Novel perovskite coating of strontium zirconate in Inconel substrate

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Thermal Barrier Coatings (TBC) provides a low thermal conductivity barrier to heat transfer from the hot gas in the engine to the surface of the coated alloy component. SrZrO3 powder are prepared by Sol Gel synthesis method. The synthesized powder sample is characterized by X Ray Diffraction Technique (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) and the results are interpreted. The Polycrystalline nature of SrZrO3 is confirmed and lattice spacing are determined in XRD. SEM shows sub-micron sized particles and a fringed pattern is observed in TEM. The IN718 specimen is Wire Cut and Sand Blasted. A SrZrO3 double layer is coated over the Inconel specimen through a Bond Coat made of NiCoCrAlY by Plasma spraying Process and also characterized. SEM analysis of the Coating shows diffusion of Fe, Sr into the substrate.

Keywords: Thermal Barrier Coatings (TBC), Strontium Zirconate, Ceramic coatings, Sol gel synthesis, Atmospheric plasma spraying.

1. Introduction

A protective coating deposited to act as a barrier between the surfaces of the component and the aggressive environment that it is exposed during operation is now globally acknowledged to be an attractive means for reducing damage to the actual component. Thermal Barrier Coatings(TBC) provide an insulation barrier to heat transfer from the hot gas in the engine to the surface of the coated alloy component, whether in the specific applications such as in combustor or the gas turbines [14]. They are provided to protect the base material in various applications such as internal combustion engine bodies, gas turbine blades etc. at very high temperatures thus extending the life of alloy components in the these super temperature regimes by decreasing their surface temperatures [6]. The perovskite Zirconia (ZrO2) is been used as the best suit for coatings where it is used as the top coat, over a bond coat. As wear resistant coatings are used to prevent wear mainly in textile mill rollers, cylinder liners, pistons, valves, spindles etc. Alumina (Al2O3), Titania (TiO2) and Zirconia (ZrO2) are the some of the conventional wear resistant coating materials which is presently used for study of novel ceramic coatings for high temperature applications [16].

There are various methods for synthesizing these Perovskite coatings. Molten Salt Synthesis and Sol Gel synthesis are the most commonly used processes. YSZ is the commonly used coating materials due to their thermal properties such as low thermal conductivity, thermal expansion coefficient and an excellent corrosion resistance. CYSZ is an alternate TBC's powder and it has good thermal cycle properties because the addition of ceria makes zirconia more stable at higher temperatures [6]. Calcium titanate synthesized and deposited from conventional powder feedstock by Jiri Kotlan et al. is found to be the best choice for plasma spraying when compared with other perovskite structures [12]. Doping with materials such as of Yb2O3, Gd2O3 are more effective in reducing the specific heat capacity and thermal conductivity for Ceramic powders leading to higher efficiency [2]. The NiAl sprayed coatings are harder than the substrate and hence forms the basis for tribological and wear resistant applications [15].

The method of thermal spraying depends on the type of Thermal type of process employed and consequently flame spraying (FS), high velocity oxy-fuel spraying (HVOF), plasma spraying (PS) etc. are the available choices for material spraying [16]. The study can be extended on degradation of parts and their failure caused due to high relative motion between mating surfaces, degrading environment, peak temperatures
and repeated stresses [1]. The plasma spraying process can be conducted by varying several process parameters such as oxygen flow rate, spraying speed, fuel gas flow rate, powder carrier gas flow rate, arc current, powder feed rate, nozzle length and stand-off distance [3,4,10]. These parameters have influence on thickness, hardness, microstructure and wear resistance on the coatings [6,9,10]. The powder that is coated fail at different locations due to various reasons. In Optimized functionally graded ceramics spalling occurs at the ceramic and bond coat interface along the thermally grown oxide layer(TGO) whereas in double ceramic layer coatings, it occurs along the bilayer [5]. In double layer coatings failure occurs due to mismatch due to thermal expansion and this can be avoided by formation of a functional gradient coating [7,8].

Based on the literature survey, it is found out that studies on thermal barrier coating using Strontium zirconate has not been explored. Also, several researchers reported only on single layer coating hence in the present study, a novel perovskite double layer has been coated over Inconel substrate and characterization is done.

2. Materials and methods

2.1. Sol gel method

2.1.1. Raw material synthesis

The precursors were chosen based on the processing techniques and the compound formation. The chosen raw materials are ZrOCl₂·8H₂O-98% pure, SrCl₂-98% pure and EDTA. The precursors were weighted on the basis of stoichiometry for the sol gel reaction and were taken for further process.

