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Influence of zircon on cristobalite crystallization of silica-based ceramic cores

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Zircon is usually used as a main additive to silica-based ceramic core materials in precise investment casting in order to improve their high temperature properties. But there is still a disagreement in its effect on crystallization behavior of fused silica. In this study, cristobalite crystallization of fused silica in three silica-based core materials containing 10, 30 and 50 wt% zircon respectively were investigated through X-ray diffraction (XRD) and scanning electron microscopy equipped with energy dispersive spectrometer (SEM/EDS). Results showed that zircon addition had neglected effect on cristobalite crystallization during sintering at 1180 °C, 1200 °C, and 1220 °C, but could decrease crystallization during simulated casting process at 1500 °C. It was suggested that diffusion of zirconium atoms played a crucial role in this suppressing behavior of zircon on the cristobalite crystallization. During cooling from 1500 °C, cristobalite transformation from β to α caused microcracks in these samples that containing 10% or 30% zircon. But when zircon content increased to 50%, crack was prevented. Less phase transformation of fused silica \rightarrow cristobalite and enhanced strength by zircon was supposed to be the reason that was responsible for prevented cracks.

Key words: Silica-based ceramic cores, Zircon, Cristobalite transformation.

Introduction

Silica-based ceramic cores play a vital role in manufacturing superalloy gas turbine components with internal cooling passages during precise investment casting. They are usually used with casting temperatures lower than 1550 °C [1, 2]. In order to produce acceptable inner surface finish and thickness of the wall for superalloy components, the properties of the ceramics have to be balanced carefully, such as dimensional conformity, mechanical strength, thermal shock resistance, thermal stability, chemical inertness against the superalloy, enough mechanical weakness during solidification, and easy removability by a process that is not harmful to the metal [3-6]. Many studies have been conducted to prepare ceramic cores with appropriate performance.

Crystallization behavior of fused silica (fused silica \rightarrow cristobalite) in the silica-based ceramics during sintering has a crucial effect on their performance. It is reported that the cores consisting of $10 \sim 20$ wt% cristobalite have balanced properties and could be applied for superalloy casting [7]. Since the amount of cristobalite plays a vital role in determining the performance of the ceramics, it is necessary to study the factors that influence the cristobalite crystallization.

Zircon, or zirconium silicate (ZrSiO₄), has low

coefficient of thermal expansion, high thermal stability and chemical stability, and it is a crucial component in the silica-based ceramic cores [8-12]. Wang and Hon [13] determined the effect of zircon addition on phase transformation kinetics of fused silica \rightarrow cristobalite in the silica-based cores through quantitative X-ray diffraction (XRD) analysis. They found that the presence of zircon could assist the crystallization of fused silica in the initial stage of heating, but retarded the crystallization when the soaking time was increased. Wilson and his coworkers [11] observed the growth front of cristobalite into fused silica grains by optical polarizing microscopy. Their results indicated that zircon had undetectable influence on the transformation of fused silica to cristobalite. And It is pointed out that the promoting behavior of zircon on crystallization of fuse silica in the initial stage of heating reported by Wang and Hon [13] was not affected actually by zircon itself, but by impurities in the zircon grains. There was another work [14] suggested that zircon decreased the formation of the in-situ cristobalite at 1400 °C and higher temperatures, but did not have considerable effect on the crystallization behavior at 1220 °C.

From the above information, it can be seen that although lots of studies has been conducted about the influence of zircon on the crystallization behavior of the silica-based ceramics, there is still a discrepancy in it. Therefore, in this present study, the crystallization behavior and the corresponding microstructure changes of injection moulded silica-based ceramics with different zircon additions (10, 30, 50 wt%) were investigated.

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Table 1. Weight percentages of compounds of the raw materials.

Particle size (µm) Fig. 1. The particle size distribution of the materials to be used.

