High-Performance Ceramic-Lined Composite Pipes with ZrO2 Additive Prepared by Centrifugal-SHS Process

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High-performance ceramic-lined composite steel pipes (CLCSPs) were fabricated by self-propagating high-temperature synthesis and centrifugal casting technique. ZrO2 powders doped by 3 mol\% Y2O3 were added into Al-Fe3O4 thermit to improve the mechanical properties of CLCSPs. The phase constituents and microstructural evolution of ceramic layers after addition of ZrO2 were analyzed by means of X-ray diffractometer, optical microscope, scanning electron microscope and energy dispersive X-ray spectrometer. The effects of ZrO2 on fracture toughness of ceramic layers, and crushing strength as well as mechanical shock of CLCSPs were investigated using Vickers indentation microscopy method, squeezing test and repetitive impacting method. The results show that addition of ZrO2 changes the morphology and preferential orientation of Al2O3 dendrites, and reduces the width of Al2O3 dendrites, leading to the microstructure of Al2O3 dendrites with fine t-ZrO2 phase particles distributed at boundaries. The hardness of ceramic layer decreases, while the crushing strength of CLCSP changes slightly after addition of ZrO2. The fracture toughness of ceramic layer is significantly enhanced; meanwhile the mechanical shock resistance of CLCSPs was also greatly improved by adding more than 2\% ZrO2. The optimum adding amount of ZrO2 is 4\%–6\%. [doi:10.2320/matertrans.MC201503]

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1. Introduction

Centrifugal self-propagating high-temperature synthesis (Centrifugal-SHS) is a new technology for preparation of ceramic-lined composite steel pipes by combining SHS with the centrifugal casting technique. CLCSPs have pronounced advantages such as long life cycle, light weight, low cost, and high resistance to abrasion, corrosion, erosion and heat. Using the novel technology, Odawara \textit{et al.} successfully developed 5.5 m long Al2O3 ceramic-lined composite steel pipes, which have been recommended for industrial applications to transport the coal cinder, mineral powder, limestone flour and oil-water mixture.\textsuperscript{1–3} However, a serious problem has faced this kind of composite pipes since they were initially invented. It is the poor fracture toughness of Al2O3 ceramic layer. Cracking and spallation of the Al2O3 lined layer are often caused by the large thermal stress in preparation and/or careless mechanical shock in subsequent processes including machining screw thread, transport and installation. The problem must be addressed if large-sized CLCSPs are applied in oil and mineral industries, where mechanical shock is inevitable during the transport and construction of CLCSPs.

Various additives such as MgO, SiO2, Na2B4O7 and Si (silicon sludge) have been used to reduce the melting temperature of Al2O3 ceramic layer, decrease the porosity, and increase the densification and fracture toughness.\textsuperscript{4–7} However, the effects of these additives on improvement of fracture toughness of Al2O3 ceramic layer are typically limited due to the brittle nature of Al2O3 ceramics. It is well known that introducing of fine zirconia (ZrO2) particles in Al2O3 matrix results in a large enhancement of basic mechanical properties like flexural strength and fracture toughness.\textsuperscript{8,9} Zirconia-Toughened-Alumina (ZTA) ceramics consists of an alumina matrix in which there are embedded zirconia particles, either unstabilized or stabilized. The main toughening mechanisms associated with zirconia toughening alumina are mainly based on the stress-induced tetragonal$\rightarrow$monoclinic martensite transformation toughening and microcrack toughening. The main toughening source of toughening mechanisms is the presence of retained tetragonal zirconia (t-ZrO2) phase particles dispersed in Al2O3 matrix; hence the toughening effect is intensely dependent on the content of retained t-ZrO2 phase particles. Only few works have been reported so far on microstructure and mechanical properties of ZTA ceramic-lined composite steel pipes produced by centrifugal-SHS process. Yu \textit{et al.} investigated the toughening mechanism of lined Al2O3-ZrO2 multiphase ceramics in gravitational separation SHS composite steel pipes.\textsuperscript{10} They prepared the hypo-eutectic and hypereutectic Al2O3-ZrO2 multiphase ceramic layers by adding large amounts of 2 mol\% doped ZrO2 powders to the thermit powder mixtures, i.e. 20\% and 40\% respectively. There were 81.44 vol\% and 71.04 vol\% ZrO2 particles retained in metastable tetragonal form for the hypo-eutectic and hypereutectic Al2O3-ZrO2 multiphase ceramic layers, respectively. The fracture toughness was improved considerably, 15.96 and 15.23 MPam\textsuperscript{1/2} for hypo-eutectic and hypereutectic Al2O3-ZrO2 multiphase ceramic layers, respectively via mechanisms of bridging toughening, stress-induced transformation toughening and microcrack toughening. However, adding such a large amount of ZrO2 powders in the thermit may greatly raise the production cost of CLCSPs, which limits the application of CLCSP.

