

Study on Thermal Shock Resistance of Plasma Sprayed ZrO₂ Coating

Yuan Donglin, Li Wenge, Zhao Yuantao

Abstract— In this paper, the research progress of thermal shock resistance of zirconia ceramic materials is summarized, and the effects of different stabilizers on the thermal shock resistance of zirconia ceramic materials are briefly described. Through research, it is found that when adding cerium oxide with a mass fraction of 5.5% in the zirconia ceramic coating, the thermal expansion property of the coating can be minimized to improve the thermal shock resistance of the coating.; A 25% mass fraction of CeO₂ is dissolved in the nano-yttria partially stabilized zirconia coating to form a stable tetragonal phase compound, which improves the thermal shock resistance of the coating.; adding a mass fraction of 3.0% SiO₂ to the zirconia ceramic coating, the coating produces uniform pores, The modulus of elasticity and the stresses received are minimal, making the coating best resistant to thermal shock.

Index Terms— high temperature coating; ceramic material; stabilizer; thermal shock resistance

I. INTRODUCTION

With the rapid development of aerospace and marine shipbuilding, the application environment conditions of aerospace and marine ship engines will become more and more severe. The hot end components (turbine discs, turbine blades, combustion chambers, etc.) on the aero engine are one of them. The working temperature of the hot end components is as high as 1400 °C or higher, which exceeds the normal working limit temperature of the high temperature nickel base alloy by about 350°C^[1]. Ceramic materials have excellent properties such as high temperature resistance, wear resistance and corrosion resistance. They are ideal high temperature structural materials and are widely used in high temperature engineering. However, due to their brittleness and poor thermal shock resistance, their applications are limited. Thermal shock resistance refers to the ability of a material to withstand rapid changes in temperature without being destroyed. In the environment of temperature change(thermal shock), the strength of structural ceramic materials will be greatly reduced, and peeling or even brittleness will use.

Therefore, to study the effect of thermal shock resistance on the properties of high temperature structural ceramic materials, and to explore ways to improve the thermal shock resistance is a problem to be solved. In this paper, the research progress of thermal shock resistance of zirconia ceramic

materials is summarized. The main factors affecting the thermal shock resistance of zirconia ceramic materials are briefly described, and the future development direction of zirconia ceramic materials' thermal resistance is pointed out.

II. RESEARCH STATUS AT HOME AND ABROAD

After decades of research, the composition and structure of high temperature resistant coating materials have been greatly improved. According to the selection of components and the optimization of structure, the development research experience of high temperature resistant coatings can be simply divided into the following periods:

In the 1960s, the β₂NiAl-based aluminide coating was successfully developed. However, the 1NiAl phase is brittle and easily cracked, and the Al atoms diffuse rapidly toward the substrate in a high temperature environment, resulting in a short coating life.^[2-3]

In the 1970s, improved aluminide coatings, such as Al₂Cr, Al₂Si, Al₂Ti, and Pt₂Al, were introduced. Among them, the platinum-aluminum compound coating formed by Pt-plated Al has a longer service life and became popular. Hot spots, there are still relevant research reports.

In the 1980s, a plasma sprayed MCrAlY coating that could adjust the coating composition and provide high temperature oxidation resistance at higher temperatures was developed. This is also the most common metal bonding layer they have used in TBCs. It overcomes the weakness of the traditional aluminide coating and the matrix, and has a significant improvement in resistance to high temperature oxidation.

Ceramic thermal barrier coatings (7% Y₂O₃ partially stabilized ZrO₂ coated TBCs), which have been widely studied and used since the late 1980s, have significant thermal insulation effects and are stable in high temperature environments, showing great advantages^[4-5]

A. Research status of Zirconium Oxide ceramics

Zirconium dioxide series coating is one of the most widely used high temperature resistant ceramic coatings. It has high temperature insulation performance, stable phase at high temperature, erosion resistance, and is not easily wetted by liquid metal. Since its inception in the early 1970s, it has been widely used in high temperature working parts such as gas turbine hot end parts and turbine blades. About 300t ZrO₂ is used annually on high temperature ceramic coatings (2003), and thermal barrier coatings will reach an annual growth rate of 12% in the next 10 years, with an annual growth rate of 25% in engine components has broad application development prospects. Many researchers have conducted in-depth research on the thermal shock resistance and high temperature oxidation resistance of ZrO₂ series coatings in atmospheric high temperature environment^[6-8].

