Effect of Air Plasma Spray Parameters on the Properties of YSZ and CYSZ Thermal Barrier Coatings

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Abstract
In this study; effects of plasma spray distance and Ar/H₂ gas mixture ratio on YSZ and CYSZ thermal barrier coating properties are investigated with the experiments and characterization studies. Within the scope of characterization studies; SEM analysis, porosity analysis with ASTM 2109 standard, adhesion strength tests compliance with ASTM C633 and also thermal shock tests were performed. The best thermal shock performance is observed in YSZ coated specimens which are produced from 75mm spray distance and it is 52 cycles. It was determined that, in this study, bonding strength of the coatings is between 4 and 10 MPa.

Keywords: Thermal barrier coating, Plasma spray, Thermal shock

1. INTRODUCTION
Thermal Barrier Coatings (TBC) find a wide application area as a protection shield against high temperature for the structural components in stationary and aerospace gas turbines. The TBC concept is based on placing a thermally insulating layer between a cooled metallic component and the hot working gas with the aim of reducing the heat transfer to the component. A metallic layer is coated on substrate surface as a bond coat (MCrAlY (M = Co, Ni)). Bond coat is applied in order to improve adhesive strength, oxidation and corrosion resistance. It also reduces the thermal expansion differences between substrate and ceramic coat. Ceramic layer, known as thermal insulating layer is applied on bond coat. Plasma spray process parameters have vital impact on the quality of thermal barrier coatings due to the powder particles and plasma flame interactions [1-3].

YSZ and are known as the most commonly used coating materials due to their low thermal conductivity and having close characteristics like metals in terms of thermal expansion coefficient, good corrosion resistance. CYSZ is an alternative TBCs powder and it has good thermal cycle properties because the addition of ceria makes zirconia more stable at higher temperatures.

From the literature, the predominant factors (APS process parameters) that have a greater influence on the coating properties were identified. They are the power (kW), the primary gas flow rate (lpm), the standoff distance (mm), the powder feed rate (gpm), and the carrier gas flow rate (lpm) [4,5].

Li et al reported within the scope of the uniform design of experiments, the argon flow rate and the hydrogen flow rate are the most significant two parameters affecting the deposition efficiency, porosity and microhardness among the arc current, spray distance and powder feed rate process parameters [6].

Ar/H₂ gas mixture ratio (known as plasma power) and also plasma spray distance play a key role on the quality of TBCs. Taking into account the effect of spray distance on the particle properties, it is indicated that the particle velocity and particle temperature decreases because of the increase in spray distance. This means that spray distance determines cooling rate of in-flight particles and accordingly long spray distance causes more cooling. On the other hand, due to the heating of the substrate surface by plasma flame, much more melting particles and low density TBCs occur resulting from short spray distance. Spray distance also affects adhesion strength of the TBCs on account of both fast cooling at long spray distance and also the overheating of substrate material at short spray distance. Therefore, determination of the optimum spray distance is very important in terms of TBCs quality [7-9].
Based upon the high thermal conductivity and specific heat capacity of the H\textsubscript{2} gas, the ratio of H\textsubscript{2} in the Ar/H\textsubscript{2} gas mixture is more influential on plasma power than Ar. As the flow rate of H\textsubscript{2} gas increases, plasma power and in-flight particle temperature also increase [10-12]. From the point of ascent in Ar flow rate; despite the increase in kinetic energy of plasma, plasma temperature decreases depending on particle velocity acceleration. Particles move at a very fast speed in the plasma jet areas and in parallel with this, the heat transfer between particles and plasma flame may not be sufficient. Poor heat transfer causes poor adhesion of the splats and in the microstructure more porosity and more melted particles are observed [11,12].

In this study, we investigated the effect of spray distance and Ar/H\textsubscript{2} ratio on microstructure, thickness, porosity, adhesion strength and thermal shock behavior of YSZ and CYSZ TBCs.

2. METHODS AND PROCEDURES
Disc shaped 316L stainless steel samples with a diameter of 25.4 mm and thicknesses of 2mm were used as a substrate material. Prior to bond coat production, the substrate was grit blasted with using 50-80 grain mesh alumina. After grit blasting, the surface roughness of the base material is measured with optical profilometer (Veeco WYKO NT1100) device. Surface roughness profiles of base material before and after the grit blasting is given in Figure 1.

![Fig. 1. Surface roughness of base material before and after grit blasting.](image)

Surface roughness of base material before and after grit blasting is 358.68 nm and 2.69 \( \mu \)m respectively. Commercial Sulzer Metco Amdry 997 (Ni-23Co-20Cr-8.5Al-4Ta-0.6Y) powders were used for the bond coats. SEM images of AMDRY 997 powder is given in Figure 2. According to the image, powder have a spherical morphology.