The unique characteristics associated with centrifugal-SHS technique can be utilized for preparation of high-toughness CLCSP by adding only a small amount of ZrO2 powders in the thermit. As it is known that there is a great difference in
cooling rate and thermal stress between centrifugal-SHS and gravitational separation SHS. During the centrifugal-SHS preparation of CLCSP, the cooling rate of CLCSP is rapid due to high rotational velocity of the centrifuge machine. Since the melts of ceramic layer and Fe-rich layer solidify at different temperatures, a unique residual thermal stress distribution is produced due to a large difference in coefficient of thermal expansion between the two layers. The steel substrate pipe is subjected to residual tensile stress, while the ceramic layer and Fe-rich layer suffer from a large residual compressive stress. Compressive stress is reported to be beneficial for existence of ZrO2 in metastable tetragonal form. Therefore, it is expected that employing centrifugal-SHS technique can have a high volume ratio of t-ZrO2 in Al2O3 ceramic layer, and enhance the fracture toughness by adding only a small amount of zirconia to Al-Fe2O3 thermit.

In this paper, centrifugal-SHS CLCSPs were produced by adding small amounts of 3 mol% Y2O3 doped ZrO2 powders to the thermit. The adding amount of ZrO2 powders ranged from 2% to 8%. The effects of ZrO2 addition on the microstructures, hardness and fracture toughness of ceramic layers as well as mechanical shock resistance of CLCSPs were investigated.

2. Experimental Procedure

The substrate material was a J55 steel with chemical composition as listed in Table 1. The testing pipes of 400 mm in length were cut from a 10 m long J55 steel oil pipe with 73.02 mm diameter and 5.51 mm wall thickness for usage of centrifugal-SHS process. The pure powders, Fe2O3 (≥99%, 75–150 μm) and Al (≥99.5%, 75–150 μm) were used as the based thermit reactants, and 3 mol% Y2O3 doped ZrO2 powder was done as an additive. The as-received ZrO2 powders doped by 3 mol% Y2O3 were prepared by a titration reaction process. The adding amount of ZrO2 ranged from 2% to 8% for the thermit reactants of Al+F2O3. The chemical mole ratio of the Al and F2O3 powders conformed to the following chemical reaction:

\[ \text{Fe}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Fe} \quad \Delta H = -836 \text{ kJmol}^{-1} \]  

Prior to each preparation of centrifugal-SHS CLCSP, the thermit reactants with different amounts of ZrO2 additive were mixed for 1 h using a barrel mixer, and then dried thoroughly at 373 K for 2 h. The J55 steel pipe was loaded with the thermit mixture, and placed horizontally on the SHS-centrifugal apparatus. When the required rotational velocity of the centrifuge apparatus was reached, the thermit mixture was ignited by a tungsten filament at one end of the pipe. Upon the completion of the reaction, the centrifuge apparatus was allowed to run for 10 more minutes until the CLCP cooled down.

The phase constituents in 3 mol% Y2O3 doped ZrO2 powders and Al2O3 ceramic layers adding with ZrO2 were identified by means of a Ragaku D/MAX 200PC diffractometer using CuKα radiation. The volume fractions of monoclinic ZrO2 (Vm) in Al2O3 ceramic layers adding with ZrO2 were calculated using the following relation:

\[ V_m = \frac{I(111)_m + I(1\bar{1}1)_m}{I(111)_m + I(11\bar{1})_m + I(111)_t} \]  

where \( I \) is the integral intensity and the subscripts \( m \) and \( t \) refer to the monoclinic and tetragonal ZrO2 phases, respectively. The intensities were corrected for the background. The morphology and phase constituents of ZrO2 powders doped by 3 mol% Y2O3 were analyzed by SEM and XRD, as shown in Fig. 1 (a) and (b), respectively. From Fig. 1 (a), it can be seen that the size of ZrO2 powders ranges from 30 to 100 nm. The XRD analysis reveals that there are two phase constituents in ZrO2 powders, i.e. the tetragonal and monoclinic ZrO2 phases. The volume fractions of m-ZrO2 and t-ZrO2 are 32.1% and 67.9% by eq. (2), respectively.