The first ceramic layer material used for TBCs was MgO or

Yuan Donglin Merchant Marine academy & Naval Architecture and Ocean Engineering, Shanghai Maritime University, Shanghai Lingang new city 21306, China

Li Wenge Merchant Marine academy, Shanghai Maritime University, Shanghai Lingang new city 201306, China

Zhao Yuantao Merchant Marine academy, Shanghai Maritime University, Shanghai Lingang new city.201306, China

CaO fully stabilized ZrO₂ (MSZ or CSZ), but it was later found that due to the higher vapor pressure of MgO or CaO, it is easy to cause loss due to high arc temperature during spraying. The stability of ZrO₂-CaO is impaired. During the thermal cycle cooling process, MgO or CaO will be dispersed from the solid solution, which not only affects the stabilization effect of ZrO₂, but also increases the thermal conductivity of the coating material, thereby reducing the thermal insulation performance of the thermal barrier coating. Coating in order to improve the thermal cycle of life, and now part stabilizer instead of Y₂O₃ gradually stable ZrO₂ (YSZ), stability of ZrO₂ coatings with Y₂O₃ part, to a certain extent to avoid the stability of CaO and MgO style stabilizers of ZrO₂ loss problem, can make the system of high temperature and low temperature to maintain stable phase state, thus has good stability At present, YSZ is the most widely used material in thermal barrier coatings. It has a low thermal conductivity (4.2W / mk) and a high thermal expansion coefficient (10.7×10⁻⁶ / °C⁻¹)^[9-10] high melting point. High temperature phase stability, good corrosion resistance and high thermal cycle life.

B. Theoretical study on thermal shock resistance of ceramic materials

Thermal shock resistance refers to the ability of materials to withstand temperature fusion, and is a comprehensive response of mechanical properties and thermal properties to heated conditions^[11]. Thermal shock damage of ceramic materials can be divided into two types: instantaneous fracture under thermal shock and cracking, spalling, and overall damage under thermal shock cycle. Due to the different thermal shock damage modes of ceramic materials, there are two kinds of thermal shock evaluation theories widely used: one is the critical stress fracture theory based on elastic mechanics, and the other is thermal shock damage based on fracture mechanics.^[12-13] Thermal shock fracture refers to the instantaneous fracture of a material caused by the inherent strength of the material to resist thermal stress caused by thermal shock temperature. Thermal shock damage of materials refers to the thermal damage process of cracking and spalling of materials until bursting or overall fracture under thermal shock stress^[14-16].

III. EFFECT OF DIFFERENT STABILIZERS ON THERMAL SHOCK RESISTANCE OF ZrO₂

Pure ZrO₂ generally has three crystal structures^[17], namely, a monoclinic phase (m phase), a tetragonal phase (t phase) and a cubic phase (c phase). The phase transition temperature is as follows (if there is other oxide doping in ZrO₂, the phase transition temperature is generally lower).