The spray torches (APS and DJ2700 HVOF gun) were fastened on a three-axis CNC robot and gun speed is 600 mm/min. Grit blasted samples were clamped on the turntable and the number of passes was 12. HVOF process parameters were given at Table 1.

![Table 1. Process parameters of HVOF](image)

Surface roughness profiles of bond coated material is given in Figure 3. Surface roughness of bond coated material is 6.1\( \mu \)m. According to literature, this roughness value is suitable for the application of ceramic top coat on bond coated material [13]. Commercial Sulzer Metco 204NS (ZrO\textsubscript{2}-8 wt.%Y\textsubscript{2}O\textsubscript{3}) and Sulzer Metco 205NS (CYSZ) powders were used for top coats. SEM images of YSZ and CYSZ powders are given in Figure 4.

![Fig. 3. Bond coated substrate’s surface roughness profile.](image)

![Fig. 4. SEM images of YSZ (a) and CYSZ (b) powders.](image)
As it can be seen in SEM images, all powders have spherical morphology. XRD patterns of YSZ and CYSZ powders are given in Figure 5.

![XRD patterns of YSZ and CYSZ powders](image)

**Fig. 5. XRD patterns of YSZ and CYSZ powders.**

YSZ powder occurs mostly of tetragonal Zr$_{0.9}$Y$_{0.1}$O$_{1.96}$ (JCPDS card no:010-082-1241) phase and also monoclinic ZrO$_2$ (JCPDS card no:010-086-1450) phase. CYSZ powder occurs mostly of tetragonal Zr$_{0.86}$Ce$_{0.14}$O$_{2}$ (JCPDS card no:010-038-1437), monoclinic ZrO$_2$ (JCPDS card no:010-086-1450), and cubic CeO$_2$ phase. YSZ and CYSZ TBCs were produced by air plasma spray (APS) method with the usage of Sulzer Metco 9MB plasma spray gun. Sulzer Metco Commercial 730C gun nozzle has been used. Powder injection angle was placed perpendicularly to plasma flame. Current is 500 A, carrier gas (Ar) flow rate is 13.5 scfh, number of passes are 12, gun speed is 200 mm/min, turntable speed is 200 rpm for all specimens. Process parameters of plasma spraying were given in Table 2.

![Table 2. Process parameters of plasma spray](image)

<table>
<thead>
<tr>
<th>M</th>
<th>Sample Name</th>
<th>P. Gas Ar (scfh)</th>
<th>S. Gas H$_2$ (scfh)</th>
<th>S.D (mm)</th>
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<tr>
<td>CYSZ</td>
<td>C465</td>
<td>80</td>
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<td>C675</td>
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<td>C8100</td>
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<td>Y865</td>
<td>80</td>
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</table>

M: Materials, P.Gas: Primary Gas, S.Gas: Secondary Gas, S.D: Spray Distance

Figure 6 shows XRD pattern of as-sprayed YSZ and CYSZ TBCs. As it is seen in Figure 6, as-sprayed YSZ coating has tetragonal Zr$_{0.9}$Y$_{0.1}$O$_{1.96}$ (JCPDS card no:010-082-1241) and monoclinic ZrO$_2$ (JCPDS card no:010-086-1450) phases. As understood from the Figure 5 and Figure 6, some of the monoclinic phase of zirconia in the YSZ powder, transform into the tetragonal phase after sprayed with APS method because of rapid solidification of YSZ powders during the APS process [14-23].

As-sprayed CYSZ coating has only tetragonal Zr$_{0.84}$Ce$_{0.16}$O$_2$ (JCPDS card no:01-038-1437). Monoclinic and cubic phases in the CYSZ powder disappear due to the evaporation of part of CeO2 and part of CeO2 disperse in the coating during the APS process [20-26].

![XRD patterns of as-sprayed YSZ and CYSZ coatings](image)

**Fig. 6. XRD patterns of as-sprayed YSZ and CYSZ coatings.**

The thermal shock test of TBCs was performed by heating and the water quenching method. The TBCs samples with substrate were heat treated at an evaluated temperature of 1000 °C in a tube furnace for 20 min. and then directly water quenched at an ambient temperature. Then, TBCs samples placed into the furnace again. When a visible delaminated region is seen, surface micrographs of the samples were captured using a digital camera. When the delaminated region reached about 50% of the total coating surface, the test was stopped.
3. RESULT AND DISCUSSION

3.1 Microstructure, Thickness and Porosity of TBCs

The cross-sections of the YSZ and CYSZ TBCs including bond coats and top coats were given in Figure 7.

