Effect of the composition profile and density of LPPS sprayed functionally graded coating on the thermal shock resistance

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Abstract

Low Pressure Plasma Spraying (LPPS) is a promising coating method for Functionally Graded Material (FGM) expected to be able to reduce the thermal stress in high temperature environments such as a gas turbine. In this paper, we report the effect of the composition profile and coating density of LPPS sprayed FGM, consisting of ZrO$_2$–8 wt%Y$_2$O$_3$ (YSZ) top coating, YSZ–Ni–20 wt%Cr (NiCr) FGM coating, NiCr under coating and copper substrate, on the thermal shock resistance evaluated by a modified temperature difference test. The density of YSZ and NiCr coating was successfully controlled by the chamber pressure and initial particle size in the range from 5.43 to 5.79 g/cm$^3$ and from 7.89 to 8.09 g/cm$^3$, respectively. For an YSZ composition profile from NiCr under coating to YSZ top coating (in FGM), the highest thermal shock resistance was obtained when the fraction of YSZ increased with gentle slope just over NiCr coating and acute slope just under YSZ coating. Also, the higher density coatings tended to perform the higher thermal shock resistance. Initial cracks formed in the YSZ top coating propagated into YSZ parts in FGM coating through the grain boundary of YSZ and/or the interface between flattened NiCr and YSZ particles. After the cracks connected, the coupled cracks caused the coating spallation.

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1. Introduction

Many of today’s machines, of industrial, commercial, and consumer use, have components that are subjected to severe conditions. In order to protect the surfaces of these components, novel-coating techniques are strongly desired. Among many advanced spray-coating technologies that are used to deposit thick chemical and thermal protective barriers, plasma spraying is considered to be one of the most effective and most widely used. Especially, Low Pressure Plasma Spraying (LPPS) is a promising method of applying coatings to surfaces for their protection [1–3].

LPPS processing can accommodate a wide range of materials, including refractory metals and ceramics, with its high capacity for melting and fusing particles. Due to several factors, LPPS coatings thus often demonstrate higher adhesion strength, higher bulk strength, and lower porosity, especially in metallic systems, than do APS coatings. Moreover, studies have shown LPPS to improve the overall properties of sprayed metallurgical coatings [4]. Hence, LPPS technique has been already applied to a turbine blade and vane in an engine of airplane to improve surface resistance against abrasion or thermal damage [5,6].

For thermal barrier coatings (TBCs), it is required to use higher temperature turbine inlet gas, in order to reduce in fuel consumption. However, conventional ceramic/metal TBCs have a disadvantage in cracking and spalling of the ceramic coatings caused by the thermal stress due to the thermal expansion coefficient difference between ceramic and metal. Functionally graded material (FGM), which has a gradual composition variation interface from the metallic layer to the ceramic layer, is expected to be able to reduce the thermal stress [7,8].

An optimization of a compositional profile, to reduce the thermal stress, of FGM has been carried out by Finite Element Method (FEM) analysis [7]. Polat, additionally, reported that porosity in coating can reduce the thermal stress [9]. However, the numerical result might include errors due to uncertainty of the values of thermal properties (thermal expansion coefficient, thermal conductivity, heat capacity, and density) and mechanical properties (Young’s
properties for varied composition [10] although the effect of temperature and porosity on the properties has not been completely measured yet. These parameters bear a complex relation to the thermal shock resistance each other, and the optimum compositional profiles and coating density of FGM must therefore be determined by experiments.

The coating density of YSZ or NiCr reflects on the density of FGM. After investigating the effect of spraying conditions on the coating density, we found that there was relationship between chamber pressures and density, and between initial particle size and density.

A gas burner heating test [11] and a temperature different test heating a sample by Xe lamp in vacuum chamber [12], has been an established method to evaluate the fracture behavior of TBCs of FGM. The burner heating test can estimate the thermal shock resistance in an oxidizing environment and TBCs are subjected to actual environment. On the other hand, temperature different test is performed in non-oxidizing environment; therefore, the temperature difference test under oxidizing environment can be useful as an actual evaluation method.

The current study is motivated by the experimental optimization of the LPPS sprayed FGM suitable for TBCs [4,13,14]. This paper describes the effects of the composition profile and coating density of TBCs in FGM on the thermal shock resistance by using a modified temperature difference test. A FGM consisting of Ni based supper alloy and Ytoria Stabilized Zirconia is one of the most common TBCs. As shown here, the thermal shock resistance is strongly dependent on the profile and coating density. Knowledge of this dependence has guided our selection of spray conditions and configurations needed to extend these TBCs to more challenging structural materials.

2. Experimental procedure

The plasma gas used here is a mixture of hydrogen and argon, which is widely used in LPPS. Hydrogen is added to argon to increase the overall plasma enthalpy at a fixed discharge current (higher operating voltage), and to increase the plasma thermal conductivity. These two effects enhance the heating of particles.

The plasma source and deposition facility consists of a 1.7 m diameter by 2.5 m long vacuum chamber equipped with feed through for the powder injection (the powder feeder is located outside of the vacuum chamber), water for substrate cooling, and robotic system to scan the substrate. The plasma discharge head is a modified commercial EPI model 3 spraying gun, with a redesigned cathode for spraying through 4 ports of powder feeder. Regulated current delivered to the arc source by a EPI model 485 plasma power supply at an arc power of 77 kW (1400 A, 55 V), argon and hydrogen plasma gas flow rate of 120 l/min and 15 l/min, respectively, an argon powder carrier gas flow rate of 15 l/min and a spray distance of 150 mm. The vacuum chamber is pumped by a mechanical pump and possible to maintain chamber pressures in the range from 0.6 to 101 kPa during spraying, although the present results are for 13–53 kPa, which is a typical range over which we have performed spray studies.