Experiment

The raw materials in the present experiment are commercially-available ceramic powders (fused silica and zircon sand), and their chemical components are listed in Table 1. The purchased fused silica and zircon sand both were ball milled first, and then sieved to obtain -300 mesh particles. The particle size distribution of the obtained particles is shown in Fig. 1. Three compositions of ceramic bar samples $(100 \text{ mm} \times 10 \text{ mm} \times 4 \text{ mm})$ with different zircon additions (10, 30, 50 wt%), denoted as CKA1, CKA2, and CKA3, respectively, were fabricated through injection moulding method at 120 °C. The prepared samples were then sintered at an electrical resistance furnace. During sintering, the samples were heated to 450 °C at a heating rate of 80 °C/hr, and then holding 4 hrs for dewaxing. After dewaxing, the samples continued to be heated up with a heating rate of 120 °C/hr until the temperature reached 1180, 1200 and 1220 °C. The samples were then sintered at these temperatures for 4 hrs. After being sintered, some of the samples were then exposed to 1500 °C for 1 hr to simulate casting process of superalloy.

The approximate quantities of phases in the investigated samples were identified by an X-ray diffractometer with Ni-filtered Cu Ka radiation (XRD, D8 Discover, Bruker, Germany). It has been proved that crystallization of the fused silica always occurs on the surface of the fused silica grains. So in order to characterize the surface microstructure of the ceramic grains, all the investigated samples were intended ruptured at room temperature through a three point bending test with a span distance of 90 mm and 1 mm/min loading rate. The microstructures of the fractured surface were characterized by scanning electron microscope (SEM, JSM-6301F, JEOL, Japan).

Result and Discussion

Phase transformation



Fig. 2. XRD patterns of the core materials after sintering at different temperatures.



Fig. 3. XRD patterns of the core materials after simulated solidification.

XRD patterns of the samples with various zircon contents before and after simulated casting process are presented in Fig. 2 and Fig. 3. It can be seen that cristobalite peaks are presented in all the samples. This confirms crystallization of fused silica (fused silica \rightarrow cristobalite phase transformation) has occurred before and after simulated casting process. But the amounts of cristobalite in these samples are greatly influenced by this simulated process. Before this process (Fig. 2), all the samples contain small amounts of cristobalite no matter what zircon content and sintering temperature is. This suggests cristobalite crystallization has occurred during sintering. However, this transformation has not proceeded completely, with some amount of fused silica left. This can be deduced from the amorphous XRD peak at 2θ of $20 \sim 30^{\circ}$. After the simulated casting process, large amounts of cristobalite appear in all the samples, which can be found through comparing the relative intensities of the XRD peaks of cristobalite before and after this simulated process (Fig. 2 and Fig. 3).



Fig. 4. XRD patterns of the core materials after simulated solidification.

In order to make clear the effect of zircon addition on the crystallization behavior of fused silica, the XRD peak intensities of cristobalite and zircon at 22.2 ° and 27.2 ° respectively were extracted from the original XRD data (Fig. 2 and Fig. 3) through software of Jade 6. It is known that XRD peak intensity ratio of two phases is in direct proportion to the content ratio of the two phases, so the content of one phase can be obtained by

$$w_c = k \frac{I_c}{I_z} \times w_z \tag{1}$$

in which, w_c and w_z are the contents of cristobalite and zircon, respectively.

 $I_{\rm c}$ and $I_{\rm z}$ are the peak intensities of the two phases, respectively.

k is a proportional constant.

In this present study, the content of zircon (w_z) is given, and thus the relative magnitude of w_c can be calculated. The calculated results are presented in Fig. 4. It is seen that the addition of zircon has negligible influence on the amount of cristobalite during sintering at 1180 °C/4 hr, 1200 °C/4 hr, and 1220 °C/4 hr. This result agrees well with Kazemi's [14].