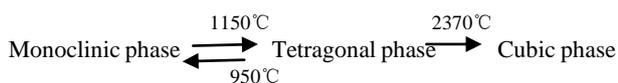


Figure 1. Schematic diagram of temperature conversion of ZrO₂ phase

In the process of heating and cooling, ZrO₂ ceramics will undergo a high-temperature t-phase to m-phase transition, and a phase change stress will occur with a 3-5% volume change. In the case of thermal cycling, when such a phase change occurs, The phase transformation stress will cause cracks and spalling of the ceramic layer during thermal shock^[18-19],

which will invalidate the coating. In order for the thermal barrier coating to work under the thermal cycling conditions near the phase transition temperature and extend the service life of the coating, it is necessary to reduce the occurrence of such phase transitions and maintain ZrO₂ as cubic or square phase at high temperatures. In order to prevent the conversion of ZrO₂ from tetragonal ZrO₂ to monoclinic ZrO₂, oxides such as yttrium oxide (Y₂O₃), calcium oxide (CaO), magnesium oxide (MgO) and oxidation decoration (CeO₂) were used as tetragonal stabilizers and dissolved into ZrO₂. It has been found through research that adding a small amount of oxides such as MgO, CaO, Y₂O₃ or CeO₂ to ZrO₂ can stabilize or partially stabilize ZrO₂ to a certain extent. Different stabilizers have different phase stabilization effects, and the respective stabilization mechanisms may also be different.

A. Effect of Y₂O₃ on Thermal Shock Resistance of Zirconia Ceramics

Different mass fractions of cerium oxide were added to zirconia, and sintered at a pressure of 1460°C for 4h to obtain yttria-stabilized zirconia ceramics^[20].

For the study of thermal shock resistance of brittle ceramic materials^[21-23], the theory of thermoelasticity is generally adopted. This theory refers to the balance between thermal stress and the strength of the material itself as the reference. The smaller the thermal stress, the strength of the material itself. The more balanced, the better the thermal shock resistance of the material^[24]

Thermal stress formula:

$$\sigma_h = E \cdot \alpha \cdot \Delta T / (1 - \nu)$$

In the formula:

- E— Young's modulus of elasticity
- α — Thermal expansion coefficient
- ΔT —Thermal shock temperature difference
- ν —Poisson's ratio

The smaller the modulus of elasticity, the coefficient of thermal expansion and the Poisson's ratio, the smaller the thermal stress of the material and the higher the strength of the material. Therefore, the better the balance between the thermal stress and the strength of the material itself, the better the thermal shock resistance of the material.

The high-purity Y₂O₃ powder (purity ≥99.99% is completely dissolved by concentrated nitric acid (68%), the Y(NO₃)₃ solution is diluted, and the diluted solution is mixed with ZrOCl₂ aqueous solution, and prepared by chemical coprecipitation method^[25]. Different mass fractions of Y₂O₃-ZrO₂ powder. The prepared powder was subjected to high temperature calcination at 1100 °C. After the powder was dry-formed, it was pressed and formed by cold isostatic pressing of 180 MPa. Finally, the sample was placed in an electric furnace at 1460 °C for normal pressure sintering, heat-sealed for 4h, and finally cooled with the furnace. The linear expansion coefficient of the zirconia ceramic material was measured by a PLY high temperature horizontal expander. A curve between the average linear expansion coefficient of the material and the cerium oxide content, As the thermal expansion device continues to heat up, the coefficient of expansion of the material first rises rapidly and then gradually becomes flat until it becomes substantially constant.

By adding cerium oxide to the zirconia ceramic, the densification degree, hardness, and bending strength of the material can be improved. Y_2O_3 forms a displacement solid solution with ZrO_2 , which makes the material more dense Wu Shan and other research found that ^[26] when the mass percentage reached 5.5%, the densification degree of the material reached the highest, and the material properties here also obtained the maximum. When the mass percentage of cerium oxide reaches 5.5%, the thermal expansion property of the material is the smallest, and the strength of the material itself is high, so the zirconia ceramic material obtained at this content has better thermal shock resistance.

