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Experimental Study on the Re-bonded Magnesia - Zirconia Refractory for New Dry Process Cement Kiln

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Abstract. The use of magnesia-chrome refractories of the cement kiln can generate harmful hexavalent chromium in the environment and be hazardous to your health, so the study on the instead of magnesia-chrome refractories have become urgent issues. The raw material is made up of fused magnesite particles (particle size 0 to 3 mm), fine fused magnesite powder with the size less than 200 meshes and fine fused magnesia-zirconia's powder with the size less than 320 meshes, polyvinyl alcohol and calcium lignosulfonate liquor being used as the combine. This paper discusses the effect of sinter temperature on sinter character of products.

Introduction

Cement is important building material, and its consumption is increasing rapidly, correspondingly, cement industry is also required for growth in consumption of basic refractories. In the cement rotary kiln, the basic configuration of its basic blocks are: magnesia chrome bricks for the firing zone, the periclase-spinel brick for transition zone. Magnesia-chrome materials under this condition occurs in the trivalent chromium into hexavalent chromium ions, causing environmental pollution.Therefore, in the recent ten years ,basic brick for cement kiln is in a fundamental change[1,2]. The importance of Cr^{6+} pollution of the environment's has long been developed, but some key parts of the industry, such as iron and steel industry in the RH refining equipment, cement rotary kiln at high temperature and some non-ferrous metal smelting furnace with a still widely used on the magnesia-chrome refractories[3-5].

In this experiment we use the fused magnesia, periclase - zirconia eutectic material as raw material to study sintering temperature and holding time on properties of sintered products.

Test Materials and Process

Test Materials. The raw material is made up of fused magnesite particles (particle size 0 to 3 mm), fine fused magnesite powder with the size less than 200 meshes and fine fused magnesia-zirconia's powder with the size less than 320 meshes, polyvinyl alcohol and calcium lignosulfonate liquor being used as the combine. Table 1 shows the chemical composition of raw materials.

Test Process. Table 2 shows proportion of grain composition, according to proportion of grain composition, First, join the coarse aggregate, then add wetting agent with the amount of 3.3 millilitre per 100 gramme to coarse aggregate for wetting the particle surface, finally put the fine powder to coarse aggregate; after sufficiency mixing, tewing, pressure forming and sintering at 1550 to 1800 ^{o}C, Magnesia - Zirconia Refractory were obtained.Burning products should be test the bulk density, porosity, flexural strength and other performance tests, and made SEM scanning electron microscope to study the sintering process parameters on the performance of products.

Table 1 The chemical composition of raw materials,%

raw materials	MgO	CaO	SiO_2	Fe_2O_3	Al_2O_3	L.O.I	ZrO_2
fused magnesia B	98.34	0.78	0.35	0.28	0.12	0.13	—
magnesium zirconium powder(<320 mesh)	84.97	1.31	0.69	0.81	—	—	11.71

Table 2 Proportion of grain composition,%

coarse particles (fused magnesia B)				fine powder	
3～2mm	2～1mm	1～0.5mm	<0.5mm	fused magnesia (<200mesh)	Magnesium zirconium powder (<320 mesh)
10	15	25	10	20	20

Results and Discussion

Fig.1 shows that effect of sintering temperature on bulk density of samples, Fig.2 shows that effect of sintering temperature on apparent porosity of samples, Fig.3 shows that effect of sintering temperature on modulus of rupture of samples.

