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Effect of Some Additives on the Microstructure and Properties of Andalusite-cordierite Refractory

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Abstract: The effect of some additives on the microstructure and properties of andalusite-cordierite refractory is concerned with. A study has been made on Al_2O_3, Cr_2O_3 and SiC powders, which are selected as additives and added respectively to the standard formulation in varying amounts as extra content (2%, 4%, or 6%). As the results indicate, Al_2O_3 (best at 4%) and SiC (best at 2%) can improve the microstructure and the properties of the material. But Cr_2O_3 shows the effect to the contrary.

Key words: andalusite-cordierite refractory, additive, microstructure, property

Mullite-cordierite refractory is a top-grade material for kiln furniture. It is used in large amounts, but its cost is quite high. At high temperature, andalusite is transformed into mullite. Andalusite cordierite refractory, a low-cost and high-quality new type of kiln furniture, can be developed by replacing mullite with andalusite. To improve the properties of the material, proper additives should be selected.

Research work done by Knickerbocker and others[1] revealed that modifying the content of the Al_2O_3 component will alter some properties of cordierite. Study made by I. Wadsworth and others shows that SiC contributes to the improvement of the mechanical property of cordierite[2,3]. Cr_2O_3 itself possesses fine properties as refractory. Refractories containing Cr_2O_3 are widely used in industrial kilns, as the addition of Cr_2O_3 can improve certain properties of such materials[4].

The effect of these additives on the microstructure and properties of andalusit-cordierite refractory are discussed in this paper.

1 Experiment and results

1.1 Raw materials and Procedure

Cordierite, Andalusite and Clay are selected as basic materials whose chemical components are shown in table 1.

Al_2O_3, Cr_2O_3 and SiC powders are selected as additives, with purity all above 99%.

Table 1 Chemical components of raw materials %

Component	Cordierite	Andalusite	Clay
Al_2O_3	35.2	59.02	34.03
SiO_2	46.6	37.84	47.80
MgO	13.1	0.14	0.07
CaO	0.75	0.36	0.17
TiO_2	0.60	0.21	0.36
K_2O	0.12	0.18	1.17
Na_2O	0.05	0.12	0.14
TFe	2.99	1.50	0.77

According to a certain grain size and content, raw materials are evenly mixed and then compacted into a cylinder 25 mm in height and diameter. The compacts are sintered at 1 380 ℃ for 5 h.

1.2 Results of experiments

As tandard andalusite-cordierite sample is made according to the standard formulation determined through experiment. Al_2O_3, Cr_2O_3 and SiC, all in fine powder, are added respectively to the standard formulation in varying amounts as extra content (2%, 4%, or 6%), thus obtaining a series of additive andalusite-cordierite samples. Then analyses are made about the effect of these additives on the microstructure and room temperature properties of these additive samples, as compared with the standard sample. Also, tests are made in regard to the two room temperature properties of all additive samples: firing shrinkage and compressive stress. Part of these samples are examined for their refractoriness. The results are shown in table 2.

Table 2 Properties of Samples

Additives	Extra content/%	Firing shrinkage/%	Compressive shrinkage/%	Refractoriness/℃
None	0	2.01	65.2	1580
Al_2O_3	2	2.97	52.8	1630
	4	2.42	70.1	
	6	2.70	49.8	
Cr_2O_3	2	2.91	57.5	
	4	2.99		
	6	2.78	60.4	
SiC	2	2.71	97.3	1580
	4	2.32	95.0	
	6	2.14	86.2	

Note: Firing shrinkage is controlled at about 0.5% in following experiments.

2 Microstructure and analysis

For convenience code names are used to stand for additive samples. Such names are indicated by the general form [A]B, in which A stands for an additive and B, for amount of extra content. [SiC]4, for example, indicates an additive sample with 4% of SiC powder added as extra content.

2.1 Microstructure and analysis of the standard sample

The microstructure of the standard sample is shown in Fig. 1.

Fig.1 Andalusite transformed and cracked
★ andalusite and its crack;
● mullite edge of andalusite;
■ andalusite transformated completely

The central part of large grain andalusite is cracked under thermal stress, with its edge transformed into mullite with wool-like crystals arranged in a direction parallel to the cleavages. Small grain andalusite becomes completely transformed into mullite looking like an aggregate of nets or tree branches. Found in the cordierite substrate are mullite and broad-striped pyroxene crystals, as shown in Fig. 2.