2.1.2. Preparation

The weighted materials are taken for the preparatory steps through sol gel method. Initially the required glass wares were cleaned well by distilled water and acetone to ensure the purity. 1.0 M solution of zirconium oxychloride and Strontium chloride in water is prepared by vigorous stirring. In the clear solution, EDTA is added in the proposed ratio (1:1) to the molten solution under continuous stirring to induce the chelation pH of the solution was increased to 7 and by addition of 5M solution of NaOH, turns the PH till 10. The complete setup was setup at 80°C. This continuous stirring and the effect of the PH converts the solution into gel formation. Then the resultant gel is dried overnight at 350°C for 8 hours in hot air oven for complete removal of water molecules. The obtained mass is grounded to ensure the homogeneity before final calcinations followed by intermediate grinding, the sample is subjected to calcination at 600°C for 4 hours. Resultant powder is grounded well and subjected to sequence of characterization to analyze the desired properties.

2.2. Plasma Coating

SrZrO₃ exhibits pseudo tetragonal structure at 750°C and exhibits tetragonal structure at high temperatures of 840°C. The pseudo tetragonal structure creates lattice mismatch between Sr-O atoms, so that coating delaminates easily. So, during the service temperature of the material is subjected to fail at an earlier circumstance. This type of failure requires further modification of coating or a coating interlayer to be sprayed above the bond coat. For this we are going for a multilayer coating with varying feed rates.

The Inconel specimens are wire cut to the desired dimensions and are sand blasted with silica sand to improve its surface roughness for coating adherence. The powder synthesized after conformation of phase purity are then coated onto the Inconel 718 substrate. The coating is done by APS (Air Plasma Spray) technique. The parameters are mentioned in table 1. Initially bond coat of NiCoCrAlY of about 100µm are coated onto the substrate with standard parameters. On top of the bond coat SrZrO₃ powder thickness up to 150 µm is deposited with higher powder feed rate and is then cooled. Again, the coating of SrZrO₃ powder of thickness 150 µm atop of pervious coated layer with lower powder feed rate. The substrate (Figure 1) along with coating is then cooled and further characterization is done to determine the microstructure of them.
o Substrate - INCONEL 718
o Coating - Strontium Zirconate (SrZrO₃) - Double Layer
o Bond Coat – NiCoCrAlY

Specimen Dimensions (Substrate) - 60mm x 38mm x 6mm

Figure 1. SrZrO₃ Coated Inconel Specimen.

Table 1. Various Parameters used in Double Layered Coating.

|                     | Bond Coat | Top Coat 1 | Top Coat 2 |
|---------------------|-----------|------------|------------|
| Current (A)         | 500-550   | 500-600    | 500-600    |
| Voltage (V)         | 60        | 60         | 60         |
| Spraying Distance (mm) | 100      | 100        | 100        |
| Spraying Speed (mm/sec)  | 10       | 10         | 10         |
| Powder Feed Rate (g/min) | 35      | 35         | 20         |
| Ar/He Ratio         | 15/50     | 15/50      | 15/50      |
| Oxygen (kg)         | 4         | 4          | 4          |
| Acetylene (kg)      | 1.8       | 1.8        | 1.8        |
| Air                 | 3         | 3          | 3          |

2.3 Characterization
The Crystal structure and Phase of the synthesized SrZrO₃ Powder particles is determined using XRD Copper K alpha radiation and Cobalt K alpha radiation and the Phase Purity is confirmed. The surface Morphology of the powder particles are determined using SEM with an EDS attachment in secondary electron mode. The Particle morphology is analyzed using JEOL JEM 2100 High Resolution Transmission Electron Microscope (HRTEM). The Coated specimen is subjected to SEM analysis and the Elemental Distribution along the Top Coat and Bond Coat interface were determined.

3. Results and discussion
3.1 Characterization of SrZrO₃ Powders

3.1.1 Phase Analysis-XRD
Figure 2. Phase analysis of synthesized SrZrO$_3$

The XRD pattern reveals presence of SrZrO$_3$ phase with Orthorhombic system. The strong diffracted peaks as obtained in Figure 2. represents Strontium Zirconate phases with space group of pbnm thereby the lattice parameters are computed. Existence of the narrow diffracted peaks resembles coarser crystallites which are in the range of few micro meters (µm) which is evident from the SEM analysis. The crystallite size is determined from x-ray line broadening using Debye Scherer’s formula, and was found to be 5.20nm.

3.1.2. Scanning Electron Microscope (SEM)

Figure 3. SEM Analysis of SrZrO$_3$ powders.

From figure 3, the particle size is approximately in the sub-micron size with particles being agglomerated. The particle size is in comparison with the particle size calculated from the SEM image.
3.1.3. Transmission Electron Microscope (TEM)

Figure 4. SAED pattern of SrZrO$_3$.

The synthesized SrZrO$_3$ powders are analyzed in TEM to confirm the presence of its Crystalline nature. The presence of rings confirms the Polycrystalline nature of SrZrO$_3$.

Figure 5. Particle morphology using TEM. Figure 6. HRTEM image of Strontium Zirconate.