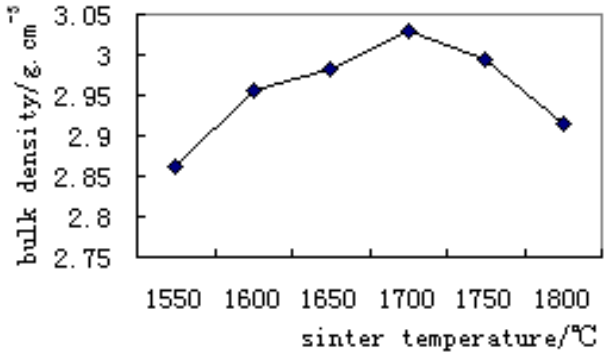

Fig.1 Effect of sintering temperature on bulk density of samples

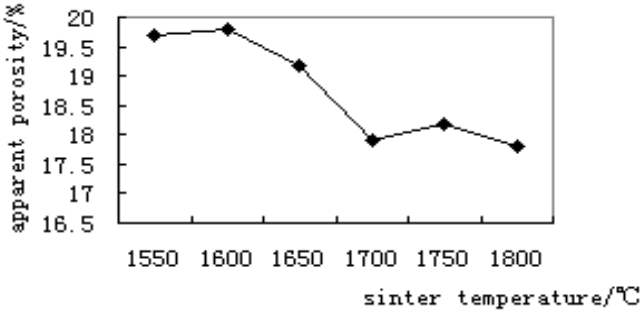

Fig.2 Effect of sintering temperature on apparent porosity of samples

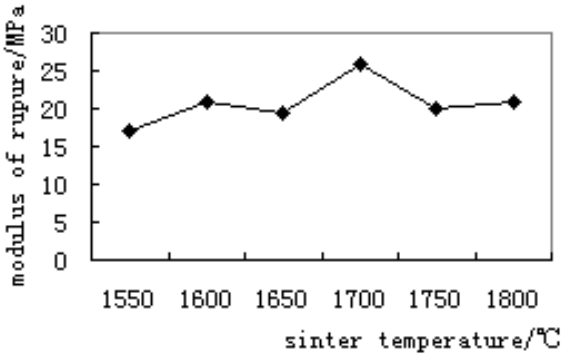

Fig.3 Effect of sintering temperature on modulus of rupture of samples

Sinter process of magnesia is a sinter process of solid phase, the growing of crystal grain and the elimination of pore mainly to realize through the diffusion of ions. Energy of intrinsic defects in magnesia is very high, so the defect concentration are controled by the content of impurities. Solid solution of zieconia in the magnesia raises the propagation rate and accelerate sintering ,on the one hand, the price difference will produce the corresponding cation vacancy in the magnesia lattice ;on the other hand, differences in the ionic radius of magnesia will also have a certain degree of lattice distortion.

