Development Trend of Low Thermal Conductivity Ceramic Materials

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Abstract. In recent years, high entropy ceramics have become one of the research hot spots in the ceramic field due to its superior high entropy characteristics, and the use of blast furnace slag as high entropy material is also in line with the general trend of energy conservation and emission reduction in today's society. This paper will briefly introduce the preparation and properties of several common porous ceramics by studying the low thermal conductivity mechanism of traditional ceramic materials. The high entropy ceramic materials are further introduced. By introducing its low thermal conductivity principle, preparation process and its low thermal conductivity related experiments, the superior performance of low thermal conductivity high entropy ceramic materials compared with traditional porous materials is demonstrated, the development trend of low thermal conductivity ceramic materials is analyzed, and finally the application prospect of blast furnace slag in high entropy materials is prospected.

1. Introduction
In recent years, materials with low thermal conductivity, especially oxide ceramics, have attracted much attention due to their potential as thermal barrier coatings for high-temperature engines. Traditional ceramic materials use porous structures to reduce thermal conductivity, while new high entropy ceramics use their high entropy characteristics to achieve low conductivity. This article will analyze the development trend of low thermal conductivity ceramic materials from the related introduction of traditional porous ceramics to low thermal conductivity and high entropy ceramics.

2. Development of Traditional Porous Ceramics with Low Thermal Conductivity
When it comes to low thermal conductivity ceramic materials, we have to talk about its low thermal conductivity. Reducing the thermal conductivity of ceramic materials is to make the materials have better thermal insulation performance and can be applied to the required fields. This article will explore the low thermal conductivity mechanism of traditional porous ceramic materials and briefly introduce several porous ceramic materials.

2.1. Low Thermal Conductivity Mechanism of Porous Ceramic Materials
In this paper, the low thermal conductivity principle of traditional ceramic materials will be explained by the microstructure and room temperature thermal conductivity of porous yttria stabilized zirconia ceramic (YSZ) with thermal conductivity close to the lower thermal conductivity limit (0.06 W/m·K) [1].

Firstly, we have to measure the pore diameter distribution and pore diameter ratio of the sample to determine its density, and then compare it with the density of the fully dense ceramic of the material, wherein the pore diameter distribution can be obtained by mercury ion implantation method, and the
Porosity can be calculated by measuring the volume and mass, and the density of the fully dense ceramic of the material is known as 6.0 g/cm³.

From the details of pore morphology and intergranular bonding in the sintered ceramic of Figure 1, it can be seen that as the sintering temperature increases from 1450°C to 1550°C, the crystal grains gradually grow and the porosity decreases.

Figure 1. Porous Image of YSZ Sample at Different Temperatures: Interconnection of a 1450 °C, B 1500 °C, C 1550 °C and D typical grains.

Figure 2 shows the pore size distribution of the sample at different sintering temperatures. From the figure one narrow half-peak width single peak can be seen, indicating that the pore size distribution is uniform. Among them, the total volume fraction of the sample pores is reflected by the area range under the curve, and due to the increase of temperature, the crystal grains grow rapidly, resulting in the total volume fraction and average pore diameter of the sample pores decrease with the increase of sintering temperature.

Figure 3 and Figure 4 show the change trend of porosity and room temperature thermal conductivity of the material with solid loading of 10vol% and 15vol% respectively as the temperature increases from 1450°C to 1550°C.

When studying the microstructure of porous yttria stabilized zirconia ceramic, we found that the pores trapped a large amount of air, and the thermal conductivity of air was lower than that of the material, which better blocked the heat transfer. In addition, a large number of voids are connected with each other, which makes the ceramic particles no longer continuous, thus leading to the reduction of heat conduction level. Meanwhile, a large number of pores and micro-sized interfaces provide significant phonon and photon scattering. Therefore, the lower thermal conductivity of the material is caused by the porous structure.
2.2. Porous Ceramic Materials

2.2.1. Porous Anorthite Ceramics with Low Thermal Conductivity
Ye Li [2] et al. have successfully prepared porous anorthite ceramics with low thermal conductivity by direct foaming and grouting with fly ash and gypsum as raw materials, and found that after adding 10% gypsum and 0.8% sodium hexametaphosphate, the porosity of the prepared anorthite ceramics is as high as nearly 95% and the thermal conductivity is as low as 0.042 W/m·K.