The particle shape and size of SrZrO$_3$ was observed from TEM images (Figure 5, 6). The particle size is found to be ultra-fine sized and confirms the morphology as spherical in nature. The particle size computed from the above TEM images ranges between 10nm to 100nm. Particle agglomeration prevents the size reduction factor of SrZrO$_3$.

From SAED pattern (Figure 4) of SrZrO$_3$ reveals the presence of polycrystalline nature of the sample with each diffraction spot corresponding to the reflection from the planes of orthorhombic unit cell respectively [12], (111), (002), (040) from the orthorhombic unit cell clearly confirms the phase pure formation. The bravais lattice with d-spacing value ranges from 28.23nm to 178.26nm. Hence from the d spacing and the reflection planes, the lattice parameter were calculated and found to be a=5.81nm, b=8.13nm, c=5.69nm.
The HRTEM image (Figure 6) shows the perfect stacking sequence. All atoms are in the [001] direction. The fringe pattern is observed and that justifies the atomic presence over the (111), (200), (040) observed from the SAED pattern. The size ranges from 0.5Å to 1nm.

3.2. Characterization of Coated specimen

3.2.1. Scanning Electron Microscope (SEM)
Figure 7. shows the cross-sectional view of the SrZrO₃ powder coated over the Inconel substrate. Presence of NiO or NiO₂ (spinal) and chromia at the TGO layer may lead to Thermal Spalling. The Elemental analysis as shown in Figure 8. shows Cr, Ni which are ingredients of the bond coat.

![Cross-sectional view of sprayed SrZrO₃ on Inconel](image)

**Figure 7.** Cross sectional view of sprayed SrZrO₃ on Inconel.

From figure 8., the Area analysis shows the variation in concentration of the element across the line. The Area EDS analysis confirms the range of distribution of elements along the interface of the bond and top coat.
Figure 8. Elemental Distribution along Area at Bond and Top coat interface.
Figure 9. EDS and Chemical Composition of Elements at Inconel and Bond Coat Interface.

EDS shows presence of Ni, Cr, Fe from Substrate and Ni, Co, Cr, Al from the Bond coat as in Figure 9. The presence of Si may be due to the sand blasting process, we can clearly see the difference in concentration of Sr, Cr, Fe, Ni as we move away from the substrate into the coating can be clearly seen in Figure 9. Intermediate to the coating there is a diffused layer wherein the Fe from the substrate and Sr from the top coat are diffused to some extent.

Figure 10. EDS and Chemical Composition of Elements at Bond coat and Top Coat Interface.
EDS (Figure 10) shows presence of Ni, Co, Cr, Al from the Bond coat and major content of Sr, Zr from the Top coat. The Cu alloying element in the substrate is also diffused into the top coat because of their high thermal conductivity as the plasma sprayed process is carried at higher temperature. Due to the diffusion of Cu there is a possibility of formation of intermetallic during subsequent thermal process. The whole of diffusion process is in the first coat while the second coat remains unaffected. In single layered coating, the diffusion would have concentrated in top coat that reduces the overall property of the coating, the double layered coating provides nil concentration of diffusion in top coat that can increase the lifetime of the coating and wear property of the substrate in comparison to the single layered coating.

3.2.2 Macrostructure
Figure 11. shows the cross sectional view of the SrZrO₃ coating over the Inconel substrate as observed in the image analyzer. The coated surface is porous which may be due to improper melting of large particles during spraying [2]. Figure 12. Gives the macrostructure of the coated powder samples in top view.

Figure 11. Cross sectional view of the coated powders. Figure 12. Macrostructure of the coated powders.

4. Conclusion
Perovskite oxide salt are synthesised using Molten salt synthesis method and the particle size are evaluated using SEM analysis and is found to be approximately 10.6µm which is an ideal particle size for Thermal Barrier Coating (TBC) applications.

The synthesised SrZrO₃ powders are coated atop of INCONEL 718 substrate with intermediate layer of NiCr bond coat. The coating was non-homogeneous and the adhesive property is increased due to presence of bond coat. The coating is done in two stages:

(i) First coat is done with higher powder feed rate and then cooled.
(ii) Top coat is done with slower powder feed rate.

The Polycrystalline nature of SrZrO₃ is confirmed and lattice spacing are determined in XRD. SEM shows sub-micron sized particles and a fringed pattern is observed in TEM. All atoms are in the [001] direction. The fringe pattern is observed and that gives the atomic presence over the (111), (200), (040).

SEM in Coating shows diffusion of Fe, Sr into the substrate. The Cu alloying element in the substrate is also diffused into the top coat because of their high thermal conductivity as the coating process is carried at elevated temperatures. Due to the diffusion of Cu there is a possibility of formation of intermetallic during subsequent thermal process if ever undergone. In single layered coating, the diffusion of elements is concentrated in immediate top coat that reduces some property of the coating while in the double layered coating the top coat is not subjected to diffusion which increases the lifetime of the coating and wear property of the substrate in comparison to the single layered coating.
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