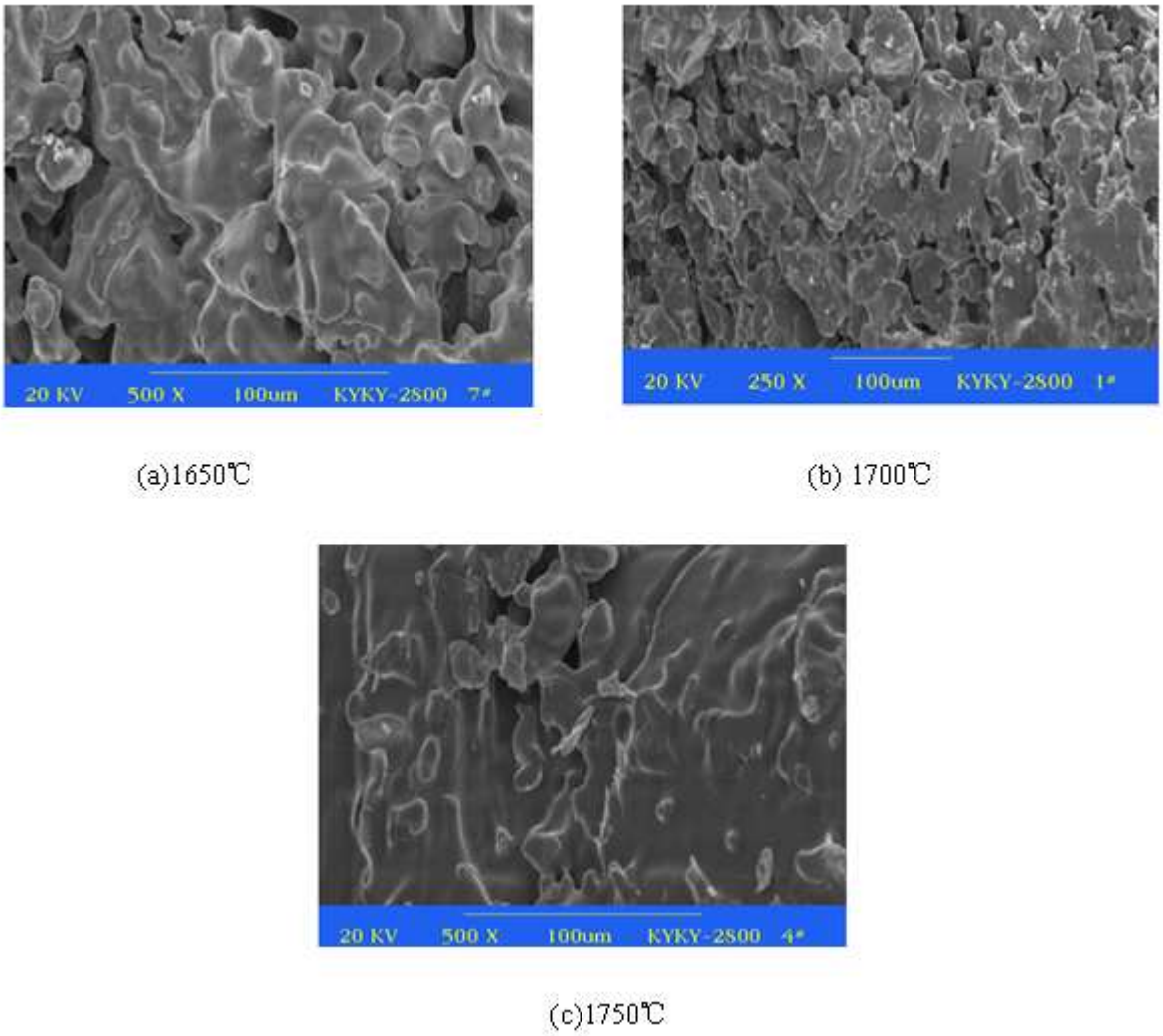

Fig. 4 SEM photos of speciments after fired at different temperature

Larger lattice energy is in the crystal, ion binding is also more solid, ion diffusion is also more difficult, required higher sintering temperature. Increase of sintering temperature for both the solid phase diffusion or dissolution - precipitation is beneficial to mass transfer. But the mere increase of sintering temperature is not only a waste of fuel, not economic, but also to promote secondary recrystallization and create deterioration of the sample. In liquid phase sintering, the excessive high temperature makes liquid content increased, viscosity decreases, create the sample deformation.

Fig.4 shows that SEM photographs of speciments after fired at different temperatures. In the magnesia - zirconia (MgO-ZrO_2) refractories, because of` the introduction of fused magnesia and impurities of magnesium zirconium powder, lower the temperature of liquid appeared, for 1470 ^oC to1555^oC, which would harm the high temperature properties of materials. However, with the second solid phase zirconia, solid - solid combination between them will increase, which ensures the continued existence of the second solid phase under the temperature (which is shown in Fig.4b), which eliminates inherent weaknesses that formed liquid can penetrate between the grains of periclase in the use and improve the material strength, thermal shock resistance and corrosion resistance, and can guarantee the disappearing of crack, cracking and peeling. From the photos of the microstructure, we know that zirconia particles are spherical and the size is small, the majority distributed in the magnesia grains. Because of the role of the solid solution, the volume diffusion rate of magnesia increased at high temperature, wrapped stomatal is much small compared with non - zirconia specimens, The grain size of magnesia is similar to non- zirconia specimens[6] . The addition of zirconia promotes holes' s migration and exclusion to grain boundary in the sintering process. It can be seen that the best sintering is at 1700^oC.

Conclusions

According to experiment and analyzing, the following conclusions are considered:The critical granularity of aggregates is 3 mm and the composition includes 4 classes, such as 3mm to 2 mm about 10 percent, 2mm to 1 mm about 15 percent,1mm to 0.5 mm about 25 percent, less than 0.5 mm about 10 percent; Fine fused magnesite powder with the size less than 200 meshes about 20 percent and fine fused magnesia-zirconia's powder with the size less than 325 meshes about 20 percent are carried on composition, burned samples that sintered at 1700 ^oC can get magnesia - zirconia heterogeneous material of fine bulk density, modulus of rupture and lower apparent porosity.

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