The transformation of andalusite starts from the grain edge and then extends to the central part, so under the same sintering system, small grain andalusite is transformed into mullite completely, while the large grain andalusite becomes transformed only around the edge, thus to a certain degree decreasing the compressive stress of the standard sample. But the sample's mineral components and small grain net-like mullite structure contribute to improving the high temperature properties of the material. At the same time, the transformation results in an increase in volume, so as to compensate for the firing shrinkage resulting from sintering of the standard sample.

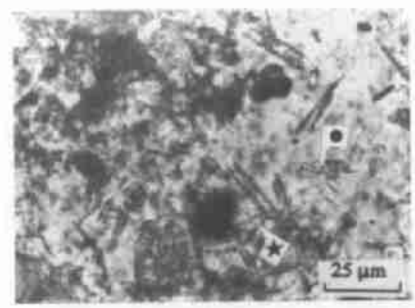

Fig.2 Crystallization in substrate
★ mullite; ● pyroxene

2.2 Analysis of effect of additives on the microstructure and room-temperature properties of the material

(1) Analysis of fine powdered Al_2O_3 on the microstructure and room-temperature properties of the material.

As compared with the standard sample, $[Al_2O_3]4$ shows two outstanding characteristics: (a) Greater transformation of andalusite into mullite, as contrasted by Fig. 3 with Fig. 1. (b) In the substrate there are relatively more needle-like mullite crystals; and the net-like structures are better developed.

As compared with the standard sample, the compressive stress resistance and firing shrinkage

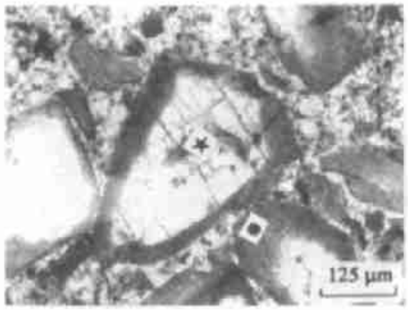

Fig.3 Transformation of andalusite in $[Al_2O_3]4$

★ andalusite; ● mullite edge of andalusite

of $[Al_2O_3]4$ are found to be greater (See Table 2).

At high temperature, andalusite is decomposed into mullite and SiO_2; and the added fine powder of Al_2O_3 reacts with SiO_2 dissociating from transformed andalusite to form mullite in the substrate. The chemical reaction equations are respectively:

$$\underset{\text{(Andalusite)}}{3Al_2O_3 \cdot SiO_2} \xrightarrow{\text{Sintering}} \underset{\text{(Mullite)}}{3Al_2O_3 \cdot 2SiO_2} + SiO_2$$

$$2SiO_2 + \underset{(Al_2O_3\text{ fine powder})}{3Al_2O_3} \xrightarrow{\text{Sintering}} \underset{\text{(Mullite)}}{3Al_2O_3 \cdot 2SiO_2}$$

Because of the addition of Al_2O_3 the above equations are promoted to the right, thus promoting the andalusite-into-mullite transformation. And Al_2O_3 reacts with the SiO_2 that has dissociated from decomposed clay in the substrate to form mullite, so as to bring about greater amount of mullite crystals in the substrate. $[Al_2O_3]4$, so far as its change in compressive stress is concerned, is affected by the extent of the transformation and by the crystallization in the substrate. The greater the extent of the transformation is, the smaller the shrinkage and the lower the compressive stress will become. And the more mullite crystals are formed in the substrate, the greater the shrinkage and the higher the compressive stress will become. The reason is that the net-like mullite crystals serve to accelerate the densification of the substrate, as well as to strengthen the substrate. In the substrate of $[Al_2O_3]4$, mullite crystallization plays a principal role and therefore, as compared with the standard sample, this powdered substance has greater shrinkage and greater compressive stress resistance.

As observed under optical microscope, the extent of the transformation of the additive sample becomes greater with the increase of the extra content of Al_2O_3 in fine powder; and the mullite crystals in the substrate also increase accordingly.

Shown in Fig. 4 are the effect of the varying amounts of Al_2O_3 as extra content on the properties of the material.