After the simulated casting process at 1500 °C for 1 hr, the quantities of cristobalite in the samples decrease as zircon addition increases. It is known that, before simulated casting, these samples have already experienced a thermal process (sintering), and there is already some amount of cristobalite. And the amounts of the pre-existed cristobalite are almost the same (Fig. 4). So the influence of this pre-existed cristobalite on the reduced amount of cristobalite in the samples after the simulated casting should be excluded. So it is only zircon that is probably responsible for the reduced crystallization of fused silica.

It is reported [13] that zirconium (Zr) in zircon can diffuse into the surface layer of silica grains to form solid solution, resulting in lattice distortion which may generate compressive stress on the surface layer. And this compressive stress retards further crystallization of the silica particles. So element diffusion of Zr is a precondition for zircon to affect crystallization of fused silica. In the present study, sintering is conducted at temperatures of 1180, 1200 and 1220 °C for 4 hr. These sintering temperatures and holding time are presumed not enough for Zr atoms to diffuse sufficiently into the surface of silica grains to affect crystallization of fused silica. However, during simulated casting at 1500 °C, the temperature is much higher, and Zr atoms can diffuse easily and sufficiently. So in this case, these diffused and solid solution Zr atoms into the silica grains suppress cristobalite crystallization at 1500 °C. The above proved by suggestion can be the following microstructure observation.

Microstructure change

It is well known that during being sintered, crystallization of fused silica in the ceramics occurs on the surface of the fused silica grains. This can be observed on the polished surface of the ceramics, and has been reported by other researchers [4, 11, 14]. In the present study, in order to characterize the surface microstructure of the ceramic particles, the samples were intended ruptured at room temperature through a three point bending.

SEM microstructures of the fractured surface before the simulated casting are shown in Fig. 5. From these figures, it is seen that both the grains of silica and zircon display irregularly sharp-edged shape and the cavities among the grains also have irregular appearance too in all the investigated samples. The XRD results discussed above suggest partial amount of fused silica transforms to cristobalite in these samples. So the irregularly sharpedged grains and cavities here suggest that it is solid phase sintering, not viscous flow sintering, that happens to these samples during sintering process. In addition, the sharp-edged microstructure also indicates elements, such as Zr or impurities in zircon, cannot diffuse easily from zircon to silica grains due to the spacing between the two grains. This confirms the presuming in the above section.

Fig. 6 shows the microstructures of CKA1 samples after simulated casting process. The microstructures of these samples differ greatly from those before the simulated casting (Fig. 5). No sharp-edged grains and cavities were observed. It is deduced that during this simulated casting, viscous flow sintering occurs when exposed temperature is above 1300 °C. This viscous flow sintering leads to a big amount of the left fused silica transforms to cristobalite. This result can be obtained from the XRD patterns (Fig. 3). From Fig. 6, it is also seen that there are lots of transgranular microcracks in CKA1 samples. These microcracks do not exist before simulated casting (Fig. 5), but appear in the samples after this process no matter what the

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Fig. 5. SEM of the samples after sintered at different temperatures. CKA1 sintered at (a)1180 °C/4 hr, (b)1200 °C/4 hr, (c)1220 °C/4 hr CKA2 sintered at (d)1180 °C/4 hr, (e)1200 °C/4 hr, (f)1220 °C/4 hr CKA3 sintered at (g)1180 °C/4 hr, (h)1200 °C/4 hr, (i)1220 °C/4 hr



Fig. 6. SEM of CKA1 samples after simulated casting at 1500 °C. The sintering temperatures before simulated casting are (a) and (d) 1180 °C/4 hr, (b) and (e) 1200 °C/4 hr, (c) and (f) 1220 °C/4 hr.

previous sintering temperature is (Fig. 6). So the thermal exposure experience at 1500 °C should be responsible for this phenomenon.