The microstructures of ceramic layers adding with ZrO2 were observed under a LEXT-OLS3000 confocal scanning laser microscope. The mechanical properties of the CLCSPs prepared with adding different amounts of ZrO2 were investigated through hardness test, squeezing test and mechanical shock test. The Vickers hardness of ceramic layers was measured using a load of 500 gf for a dwell period of 15 s. Squeezing test represents the crushing strength of the ceramic layer. The crushing strength of CLCSPs was measured using

| Table 1 Chemical composition of J55 steel oil pipe. |
|-----------------|---|---|---|---|---|---|---|
| Element | C  | Si | Mn | P  | S  | Al | V  |
| Content (%)  | 0.370 | 0.240 | 1.290 | 0.013 | 0.006 | 0.040 | 0.015 |

Fig. 1 SEM image (a) and XRD pattern (b) of 3 mol% Y2O3 doped ZrO2 powders.
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MTS810 material test system. In the crushing test, a piece of pipe of 50 mm length was compressed in the radial direction, the corresponding schematic diagram and photograph of the compression test are shown in Fig. 2. The crushing strength was calculated using formula described by Odawara

\[ \sigma_c = \frac{F}{L t} \times \frac{1}{\pi(1 + k)} \times \left( 1 + \frac{1}{k} \left( \frac{t}{D + t} \right) \right) \] (3)

where \( L, t \) and \( D \) are the length, thickness and average diameter of the test pipe, respectively, \( F \) is the turning point load deviated from straight line at the compress load–displacement curve, and \( k \) is a cross section factor.

\[ k = 1 + \frac{D}{2l} \times \ln \left( \frac{D + l}{D - l} \right) \] (4)

The fracture toughness of ceramic layer \( K_{IC} \) was obtained through Vickers indentation microfracture method, which correlates \( K_{IC} \) with the length of cracks emanating from the Vickers indentation corners. The Vickers indentation was obtained using a load of 10 kgf for a dwell period of 15 s. The fracture toughness was calculated using the following equations:

\[ \left( \frac{3K_{IC}}{Ha^{1/2}} \right) \left( \frac{H}{3E} \right)^{2/5} = 0.035 \left( \frac{l}{a} \right)^{-1/2} \left( 0.25 \leq \frac{l}{a} \leq 2.5 \right) \] (5)

\[ \left( \frac{3K_{IC}}{Ha^{1/2}} \right) \left( \frac{H}{3E} \right)^{2/5} = 0.129 \left( \frac{l}{a} \right)^{-3/2} \left( \frac{l}{a} \geq 2.5 \right) \] (6)

where \( E \) and \( H \) are the Young’s modulus and Vickers hardness values, respectively, \( a \) is the half-diagonal of the Vickers indent, and \( l \) is the length of surface crack.

The mechanical shock was measured with the repetitive impacting method using a steel ball in 50 mm diameter. The mechanical shock resistance of CLCSPs prepared with different amounts of ZrO2 was evaluated in terms of the impact times that the ceramic layer produced crack under an impact energy of 25 J. The impact energy of 25 J is a proper value for leaving behind an impact sign but not an evident deformation pit on the CLCPs. The impact locations were chosen at the centers and the edge ends of 200 mm long CLCPs, respectively. The cracking and spallation of ceramic layers were observed using a 500 thousand pixel USB camera, which could detect the crack length of 0.1 mm.