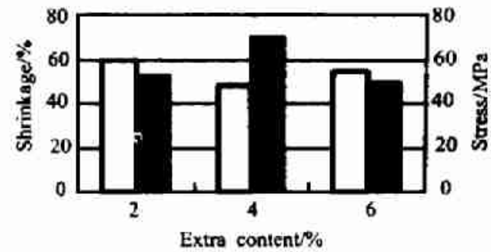

Fig.4 Effect of extra content of Al_2O_3 on the firing shrinkage (□ mutiplied 20) and compressive stress(■)

As shown in Fig. 4, with increase in extra content of Al_2O_3, the firing shrinkage of the additive samples first goes down and then comes up, while the compressive stress first goes up and then comes down. The best properties of the additive sample are achieved at 4% of Al_2O_3 as extra content. Also, with the increase of the Al_2O_3 content, the extent of the andalusite-into-mullite transformation becomes greater, and the firing shrinkage and compressive stress tend to decrease. At the same time, mullite crystals in the substrate also increase, so as to reduce the shrinkage and compressive stress. The combination of these effect plays the major role in affecting the shrinkage from the transformation, especially when the contents of Al_2O_3 are between 2% and 4%. Thus the greater extent of the transformation leads to smaller shrinkage; and the mullite crystals in the substrate plays the major role in affecting the compressive stress resistance of the additive sample, so the more such crystals are formed, the greater the compressive stress will become. But when the contents of fine powdered Al_2O_3 are between 4% and 6%, the contrary is true: greater firing shrinkage and weaker compressive stress.

In $[Al_2O_3]4$, the andalusite-into-mullite transformation is promoted, and more net-like mullite crystals are formed in the substrate. So in comparison with the standard sample, the refractoriness of the additive sample is raised by as much as 50 ℃.

(2) Analysis of the effect of Cr_2O_3 on the microstructure and normal-temperature properties of the material. Compared with the standard sample, $[Cr_2O_3]4$ has three outstanding characteristics: (a) Large amounts of pores exist in the substrate; (b) Most air pores in the substrate take on an oval

shape, without sharp angles; (c) In the substrate are found few narrow-striped or broad-striped crystals, but there are large amounts of grainy spinals whose electronic microforms are shown in Fig.5.

Fig.5 Spinel in substrate of [Cr_2O_3]
★ spinel

In comparison with the standard sample, the shrinkage of [Cr_2O_3]4 increases while its compressive stress decreases (see Table 2).

As Cr_2O_3 decomposes partly at high temperature, large amounts of air pores are formed in the substrate. The reaction equation is:

$$2Cr_2O_3 \xrightarrow{\text{Sintering}} 3O_2\uparrow + 4Cr$$

These pores should work to reduce the shrinkage of the additive sample. It can be seen that it is due to the sintering that most pores assume an oval form. The addition of Cr_2O_3 as an additive promotes the sintering of andalusite-cordierite, so as to heighten the compactness and therefore the shrinkage of the additive sample. The change in the shrinkage of [Cr_2O_3]4 is due to the combined effect of densification and shrinkage. But the effect of shrinkage is greater than that of densification. So compared with the standard sample, [Cr_2O_3]4 has greater shrinkage.

At high temperatures, low-valence Cr ion can reduce high-valence Fe^{2+}, as shown by the reaction equation:

$$2Cr + 3Fe_2O_3 \xrightarrow{\text{High temp.}} Cr_2O_3 + 6FeO$$

Hence in the Cr_2O_3 additive samples Fe should exist in the form of FeO. The grain-like mineral in [Cr_2O_3]4 is spinel, a solid solution of FeO. An analysis by energy spectrum shows that this kind of grain-like spinal is one of (Mg · Fe)O · (Cr · Al)$_2$O$_3$, which serves to lower the compressive stress resistance of the material.

The tendency of change for the firing shrinkage and compressive stress of [Cr_2O_3]2, [Cr_2O_3]4 and [Cr_2O_3]6 is shown in Fig.6.

As shown in Fig.6, with the increase of Cr_2O_3 as extra content the firing shrinkage and the compressive stress resistance both go up first and then come down, thus worsening the properties of the material.