Bond Coat thicknesses were achieved between 80 and 110 µm. As the characteristic feature of the TBCs, porosity and cracks in the top coat were observed clearly [27]. The effect of spray distance on coating thicknesses (Figure 8-a) showed that the highest thickness values of TBCs were obtained at the spraying distance of 65 mm.

Increasing spray distance from 65 mm to 100 mm resulted in coating thickness decrease. CYSZ coatings have higher thickness values than YSZ coatings at a spray distance of 65 mm. However, different Ar/H\textsubscript{2} ratio cause great changes on the TBCs thickness due to the effects of plasma spray parameters on deposition efficiency, porosity percentage and density of the TBCs (Figure 8-b). Maximum coating thickness was achieved at the spray distance of 65 mm and at the Ar and H\textsubscript{2} flow rates of 80 scfh and 20 scfh, respectively.

Figure 9 shows the effect of spray distance and Ar/H\textsubscript{2} ratio on the coating porosity percentage. The increase in Ar/H\textsubscript{2} ratio reduces the porosity % of CYSZ TBCs. However, porosity % of TBCs declines at the Ar/H\textsubscript{2} ratio of 8 and for the YSZ, there is no regular change in the porosity % of TBCs (Figure 9-a). At all spray distances, as the Ar and H\textsubscript{2} flow rate increases, porosity % decreases. Low porosity TBCs occurs in the consequence of the increase in plasma temperature, particle velocity and also Ar and H\textsubscript{2} flow rates [5,28].

![Fig. 7. SEM images of CYSZ (a) and YSZ (b) TBCs.](image)

![Fig. 8. Effect of spray distance (a) and Ar/H\textsubscript{2} ratio (b) on TBCs thickness](image)

![Fig. 9. Effect of and Ar/H\textsubscript{2} ratio (a) and spray distance (b) on TBCs porosity %](image)
the results of Ramachandran’s study, in this study increasing the Ar/H₂ rate above a critical (optimal) value leads to high porosity [5].

Porosity % declines with the rise in H₂ flow rate at the spray distance of 75 mm. On the other hand, 65 and 100 mm spray distances cause an increment in the porosity % of YSZ TBCs [29].

The porosity % of CYSZ TBCs decreases with the increasing spray distance (Figure 9-b). At short spray distances, the sample surface temperature rises with the effect of plasma flame and this leads to the formation of higher porosity % in TBCs. Also long spray distance causes a long flight time in the plasma flame for the particles. In contrast with CYSZ TBCs, YSZ TBCs does not demonstrate regular differences.

3.2 Adhesion strength of TBCs

There are many factors that affect the adhesion strength of the TBCs. Coating thickness and % porosity of TBCs are the factors that have the vital importance. As the top coating becomes thicker, the internal stress in the structure arises. Also mechanical properties of the TBCs are getting worse due to the increasing porosity of the coating [29]. Internal stresses are generated because of the molten or semi-molten splats solidify rapidly on substrate surfaces to form a coating. Plasma spray parameters affect the temperature and speed of the particles also affects internal stresses significantly. Internal stresses reduce bonding strength of the coating [30-36].

Previous studies about bonding strength of TBCs indicate that lowest bonding strength is observed between top coat and bond. Consistent with the results of other studies, all separations occurred between bond coat and top coat. Cohesive rupture occurred within the top coat at result of adhesion tests for all samples (Fig. 10).

![Surface photograph of C675 and Y675 TBCs after adhesion tests.](image)

Figure 11 shows the effect of spray distance and Ar/H₂ ratio on the adhesion strength of the coatings. Highest adhesion strength is reached at the Ar/H₂ ratio of 6.

Heat transfer between particles and plasma flame becomes excessive and particles accelerate tremendously at the flow rates of primary gas Ar and secondary gas H₂, 90 scfh and 15 scfh, respectively. It was observed that adhesion strength of TBCs decreases drastically at the Ar and H₂ flow rates in order of 80 scfh and 10 scfh.

![Effect of Ar/H₂ ratio (a) and spray distance (b) on TBCs adhesion strength](image)

Spray distance has much more influence on the adhesion strength of TBCs than Ar/H₂ ratio. Highest adhesion strength results at the spray distance of 75 mm and Ar/H₂ ratio of 6. For these mentioned parameters; adhesion strength of YSZ TBCs which have Ar/H₂ ratio of 4 and 6, is greater than CYSZ TBCs.