### 3. Results and Discussion

#### 3.1 Microstructures of ceramic layers

The thickness of ceramic layers and Fe-rich layers was measured for the prepared CLCSPs, the results are listed in Table 2. XRD patterns of ceramic layers produced by adding different amounts of ZrO2 are shown in Fig. 3. Two types of phase constituents were identified in the ceramic layer without ZrO2, Al2O3 and FeAl2O4 phases (Fig. 3 (a)), while Al2O3, FeAl2O4 and t-ZrO2 phases were found in ceramic layers with adding 2%–8% amount of ZrO2; but no m-ZrO2 phase was detected (Fig. 3 (b) to (e)). This phenomenon is interesting because the raw ZrO2 powders consist of two phases, about 32.1% of m-ZrO2 and 67.9% of t-ZrO2. The m-ZrO2 phase has been detected more or less in the ZTA ceramics or in lined Al2O3-ZrO2 multiphase ceramic layers of gravitational separation SHS composite steel pipes when they were prepared using the powder mixture of Al2O3 and ZrO2 stabilized by 3 mol% Y2O3 by conventional sintering technique or by gravitational separation SHS process. The presence of only metastable tetragonal ZrO2 phase in the ceramic layer is beneficial for enhancement of fracture toughness. The absence of m-ZrO2 phase in the ceramic layers might be related with the solidification features of CLCSPs produced by centrifugal-SHS process. The in-process of SHS centrifugal casting, the cooling velocity of CLCSP was quite fast, the Al2O3-ZrO2 melt solidified first into ceramic layer due to its higher melting temperature of about 1983–2303 K, then followed by solidification of Fe-rich melt. The steel pipe and Fe-rich layer have a higher coefficient of thermal expansion than the ceramic layer; therefore a large compressive stress can be produced in the ceramic layer during cooling to room temperature. Wang and Yang analyzed the temperature distribution and transformation during the cooling process of the CLCSP preparation with finite element numerical simulation; and they found a large compressive stress up to 152.22 MPa produced in the Al2O3 ceramic layer. It has been reported that the transformation from tetragonal→monoclinic phase can be delayed below room temperature when ZrO2 particles are smaller than the critical size of 0.7 μm and suffer from a large compressive stress in the Al2O3 matrix. Despite the raw ZrO2 powders are partially stabilized in tetragonal form in the present study, the large compressive stress produced during the rapid cooling period may inhabit the tetragonal→monoclinic martensite transformation until room temperature.

<table>
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<th>ZrO2 (%)</th>
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<th>4</th>
<th>6</th>
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<tr>
<td>Ceramic layer (t/ mm)</td>
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<td>1.73</td>
<td>1.75</td>
<td>1.78</td>
<td>1.98</td>
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<tr>
<td>Fe-rich layer (t/ mm)</td>
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<td>0.85</td>
<td>0.85</td>
<td>0.83</td>
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Fig. 2 Schematic diagram (a) and photograph (b) of the compression test.
leading to the presence of only t-ZrO$_2$ phase in the ceramic layers.

The cross-sectional microstructure evolution of ceramic layers after adding different amounts of ZrO$_2$ can be seen from Fig. 4 (a) to (f). The microstructure of ceramic layer without ZrO$_2$ consists of long columnar dendrites of Al$_2$O$_3$ with an average width of about 11.3 $\mu$m and spinel-like structure FeAl$_2$O$_4$ distributed at dendrite boundaries (Fig. 4 (a)). The columnar dendrites of Al$_2$O$_3$ demonstrate a strong preferred growth orientation, i.e. along the radial direction of the CLCSP. After addition of ZrO$_2$, the preferred growth orientation of Al$_2$O$_3$ columnar dendrites is effectively hindered along the radial direction. With increasing the amount of ZrO$_2$ to 6%, the width of Al$_2$O$_3$ dendrites is reduced to about 7.7 $\mu$m (Fig. 4 (d)). As ZrO$_2$ is increased to 8%, the columnar dendrites are transformed into the egg-shaped dendrites (Fig. 4 (e)). The refinement of Al$_2$O$_3$ dendrites is beneficial for enhancement of fracture toughness to a certain extent. In addition, most of ZrO$_2$ particles are found to be fine with a size below 1.0 $\mu$m, and they are distributed at boundaries of Al$_2$O$_3$ dendrites together with FeAl$_2$O$_4$ phase. Apparently, the preferred growth orientation considerably changed after addition of ZrO$_2$ additive. The change in preferred orientation is characterized by the preferred orientation factor $f$, which is defined as:

$$f = 1 - 2 \frac{a}{(x + a)}$$  \hspace{1cm} (7)