2.2.2. Porous Anorthite Ceramics with Low Thermal Conductivity
Yao Han [3] et al. used alumina, calcium carbonate and silicon powder as raw materials to prepare porous anorthite ceramics with low thermal conductivity, as low as 0.018 W/m·k. Then the microstructure of the ceramic samples was analyzed by scanning electron microscope and XRD. The results show that porosity, pore size, pore structure and particle size are all the reasons that lead to the decrease of thermal conductivity.

2.2.3. Porous Mullite Ceramic
Lunun Gong [4] et al. prepared porous mullite ceramic from industrial mullite powder by foaming and starch curing, and characterized its thermal conductivity and studied the effects of suspension solid content and sintering temperature on porosity and compressive strength. The results show that its thermal conductivity is as low as 0.09 W/m·K, the porosity of sintered mullite ceramic is 86%-73% of volume, and the compressive strength is 1-22 MPa. The porous has a multi-modal microstructure and the inner wall has large spherical pores and small pores.

2.2.4. Porous $Y_2SiO_5$ Ceramics
Duanyang Li [5] et al. have successfully prepared porous silica ceramics with neat straight pore structure and low thermal conductivity by TBA-based solidification casting using tert-butyl alcohol as solvent. It is found that the porosity of sintered silica ceramics can be adjusted by adjusting the initial solid load, and when the initial silica content decreases from 20% to 10% by volume, the porosity increases linearly from 45% to 71%.

The above is the principle of traditional low thermal conductivity ceramic materials and introduces some common porous ceramic materials. The following will introduce a new way to reduce the thermal conductivity of ceramic materials, namely synthesizing high entropy ceramic materials.

3. Low Thermal Conductivity and High Entropy Ceramic Materials
Correspondingly to low entropy, high entropy refers to the state where the system is highly chaotic or disordered, compared with traditional materials, high entropy materials are superior, so they have...
received considerable attention in materials science and engineering. In recent years, high entropy ceramics have been widely studied because of their interesting properties, i.e. low thermal conductivity, good high temperature stability, slow diffusion rate and serious lattice distortion.

3.1. Principle of Low Heat Conduction of High Entropy Ceramics

Previously, the research focus of low thermal conductivity materials focused on pore regulation, while high entropy ceramics (HEC) are characterized by the inherent atomic disorder of metal elements at cationic positions, resulting in complex compositions and significant lattice distortion. The following is an example of high entropy carbide ceramics to explore the low heat conduction principle of high entropy ceramics.

Xue-liang Yan et al. synthesized high entropy carbonized ceramic \((Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C\) by spark plasma sintering, in which HfC, ZrC, TaC, NbC and TiC powder are equivalent and mixed. The results show that \((Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C\) has a very low thermal diffusivity \((3.6 \text{mm}^2/\text{s})\) at 29.5 °C, which is 57% of the lowest value \((6.29 \text{mm}^2/\text{s})\) of the five binary carbides at 25°C. With the increase of temperature, the thermal conductivity of this material decreases to \(5.42 \text{W/m·K}\) at 70.8°C.

The low thermal conductivity of \((Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C\) may be caused by the high entropy effect. The main carrier of solid heat transfer is phonon and electron. For transition metal carbide, the contribution of electron at room temperature is about 25% of the total heat transfer. According to WiedemannFranz's law, it is estimated that about 75% of the phonon contribution is left [6]. When HfC, ZrC, TaC, NbC and TiC form a high entropy phase \((Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C\), the contribution of phonon changes greatly when the electronic contribution is not changed. It is found that the five independent metal atoms in the cation position have different bonding strength and size, which leads to the deformation of the atomic scale lattice of the sample, resulting in low thermal conductivity.