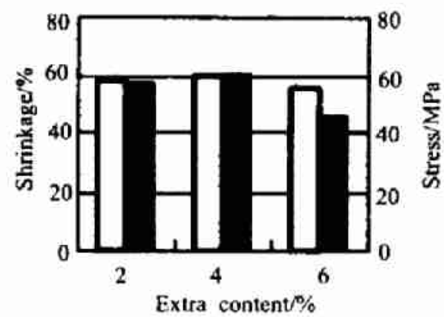

Fig.6 Effect of extra content of Cr_2O_3 on the firing shrinkage (□ multiplied 20) and compressive stress(■)

(3) Analysis of the effect of SiC on room temperature properties and microstructure of the material.

As compared with the standard sample, [SiC]4 has the following characteristics: (a) The andalusite-into-mullite transformation is somewhat checked; (b) SiC decomposes partly, leaving pores in the substrate; (c) There is a little more glass phase in the substrate than in the standard sample.

In comparison with the standard sample, the compressive stress of [SiC]4 heightens considerably, but its firing shrinkage goes up only slightly. At high temperatures and in ambiance of oxidization, SiC will be oxidized and decomposed, as shown by the reaction equation:

$$2SiC + 4O_2 \xrightarrow{\text{High temp.}} 2SiO_2 + 2CO_2\uparrow$$

Dissociated SiO_2 wraps up SiC granules, serving as a protective film checking the decomposition of SiC from oxidization. As the transformation in [SiC]4 is checked, the compressive stress of [SiC] 4 is greater than that of the standard sample. But the increase of compressive stress resistance in [SiC] 4 is not entirely due to the checking of the transformation, for the remained under composed SiC still serves to enhance the substrate in a dispersively-strengthening manner. Contrastive observation of [SiC]2, [SiC]4 and [SiC]6 under optical microscope shows that with the increase of the SiC content, more SiC is decomposed and more pores and glass phase are found.

With the increase of the SiC content, the tendency of change in firing shrinkage and compres---sive stress resistance of the additive samples is shown in Fig. 7.

It can be seen from Fig. 7 that with the increase of the SiC content, the shrinkage and compressive stress resistance all tend to become smaller.

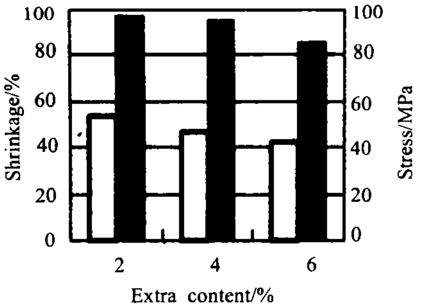

Fig.7 Effect of extra content of SiC on firing shrinkage (□ multiplied 20) and compressive stress(■)

Analysis shows that the decomposition of SiC from oxidization plays a major part in the change of these two properties. With the increase of SiC content more SiC is decomposed by oxidization, so that more air pores are formed. These pores will lower the strength of the additive sample more than the remaining undecomposed SiC will raise the strength of the additive samples. So, all in all, the compressive stress of the additive sample will become lower. The decomposition of more SiC from oxidization gives rise to the formation of more pores and thus naturally reduces the shrinkage of the additive sample.

As the addition of SiC tends to check the andalusite-into-mullite transformation, the amount of mullite, with high refractoriness, in [SiC]2 is less than in the best standard sample, and as a result, the fire resistance of the material is lowered. But the undecomposed SiC can heighten the fire resistance of the material. Thus the two opposite effect cancel each other out, leaving the fire resistance of [SiC]2 neither higher nor lower than that of the standard sample.

3 Conclusions

(1) Al_2O_3 powder can promote the transformation of andalusite into mullite as well as the crystallization of mullite in the substrate. Although this lowers the room temperature compressive stress, it will increase refractoriness and reduce the firing shrinkage of the material. The amount of Al_2O_3 as extra content is best at 4%.

(2) Cr_2O_3 in and alusite-cordierite material can promote sintering densification. But on the one hand, the decomposition of Cr_2O_3 in the substrate will form more pores, contributing unfavorably to the room temperature and high temperature compressive stress of the material as well as to its resistance to creep. And on the other hand, the grain like spinel of (Mg · Fe)O · $(Cr \cdot Al)_2O_3$ formed in the substrate by Cr_2O_3 will also tend to lower the compressive stress of the material.

(3) In andalusite-cordierite material SiC can strengthen the substrate in a dispersively-strenghtening manner. It not only can increase the room-temperature compressive stress of the material, but also can raise refractoriness under load of the material. The amount of SiC as extra content is best at 2%.

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