where $x = I_{hkl}^{(hkl)} / I_{uvw}^{(uvw)}$, $a = I^{(hkl)}_{a} / I^{(uvw)}_{a}$, $I^{(hkl)}_{o}$ and $I^{(uvw)}_{o}$ represent the integral intensity of peaks of (hkl) and (uvw) planes of Al$_2$O$_3$ phase in ceramic layers, $I^{(hkl)}_{o}$ and $I^{(uvw)}_{o}$ refer to the integral intensities of peaks of (hkl) and (uvw) planes of Al$_2$O$_3$ powder given by ASTM card. From eq. (7), it can be seen that when Al$_2$O$_3$ ceramic layer has a single preferred orientation (hkl), $x \to \infty$ and $f \to 1$; conversely, $x \to 0$ and $f \to -1$ for a single preferred orientation (uvw). When the Al$_2$O$_3$ ceramic layer has no preferred orientation (similar to the diffraction intensity of Al$_2$O$_3$ powder from ASTM card), $x \to a$ and $f \to 0$.

Three preferred orientation factors are calculated, they are $f (300)/(116), f (104)/(116)$ and $f (300)/(104)$. The preferred orientation can be determined by comparison of these three factors. The results are plotted in Fig. 5 against amount of ZrO$_2$. The ceramic layer without ZrO$_2$ has an intense preferred orientation (300) with $f (300)/(116) = 0.718$. With increasing the amount of ZrO$_2$, the preferred orientation (300) weakens and transforms to (104) at both 0.2% and 0.4% ZrO$_2$, and then comes back again to the preferred orientation (300) with $f (300)/(116) = 0.438$, but not as intense as without ZrO$_2$, and finally to a balanced state between...
the preferred orientations of (300) and (116). This indicates that ZrO₂ addition has a great influence on the solidification process of Al₂O₃ melt. The decrease of preferred orientation (300) in ceramic layer after ZrO₂ addition can improve the fracture toughness to a certain extent, because the Al₂O₃ ceramic layer usually cracks in an intergranular fracture mode along the radial direction.

In order to further identify the distribution of phase constituents in the microstructure of the ceramic layer, elemental mappings of O, Zr, Fe and Al elements were measured on the polished surface of ceramic layer specimen with adding 8% ZrO₂ using SEM and EDS, as shown in Fig. 6. Oxygen element was distributed homogeneously on the polished surface since all the three phases in the ceramic layer, Al₂O₃, FeAl₂O₄ and ZrO₂, contained a high content of oxygen element. Iron and zirconium elements were found mainly at boundaries of Al₂O₃ dendrites where the aluminum element was consequently less. This also demonstrates that both FeAl₂O₄ and ZrO₂ phases are distributed at boundaries of Al₂O₃ dendrites.

The melting temperatures of Al₂O₃, FeAl₂O₄ and Fe are 2303, 2053 and 1809 K, respectively. Based on the above observations, it is presumed that the microstructures of ceramic layers may be produced as follows: during the solidification of the thermit melt without ZrO₂, the Al₂O₃ nucleated first and grew towards the heat releasing direction i.e. along the radial direction of the pipe, forming the long columnar dendrites. Then the FeAl₂O₄ eutectic phase began to form on the boundaries of Al₂O₃ dendrites at about 2023 K (according to Al₂O₃-FeO binary diagram). After addition of ZrO₂, ZrO₂ powders completely dissolved into the Al₂O₃ melt during centrifugal-SHS reaction, and then in the process of solidifi-
cation, the Al$_2$O$_3$ nucleated first and grew into dendrites until the eutectic temperature of about 1983 K (according to Al$_2$O$_3$-ZrO$_2$ binary phase diagram), at which the remained melt was already driven to boundaries of Al$_2$O$_3$ dendrites and transformed into the eutectics which mainly contained ZrO$_2$ and FeAl$_2$O$_4$ phases.