B. Effect of CeO_2 on the seismic behavior of nano-zirconia ceramics

The cubic phase is not present in the nano- ZrO_2 coating obtained by plasma spraying. The nano-granulated powder is more fully melted during the spraying process, and is either stabilized into a non-transformed tetragonal phase or converted into a low-temperature monoclinic phase during the cooling process. The cubic phase exists in the micron ZrO_2 coating, and the micron powder is not sufficiently melted during the spraying process, and there is a residual cubic phase. Because the nano ZrO_2 coating is finer than the micron YSZ- ZrO_2 coating, the porosity is lower, the spreadability is better, the thermal shock resistance is better than that of the micron ZrO_2 coating, and the antioxidant protection of the matrix is better. Therefore, researchers have also tended to study nano-zirconia ceramics in recent years ^[27-28].

Wang Dongsheng et al. ^[29] used atmospheric plasma spraying technology to prepare two thermal barrier coatings on the surface of high temperature alloy steel using conventional nano yttria partially stabilized zirconia (YSZ) and 25 wt% CeO_2 (hereinafter referred to as CSZ) in YSZ. The two coatings were subjected to thermal shock tests at $900^\circ C$, and the thermal shock resistance of YSZ and CSZ ceramic coatings was analyzed using SEM and EDS techniques It was found that when the YSZ thermal shock test was carried out 21 times, cracks appeared at the edge of the coating. When the test was carried out 30 times, the coating peeled off at the crack. The CSZ coating showed its first peel off at the edge of the coating only when the test was carried out 63 times. CSZ failed in the 63rd heat cycle, while YSZ failed in the 21st. The thermal shock resistance of the new CSZ coating was significantly better than YSZ. CeO_2 can improve the thermal shock resistance of Y_2O_3 partially stabilized ZrO_2 .

Theoretically, the difference between the thermal expansion coefficients of CSZ and YSZ and the bonding layer material is about $(5-6) \times 10^{-6} \text{ }^\circ C^{-1}$ and $(6-7) \times 10^{-6} \text{ }^\circ C^{-1}$, respectively. The smaller the difference between the thermal expansion coefficients, the higher the material matching ratio, the better the bonding strength between the two. The analysis shows that the CSZ coating bonding strength is better than YSZ, and the CSZ coating is X-ray diffraction before the thermal shock test. According to the analysis, the thermal shock resistance of CSZ coating is stronger than that of YSZ, which indicates that the addition of CeO_2 to solid solution into YSZ forms a stable tetragonal phase compound, which improves the thermal shock resistance of the coating and prolongs the service life of the coating.

C. Effect of Silicon Oxide on Thermal Shock Resistance of Zirconia Ceramics

In the ZrO_2 , SiO_2 particles are added, and during the spraying process, the SiO_2 particles are spread on the surface of the substrate to form a flake or a coating in the form of fine particles, and then the molten ZYO particles are collided to re-melt or vaporize the SiO_2 . However, at this time, the ZYO has been spread, so that the vaporized SiO_2 cannot escape, and the pores are formed in the coating. Eking et al. given that the relationship between elastic modulus and porosity ^[30]

$$E = E_0(1 - 1.9P + 0.9P^2)$$

In the formula:

E_0 —Elastic modulus of the coating at a porosity of zero

P —Coating porosity

E —Elastic modulus of the coating when the porosity is P

During the thermal shock process, the thermal stress of the coating is proportional to the elastic modulus of the coating. The residual stress and thermal stress affect the coating at the same time, eventually leading to coating failure. The addition of SiO_2 changes the porosity of the coating, resulting in a change in the modulus of elasticity of the coating, which further causes residual stresses after coating spraying and changes in thermal stress generated during thermal shock. According to thermodynamics, the thermal shock resistance of the coating is best when the porosity in the coating is 10%-15% ^[31-32]. At the same time, the pore diameter and distribution in the coating have a significant effect on the thermal shock resistance of the coating. Only uniform distribution, pores with a diameter below $1 \mu m$ are beneficial to improve the thermal shock resistance of the coating, and unevenly distributed coarse atmospheric pores. will reduce the thermal shock resistance of the coating.