3.2. High Entropy Ceramic Materials

3.2.1. Ultra-high Hardness Dense High Entropy Boride Ceramics

Yan Zhang et al [7] prepared ultra-high hardness high density high entropy boride ceramics by spark plasma sintering self-synthesis method. Ultrafine high entropy boride powders \((Hf_{0.2}Zr_{0.2}Ta_{0.2}Cr_{0.2}Ti_{0.2})B_2\), \((Hf_{0.2}Mo_{0.2}Zr_{0.2}Nb_{0.2}Ti_{0.2})B_2\) and \((Hf_{0.2}Mo_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2\) were obtained by boron thermal reduction method. The measured yields were 89.9%, 89.6% and 97.3%, respectively. After solid phase extraction at 2000°C, it is found that high entropy boride ceramics have higher target phase yield.

3.2.2. Reactive Flash Discharge Plasma Sintering of High Entropy Ultra High Temperature Ceramics

Joshua Gild et al [8] synthesized high entropy metal diboride \((Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2\) and high entropy metal carbide \((Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C\) by reactive flash discharge plasma sintering. It is found that the addition of a small amount of carbon can synthesize and homogenize the high entropy metal borides without severe mechanical alloying, so as to avoid serious pollution and oxidation problems.

3.2.3. \((Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C\) low Thermal Conductivity High Entropy Ceramics

Xue-liang Yan et al [9] characterized the phase composition and crystal structure of a high entropy carbide ceramic \((Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C\) synthesized by spark plasma sintering with X-ray diffraction. By comparing its XRD spectrum, lattice parameters and thermal properties, it was confirmed that the single-phase halite structure of five metal elements (Hf, Zr, Ta, Nb, Ti) with cation positions, and its low thermal conductivity coefficient may be due to phonon scattering on its twisted anion sublayer.

3.2.4. High Entropy Ceramic He\((La_{0.2} Ce_{0.2} Nd_{0.2} Sm_{0.2} Eu_{0.2})_2 Zr_2 O_7\)

Zi-fan Zhao et al. [10] designed and successfully synthesized a new high entropy rare earth zirconate \(He\((La_{0.2} Ce_{0.2} Nd_{0.2} Sm_{0.2} Eu_{0.2})_2 Zr_2 O_7\)\) for the first time.XRD and SEM analysis showed that the thermal conductivity of high entropy solid solution was as low as 0.76W/m·K-1 at room temperature due to its slow diffusion effect. The grain growth rate of the material is slower than that of \(La_2 Zr_2 O_7\), making it
hopeful to be used as thermal energy barrier coating material.

With the rapid development of high entropy ceramic materials, they have virtual superior performance compared with traditional low heat conduction porous ceramic materials, which makes them more widely used, and makes them hopeful to replace traditional porous ceramics in more fields and become better low heat conduction materials.

4. Application Prospect of Blast Furnace Slag

As a by-product of steel production, the world's annual blast furnace slag production is a huge number. Different from other European and American countries, China's slag utilization rate has been very low. For example, in 2016, its utilization rate will be less than 30%, and more than 3 million tons of slag will not be utilized. This not only causes environmental pollution, but also is a great waste of resources. The author believes that if blast furnace slag is used as raw material to prepare low thermal conductivity high entropy ceramics, it not only realizes the reuse of waste slag, but also has great potential for carbon dioxide and energy conservation, and is a promising application of blast furnace slag.

5. Summary

This paper mainly introduces the traditional porous ceramics and new high entropy ceramics, reflects the development trend of low thermal conductivity ceramic materials, and forecasts the application prospect of blast furnace slag in high entropy materials.

6. References

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