of samples with 0.6% of zinc at different heat treatment temperatures for 3 h

melting–oxidation process of metal, and favor the materials forming a metal–ceramic bond. This would reduce the defects caused by the oxidation and decomposition of phenolic resin, which in turn improves the densification and strength of slide gate plate.

For this system, the reactions can be described as the equations below, and the reaction temperatures can be calculated from the Gibbs free energy (ΔG) of reactions based on the chemical thermodynamics theory.[19]

$$Zn\,(l) + 0.5O_2(g) = ZnO(s) \quad (1)$$

$$\Delta G_1^0 = -348\,360 + 103.28\,T \quad (kJ\cdot mol^{-1})$$

$$T = 419\ ℃–907\ ℃ (T<3\,100\ ℃), \Delta G_1^0<0$$

$$2Al\,(l) + 1.5O_2(g) = Al_2O_3(s) \quad (2)$$

$$\Delta G_2^0 = -1\,682\,900 + 323.24\,T \quad (kJ\cdot mol^{-1})$$

$$T = 660\ ℃–2\,042\ ℃ (T<4\,933\ ℃), \Delta G_2^0<0$$

$$2Al\,(l) + 3ZnO(s) = Al_2O_3(s) + 3Zn\,(l) \quad (3)$$

$$\Delta G_3^0 = \Delta G_2^0 - 3\Delta G_1^0 = -637\,820 + 13.4T \quad (kJ\cdot mol^{-1})$$

$$T = 750\ ℃ (T<47\,325\ ℃), \Delta G_3^0<0$$

where T is the thermodynamics temperature. The reactions (1) to (3) will be self-sustaining when T is from 600 to 750 ℃. The liquid–gas reaction and the solid–liquid reaction should occur in this temperature range, which is confirmed by Fig.4(a), which shows there are zinc oxide and alumina.

Figure 4(c) shows the microstructure of the material heat treated at 900 ℃ for 3 h, in which some columnar, needle-like (such as "3" and "4"), granular(such as "5") and massive(such as "6") substance can be observed. The EDS analysis indicated that the columnar, need-like and granular phases are mainly nitride-oxides, and the massive phase is zinc oxide and alumina. It is reasonable to consider that the reactions undergo two processes. The first was the reaction of oxygen and zinc, which results in the lower oxygen content within the system in this temperature range. The generated zinc oxide deposits on the surface of alumina. The second is the gasification of zinc, which would accelerate the oxidation of zinc and the oxidation–nitride reaction of aluminum. Consequently, the partial pressure of oxygen decreases and the nitrogen partial pressure increases, then a large number of granular, columnar and needle-like nitride-oxides form in the structure, which can be described as following:[19]

$$2Al\,(l) + 1.5O_2(g) = Al_2O_3(s) \quad (2)$$

$$\Delta G_2^0 = -1\,682\,900 + 323.24\,T \quad (kJ\cdot mol^{-1})$$

$$T = 660–2\,042 (T<4\,933℃), \Delta G_2^0<0$$

$$\lg\frac{p_{O_2}}{p^0} = -\frac{58\,579}{T} + 11.25$$

$$Al\,(l) + 0.5\,N_2(g) = AlN(s) \quad (4)$$

$$\Delta G_4^0 = -326\,477 + 116.4\,T \quad (kJ\cdot mol^{-1})$$

$$T = 660\ ℃–2\,000\ ℃ (T<2\,532℃), \Delta G_4^0<0$$

$$\lg\frac{p_{N_2}}{p^0} = -\frac{34\,108}{T} + 12.16$$

$$23Al\,(l) + 13.5O_2(g) + 2.5N_2(g) = Al_{23}O_{27}N_5(s) \quad (5)$$

$$\Delta G_5^0 = -16\,467\,302 + 3\,324.11\,T \quad (kJ\cdot mol^{-1})$$

$$T = 660\ ℃–2\,520\ ℃ (T<4\,681℃), \Delta G_5^0<0$$

$$13.5\lg\frac{p_{O_2}}{p^0} + 2.5\lg\frac{p_{N_2}}{p^0} = -\frac{860\,046}{T} + 173.61$$

where p_{O_2} is the partial pressure of oxygen, p_{N_2} is the nitrogen partial pressure and the p^0 is the standard atmospheric pressure. These reactions will be self-sustaining when T is at 900 ℃. At the same time, the partial pressure of oxygen and nitrogen should be considered. In this system, the $Al_{23}O_{27}N_5$ began to generate with decreasing the partial pressure of oxygen and increasing the nitrogen partial pressure. The $Al_{23}O_{27}N_5$ is the spinel solid solution of AlN and Al_2O_3, but the $Al_{23}O_{27}N_5$ is unstable in thermodynamic process when the temperature is below 1 640 ℃.[19] Thus, the nitride–oxides in the system at this temperature may be mixtures of AlN, Al_2O_3 and $Al_{23}O_{27}N_5$.

Due to the presence of these nitride–oxides, the bond strength and properties of materials were improved. This means that zinc has a dominant effect on the formation of the nonoxide–cermet bond phase in the intermediate-temperature range.

Table 2　EDS results of points in Fig.4　　*w*/%

Points	C	N	O	Al	Zn
1			21.15	62.09	16.76
2	0.86		15.43	66.72	16.99
3	0.88	26.15	27.31	45.66	
4	0.55	10.80	52.87	35.79	
5		17.48	30.97	51.55	
6			28.29	65.04	6.67
7	10.91	0.91	48.27	39.91	
8		0.73	28.40	68.04	2.83

In Fig.4(d), there are many fibrous aluminum carbides (Al_4C_3) (such as "7") and some zinc oxide in materials (such as "8"), which were approved by the EDS results. These fibers connect with each other and form a network structure. The effect of fiber bridging and pulling could favor the improvement of the materials strength and toughness.[20] Thus, the service performances would be enhanced.

For this system, the oxygen pressure reduces and the carbon monoxide pressure increases due to the oxidation of zinc. Thus, the formation reaction of aluminum carbide could be possibly described by three steps[21] according to the thermodynamic theory: firstly, aluminum reacts with carbon monoxide (CO) to form Al_2O (gas), secondly, Al_2O (gas) reacts with carbon monoxide (CO) to form aluminum carbide on the surface of solid or liquid phase, thirdly, the aluminum carbide dissolves into aluminum solution till the supersaturation, then it splits and grows up into whiskers on the solid phase. This phase formation process is consistent with the vapor–liquid–solid (VLS) growth mechanism of the crystal.[22]

3 Conclusions

(1) An appropriate addition of zinc into Al_2O_3–Al–C slide gate plate is beneficial to improve the strength of Al_2O_3–Al–C slide gate plate at the intermediate-temperature range. However, the excessive addition of zinc will increase the porosity, which does not favor the improvement of the service performance.

(2) Zinc changes the reaction process of aluminum. Zinc reacts with oxygen to form zinc oxide, and then deposits on the surface of aluminum, which accelerates the rate of melting, diffusion and reaction of aluminum. This process favors the formation of a metal bond phase.

(3) The microstructure of Al_2O_3–Al–C slide gate plate materials can be varied when zinc is added. A large number of granular, columnar, needle-like nitrogen–oxides form in the materials at 900 ℃, and some fibrous aluminum carbides form at 1 050 ℃, which are suggested to favor the improvement of materials performance.

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