Tang jiancheng et al. ^[33] found that when 3.0% SiO_2 was added to the coating, the number of thermal shock crack initiation and thermal shock failure of the coating reached the maximum value, which increased from 32 and 46 times without SiO_2 coating to 83 and 112 times respectively. When excessive SiO_2 is added, the thermal shock resistance of the coating will be reduced. The addition of SiO_2 will promote the formation of pores in the coating, and the porosity and diameter of pores increase with the addition of SiO_2 . The average diameter of pores in the coating of SiO_2 is about 1 micron, the porosity is about 10%, and the distribution of pores is uniform, so the elastic modulus and stress of the coating are the minimum, and the thermal shock resistance of the coating is the best.

D. Other factors affecting thermal shock resistance of ZrO_2 ceramics

In addition to adding a small amount of stabilizers such as MgO , CaO , Y_2O_3 or CeO_2 into ZrO_2 , other factors affect the thermal shock resistance of ZrO_2 ceramics. For example, the effects of bonding layer and heat treatment on the thermal shock resistance of ZrO_2 ceramics also have a certain degree of influence.

1) Effect of NiCrAlY bonding layer on thermal shock resistance of ZrO_2 ceramics. NiCrAlY is the thermal

expansion coefficient of the bonding layer between the metal matrix and ZrO₂. During the thermal shock process, the thermal expansion coefficient of the interlayer material changes from the substrate to the bonding layer and the ZrO₂ surface layer, which reduces the difference in thermal expansion. It avoids the detachment and failure of interlayer materials caused by thermal shock and exhibits the best thermal shock resistance.

2) Influence of heat treatment on thermal shock resistance of ZrO₂ ceramics. The samples of magnesium oxide partially stabilized zirconia without heat treatment have lower thermal expansion coefficient and smaller volume contraction, so the thermal stress generated by volume change is reduced, which greatly improves the thermal shock resistance of the material.

IV. FUTURE PROSPECTS

Modern ceramic materials have excellent properties such as high strength, high hardness, high temperature resistance, chemical corrosion resistance, wear resistance, oxidation resistance and thermal expansion. They have played an important role in aerospace, energy, machinery, automotive, chemical, metallurgical and other fields. But at the same time, the brittleness of materials is too great to withstand severe thermal shock, that is, its poor thermal shock resistance, which restricts the wider application and industrialization of structural ceramics in engineering.

Therefore, the study of thermal shock resistance of ceramic materials has been one of the main research directions in the field of high temperature structural ceramics.

V. SUMMARY

The thermal shock resistance of materials is closely related to the physical properties of materials. Although the physical properties of the selected material have been determined, according to the specific characteristics of the selected material, the elastic modulus and thermal expansion coefficient of the material can be reduced through optimization of the process to improve the thermal shock resistance of the material:

1) By adding yttrium oxide to zirconia ceramics, the densification degree, hardness and bending strength of the materials can be improved. Y₂O₃ and ZrO₂ form substitutable solid solution, which makes the material denser. When the mass percentage reaches 5.5%, the densification degree of the material reaches the highest, which also maximizes the properties of the material. When the yttrium oxide mass percentage reaches 5.5%, the thermal expansion property of the material is the minimum, and the material's own strength is higher, so the zirconia ceramic material with this content has better thermal shock resistance.

2) By adding 25%CeO₂ solid solution to nano-yttrium oxide nano-stabilized zirconia coating in nano-zirconia ceramics, stable tetragonal phase compounds are formed to improve thermal shock resistance of the coating.

3) By adding 3.0% SiO₂ in the zirconia ceramic coating, the coating will produce uniform pores, minimize the elastic modulus and stress, and make the coating have the best thermal shock resistance.

4) The choice of bonding layer and the effect of heat treatment also have a certain impact on the thermal shock resistance of ZrO₂ ceramics.

Because the research of thermal shock resistance of zirconia ceramics is not deep, the evaluation theory of thermal shock resistance also has fundamental defects. So there is still a lot of work to be done to improve the thermal shock resistance of zirconia materials.

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