The CKA2 samples after simulated casting display similar microstructures (Fig. 7) as CKA1. As can be seen in Fig. 7, transgranular microcracks are observed in all the CKA2 samples. But for CKA3 samples, their microstructure differ remarkably from those of CKA1 and CKA2, and no crack is observed (Fig. 8). In addition, in the CKA3 samples, there are still some distinguishable grains that have somewhat sharp edges and do not seem to experience viscous flow sintering. EDS results show the composition of these grains is Zr 16.6 at%, Si 15.2%, O 68.2%, indicating they are zircon (ZrSiO₄). In CKA1 and CKA2 samples, this kind of grains also exists, but their amounts are smaller.

As for the microcracks found in CKA1 and CKA2,

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(a) 50 um(b) 50 um(c) 50 um 50 um(c) 50 um 50 um(f) 10 um10 um

Fig. 7. SEM of CKA2 samples after simulated casting at 1500 °C. The sintering temperatures before simulated casting are (a) and (d) 1180 °C/4 hr, (b) and (e) 1200 °C/4 hr, (c) and (f) 1220 °C/4 hr.



Fig. 8. SEM of CKA3 samples after simulated casting at 1500 °C. The sintering temperatures before simulated casting are (a) and (d) 1180 °C/4 hr, (b) and (e) 1200 °C/4 hr, (c) and (f) 1220 °C/4 hr.

not in CKA3, there are two competitive reasons that may be responsible for it. One is the driving force of tensile stress caused by phase transformation; the other is strength of the material. It is reported that cristobalite transforms from β -cristobalite to á-cristobalite at around 200 °C during cooling from high temperatures [4]. This transformation causes a large volume shrinkage and introduces tensile stress on the surface of silica grains [15], and thus leads to large amount of microcracks in the ceramics. In the present study, the quantity of cristobalite in CKA3 sample is smaller than those in CKA1 and CKA2, which means the tensile stress caused by β cristobalite to α -cristobalite transformation, is smaller in CKA3. Besides, CKA3 contains much more zircon (50%) than CKA1 (10%) and CKA2 (30%). Zircon has higher strength than silica, and cracks initiate and propagate much more hard in zircon grains than in silica

grains [14]. So the much higher stress and lower strength of CKA1 and CKA2 samples are considered to be the reasons that are responsible for the observed microcracks.

The ceramic core materials should not only have enough mechanical strength to resist thermal shock of pouring alloy molten during casting, but also have enough mechanical weakness so that it would crush (crushability) during cooling otherwise it will impose deleterious and destructive stress into the metal. This kind of stress in the metal can lead to recrystallization of single crystal superalloys, grain boundary cracking in directionally solidified castings, or hot-tearing in equiaxed castings [12]. From this viewpoint, the cracks in CKA1 and CKA2 samples after simulating casting can benefit crushability of the cores while CKA3 cannot. So, for silica-based ceramic cores, in order to exhibit good crushability, the amount of zircon should 850 Jing-jing Liang, Quan-hong Lin, Xuan Zhang, Tao Jin, Xiao-feng Sun, Baig-gyu Choi, In-soo Kim, Jeonghyun Do and Chang-yong Jo

be controlled lower than 50 wt%.

Conclusions

In this work, the Influence of zircon content (10, 30 and 50 wt%) on the crystallization behavior of silicabased ceramic core materials were investigated by XRD analysis and SEM observation. The obtained results can be summarized as follows:

A small amount of fused silica transformed to cristobalite during being sintered at $1180 \sim 1220$ °C for 4 hrs, and the addition of zircon had negligible influence on cristobalite crystallization of fused silica during this process.

1. Zircon addition decreased crystallization of fused silica during simulated casting process at 1500 °C. It was suggested that it was the solid soluted Zr atoms that diffuse from zircon grains into silica grains played a vital role in suppressing the cristobalite crystallization at this temperature.

2. During cooling from 1500 °C, cristobalite transformation from β - to α -structure could bring in tensile stress, and this stress caused microcracks in the samples that contained 10% and 30% zircon. But when zircon content increased to 50%, the less phase transformation stress and enhanced strength prevented crack formation.

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