### 3.2 Hardness of ceramic layers and crushing strength of CLCSPs

The average Vickers hardness values were measured at the centers on the cross sections of ceramic layers with different amounts of ZrO$_2$, as shown in Fig. 7. The hardness of ceramic layer without ZrO$_2$ was the highest among the studied ceramic layers, because Al$_2$O$_3$ is harder than ZrO$_2$. With increasing the amount of ZrO$_2$ from 2% to 6%, the hardness of the ceramic layer decreased from 1280 to 1170 HV. The hardness of ceramic layer adding with 8% ZrO$_2$ was the lowest, only 1140 HV, this may be partly due to the low density of the ceramic layer originating from pores in the microstructure, as shown in Fig. 4 (e). In fact, ZrO$_2$ additive did not involve in the thermit reaction directly, and made no contribution to the exothermic combustion, conversely, it absorbed part of exothermic combustion for dissolution into the Al$_2$O$_3$, and decreased the melt fluidity and gas-releasing amount, leading to a low density when ZrO$_2$ additive amounted up to 8%.

In all cases, the ceramic layer is the hardest among the three zones of CLCSPs, i.e. the ceramic layer, Fe-rich layer and steel substrate pipe. It is also found that addition of ZrO$_2$ has almost no influence on the hardness of Fe-rich layer and steel substrate pipe. The hardness of Fe-rich layer is about 200 HV, a little lower than the hardness of 220 HV of the steel substrate pipe. The low hardness of Fe-rich layer may be due to its less carbon content despite a very thin layer of steel substrate could melt and dissolve into Fe-rich layer from the inner surface of the steel pipe.

The radial crushing load vs. displacement curves of CLCSPs prepared with adding different amounts of ZrO$_2$ were measured using MTS810 material test system, as shown in Fig. 8. It can be seen that two horizontal stages occurred in succession on each crashing curve. Our observation reveals that the first one corresponds to the yield deformation at top and bottom locations of the steel substrate pipe; the second one corresponds to the yield deformation at left and right corners of steel substrate pipe. The ceramic layer begins to crack firstly at the top and bottom locations when the curve turns into the rising stage, and finally cracks at left and right locations when the curve suddenly turns into a rapid drop from the climbing state. Therefore, the intersection point of the second horizontal stage and the rising stage represents the compression resistance of a ceramic-lined composite steel pipe. The second horizontal stages of CLCSPs with adding different amounts of ZrO$_2$ are very close to each other in Fig. 8, indicating that ZrO$_2$ addition has only little influence on the crushing strength. In fact, during the compressive testing process, the radial compressive load is mainly undertaken by the steel substrate pipe. Despite the fact that ZrO$_2$ addition can significantly change the microstructure and mechanical properties of the ceramic layer, the microstructure and properties of steel substrate pipe are almost unchanged. From eqs. (3) and (4), the crushing strength values were calculated and listed in Table 3. When 2% ZrO$_2$ was added, the crushing strength reached the maximum of 372 MPa, thereafter it de-
creased with further addition of ZrO$_2$ due to the decrease in elastic modulus with increasing the amount of ZrO$_2$ in Al$_2$O$_3$ matrix.

### 3.3 Fracture toughness and mechanical shock resistance

Figure 9 shows the fracture toughness of ceramic layers measured by Vickers indentation microfracture method. The average value of fracture toughness is increased from 0.56 MPa m$^{1/2}$ of ceramic layer without ZrO$_2$ to 5.74 MPa m$^{1/2}$ of ceramic layer adding with 6% ZrO$_2$, significantly improved by 925%. The indentation-induced crack extension paths of ceramic layers adding with different amounts of ZrO$_2$ were observed under optical microscope, as shown in Fig. 10. It notes that the cracks mainly initiated at top and bottom corners of indentation for ceramic layer without ZrO$_2$, and extended mainly along the growth direction of Al$_2$O$_3$ columnar dendrites in the intergranular fracture mode (Fig. 10 (a)). After adding 2% ZrO$_2$, the cracks initiated and extended in a similar mode to those without ZrO$_2$ (Fig. 10 (b)). When the amount of ZrO$_2$ was increased to a range of 4%–8%, the cracks initiated at all four corners of the indentation, and the crack extension path was a mixture mode of intergranular and intragranular fracture (Fig. 10 (c) and (d)). This may be due to the enhanced fracture toughness and the decreased preferred orientation of Al$_2$O$_3$ columnar dendrites after adding adequate amount of ZrO$_2$. In order to identify the dominant toughening mechanism operating in the ceramic layers with high fracture toughness, a comparison was made between XRD patterns of the polished and fractured surfaces of ceramic layer with adding 4% of ZrO$_2$, as shown in Fig. 11. It is found that about 33.4% volume fraction of t-ZrO$_2$ phase transformed into m-ZrO$_2$ phase after fracture. Therefore, the main toughening mechanism is the stress-induced transformation toughening.