Dokur and his friends found that the bonding strength of CYSZ-Al₂O₃ layered coatings is between 5.4 and 11.5 MPa [37]. Kwon et al. reported the bonding strength of plasma sprayed YSZ coatings is between 13 and 16 MPa [38]. In this study, bonding strength of the coatings is between 4 and 10 MPa. This results are similar to other studies.

3.3 Thermal shock performance of TBCs

Thermal shock performance of TBCs is effected by many factors like phase stability of ceramic layer, kind of substrate material, quality and kind of bond coat, and thermal expansion mismatch between metallic substrate and ceramic top coat. According to early studies, formation of TGO between bond coat and top coat as a result of bond coat oxidation and thermal stress are the main factors which effect thermal shock performance of TBCs.

Thermal shock performance of optimized YSZ and CYSZ TBCs shown in Figure 12. Thermal shock performance of YSZ TBCs is better than that of CYSZ TBCs. Coatings which are produced at 75 mm spray distance have the best thermal shock performance. Coatings which are produced at 65 mm spray distance have the worse thermal shock performance.
Ar/H$_2$ ratio also affects thermal shock performance. As seen in figure 6, YSZ TBCs which are produced by using Ar/H$_2$ ratio of 6, have worse thermal shock performance among YSZ TBCs. C875 TBCs have the best thermal shock performance in CYSZ TBCs group. C475 coatings have the worse thermal shock performance. Thermal shock performance has no relationship with adhesion strength and porosity level.

YSZ coated specimens which have Ar/H$_2$ ratio of 4, after 18 cycles, initial capillary cracks occur. After the end of the 22 cycles, new cracks occur on top coat surface. Table 3 shows specimens before thermal shock cycle test and after 23 cycles. After 38th and 39th cycle, coating starts to come off from surface of specimen which is produced at 100mm spray distance. 50% of coating comes off from surface of Y465, Y665 and Y865 after 46 cycles, so thermal shock test is terminated for this specimens. Thermal shock test is terminated after 50 cycles for YSZ coated specimen which is produced at 100mm spray distance. After 52 cycle, thermal shock test is terminated for Y475, Y675, and Y875, these specimens have the best thermal shock performance (Table 3).

Table 3. Thermal shock samples photograph of TBCs

<table>
<thead>
<tr>
<th>Spray Distance (mm)</th>
<th>Ar/H$_2$ ratio 6</th>
<th>Ar/H$_2$ ratio 4</th>
</tr>
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<tbody>
<tr>
<td>65 mm</td>
<td></td>
<td></td>
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<tr>
<td>75 mm</td>
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<td>23 cycle</td>
<td>50 cycle</td>
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<tr>
<td></td>
<td>23 cycle</td>
<td>52 cycle</td>
</tr>
</tbody>
</table>

Fig. 13. XRD pattern of coatings after thermal shock tests.

Liang and Ding indicate that thermal shock lifetime of YSZ and nano structured YSZ thermal barrier coatings at 1200 °C are 25 and 45 cycles respectively. Nejati and coworkers reported that thermal shock lifetime of CYSZ, CYSZ/microAl$_2$O$_3$ and CYSZ/nano Al$_2$O$_3$ thermal barrier coatings are 30, 45 and 60 cycle respectively. Previous studies prove that thermal shock lifetime results which found in this study are realistic and compatible [37, 39-41].

Figure 13 shows XRD pattern of coatings after thermal shock tests. As it seen in Figure 13, after thermal shock tests, while CYSZ coating has tetragonal Zr$_{0.84}$Ce$_{0.16}$O$_2$ stable phase, the amount of the monoclinic phase increases in YSZ coatings. This shows that CYSZ can be used as an alternative TBCs material instead of commercial YSZ products.
4. CONCLUSION
As a result of this study, following important conclusions can be drawn:

- Increasing the spray distance from 65 mm to 100 mm, both the thickness of TBCs and also the deposition efficiency decrease.
- Porosity level of CYSZ TBCs decreases as the spray distance ascends.
- Increasing the Ar/H₂ rate above a critical (optimal) value leads to high porosity level of CYSZ TBCs.
- Spray distance and Ar/H₂ ratio parameters did not cause a significant change in YSZ TBCs.
- Spray distance has not significant effect on adhesion strength of TBCs.
- YSZ is more resistant than CYSZ against thermal shock damage.
- Process parameters are more effective on CYSZ thermal shock damage.
- YSZ coated specimens which are produced at 75 mm spray distance have the best thermal shock performance.
- C875 has the best thermal shock performance among CYSZ coated specimens.

5. REFERENCES