The mechanical shock resistance of CLCSPs adding with different amounts of ZrO$_2$ was measured under 25 J impact energy produced by a steel ball in 50 mm diameter. The impact times that the ceramic layer was observed to crack are shown in Fig. 12. The ceramic layer of CLCSP without ZrO$_2$ began to crack after only twice and 4 times impacts at center and edge of pipe, respectively. After adding ZrO$_2$, the mechanical shock resistance was significantly enhanced, especially for the CLCSPs adding with more than 2% ZrO$_2$, the

<table>
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<td>Crushing strength ($\sigma_f$ MPa)</td>
<td>354</td>
<td>372</td>
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Table 3 Crushing strength of CLCPS adding with ZrO$_2$.

![Fig. 9 Variation in fracture toughness of ceramic layer with amount of ZrO$_2$.](image)

![Fig. 10 Indentation-induced crack extension paths of ceramic layers adding with different amounts of ZrO$_2$: (a) 0%, (b) 2%, (c) 4%, (d) 6%.](image)
ceramic layers could bear 19–22 times impacts at center and 16–20 times impacts at edge, indicating that adding ZrO$_2$ can largely improve the mechanical shock resistance of CLCSPs, improvements are above 850% at center and above 300% at edge, respectively.

The photographs of center and edge locations on the inner surfaces of CLCSPs adding with different amounts of ZrO$_2$ after impact tests are shown in Fig. 13. As can be seen, when more than 2% of ZrO$_2$ was added, the mechanical shock resistance was significantly improved at both center and edge locations. After only twice impacts, a series of cracks initiated at the impact location on ceramic layer without ZrO$_2$, and radially propagated a rather long distance up to 50 mm (Fig. 13 (a)), whereas after 19–22 times impacts, only a small spallation of about 5 mm length emerged at the impact location on ceramic layers adding with 4%–8% ZrO$_2$ (Fig. 13 (b)). Furthermore, no crack was observed forming around the spallation locations of ceramic layers adding with more than 2% ZrO$_2$. The impact tests on edges of CLCSPs adding with different amounts of ZrO$_2$ revealed that after only three times impact, a spallation of about 7 mm in length was produced at the edge of ceramic layer without ZrO$_2$ (Fig. 13(c)), while a small spallation of 5 mm in length was formed at the edge of CLCSPs adding with 4%–8% ZrO$_2$ (Fig. 13(d)).
ceramic layer adding with 4% ZrO₂ after 19 times impact (Fig. 13(d)), and a spallation of 9.7 mm in length produced at the edge of ceramic layer adding with 8% ZrO₂ after 20 times impact (not shown here). The above results suggest that ZrO₂ addition can greatly improve the resistance of the ceramic layer against the initiation and propagation of crack.

Based on the experimental results, addition of 4–6% ZrO₂ produces the optimum combination of hardness, crushing strength, fracture toughness and mechanical shock resistance for the studied CLCSPs. Therefore, preparation of centrifugal-SHS CLCSPs with adding 4–6% of ZrO₂ can maintain the required mechanical properties and keep the production cost at a reasonable level, more important is that subsequent procedures such as machining, transport and installation can be performed smoothly due to the great enhancements of fracture toughness and mechanical shock resistance of ceramic layers.

4. Conclusions

(1) CLCSPs adding with 2%–8% ZrO₂ additive were fabricated by centrifugal-SHS technique. The phase constituents of ceramic layers were Al₂O₃, FeAl₂O₄ and t-ZrO₂ phases, no m-ZrO₂ phase was detected by XRD.

(2) After adding ZrO₂, the microstructure of the ceramic layer changed remarkably. With increasing the amount of ZrO₂, Al₂O₃ dendrites decreased in width, and the morphology transformed from columnar to egg-shaped with fine ZrO₂ particles distributed at dendrite boundaries.

(3) The hardness of ceramic layer decreased, while the crushing strength changed slightly after addition of ZrO₂. The fracture toughness of ceramic layers was significantly enhanced; the mechanical shock resistance of CLCSPs was also greatly improved after adding 4–6% ZrO₂.

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