Before evaluating the thermal shock resistance of FGM, an investigation of the effect of spraying conditions on the coating density was carried out. Ni–20 wt%Cr (NiCr) powder with average particle diameters of 39, 57, 81 μm and ZrO₂–8 wt%Y₂O₃ (YSZ) powder with an average diameter of 27 μm are employed. The YSZ coating density is controlled by the chamber pressure, and the density of NiCr coating is controlled by the chamber pressure and particle diameter. At room temperature, the density corresponding to the value of each coating is measured by Archimedes method and the strength of coating is estimated by Modified Small Punch (MSP) test [15].

FGM coatings are deposited by changing the mixture ratio of NiCr and YSZ powder feed rate from NiCr under coating to YSZ top coating. Fig. 1 shows three types of FGM cross-sectional photograph and composition profile analyzed by Electron probe micro analyzer (EPMA) are shown in Fig. 2. FGM consists of a copper substrate, NiCr under coating, FGM coating, and YSZ top coating each with a thickness of 15, 0.1, 0.9, and 0.2 mm, respectively. The increasing rates of YSZ content via the thickness of FGM coating are different from each other. The YSZ content of Type B is almost proportional to the distance from the top of NiCr under coating. The YSZ increasing rate of type A is that the increasing rate above the NiCr coating is gentle, and that below YSZ coating is acute. The rate of type C is opposite to the rate of type A. Thus, the total amount of YSZ content in FGM coating of type C is the largest of the three cases.

Fig. 3 shows a schematic diagram of a modified temperature difference test. A Xe Lamp beam (Panasonic, model Light Beam 150) with an electric power of 5 kW provided a precise heat source of the coating surface, and the sample with a diameter of 30 mm is cooled from the undersurface in the course of the test. A reference beam intensity distribution was taken to be the temperature distribution, measured by thermocouples, using copper substrate without coating. This data inferred that the lamp beam was focused on the coating surface with a diameter of around 2 mm.

The thermal cycle is 15 s heating Xe irradiation and 15 s cooling, until surface temperature reaches to the temperature of cooling water. A delimitation of crack formation is defined by the number of thermal cycles at which cracks, on the coating surface, can be observed by optical microscopy with a magnification of 5.

A temperature measurement method using thermal video does not need welding process like a method using thermocouple and then it is applicable to measure...
the temperature of YSZ surface. Because the temperature, measured by thermal video, has disadvantage in the temporal/spatial resolution, then, this temperature is only used to evaluate the maximum temperature value at the center of surface during heating. The maximum temperature, measured by a thermal video: Avionics model TVS-3000, included an error of 50 K, which may have been incurred by the accuracy of the thermal video.

3. Results and discussion

3.1. Controlling coating density

Fig. 4 shows the effect of increased chamber pressure on the YSZ coating density and NiCr coating density. Coating density was maximized by an intermediate chamber pressure of 27 kPa. Above 27 kPa, the benefit of increased plasma temperature was offset by the shrink of plasma volume. Conversely, below 27 kPa, even though the expansion of plasma jet, the energy density of plasma decreased. Hence, in both cases, the lack of particle heating caused the density drops.

For YSZ and NiCr mixture coatings, a mixing rule, Eq. (1), infers that the density of mixed material is proportional to a volume fraction of each material.

\[
\rho_{\text{mixed}} = (1 - x)\rho_{\text{YSZ}} + x\rho_{\text{NiCr}}
\]  

Where \(\rho_{\text{mixed}}\) is the density of mixed coating, \(\rho_{\text{YSZ}}\) is the density of YSZ coating, \(\rho_{\text{NiCr}}\) is density of NiCr coating and \(x\) is the NiCr volume fraction. The influence of varying NiCr content on the coating density is shown in Fig. 5, for experiments performed at a chamber pressure of 13 kPa. Based on the mixing rule, the theoretical density of mixture coating was calculated from the measured values of the 100% YSZ and 100% NiCr density of bulk prepared by melting and solidifying those particles by transferred arc in vacuum. NiCr content values used here were estimated from the power feed rates of YSZ and NiCr particles.
expected, the densities of mixture coatings were almost proportional to the NiCr content. Also, for an initial NiCr particle average size, it was found that at the size of 57 μm, the density of YSZ–NiCr mixed coating was maximized. For obtaining higher density coating, the optimum particle size of NiCr being 57 μm was almost twice of the YSZ particle size (Average = 27 μm). The particle size was the only variable parameter that could be controlled separately because one plasma gun was employed for spraying YSZ and NiCr simultaneously in our study.

The density depends substantially on the state of particle melting which is preferred to be beyond melting point. Assuming that latent heat and radiation loss are negligible, a time required to heat a particle from a room temperature to the melting point, \( t_{\text{melting}} \), is expressed by

\[
t_{\text{melting}} = \left( \frac{\rho d C_p}{6\alpha} \right) \log \left( \frac{T_0 - T_g}{T_m - T_g} \right)
\]

where \( d \) is the particle size; \( C_p \), the heat capacity; \( \alpha \), the heat transfer coefficient; \( T_0 \), the room temperature; \( T_m \) the melting point; and \( T_g \) is the plasma gas temperature (assuming 3500 K). The NiCr particle size that brings the same melting time with YSZ particle size, calculated from Eq. (2), is to be almost twice that of YSZ, and this value is similar to our previous experimental result.

From these results, the density of YSZ coating and NiCr coating could be controlled in the range from 5.43 to 5.79 g/cm³, and from 7.89 to 8.09 g/cm³, respectively. By using these spraying technique, the effect of varying coating density and the composition profile on the thermal shock resistance was investigated.

3.2. Thermal shock resistance

A comparison is made on the thermal shock resistance for the composition profile and YSZ coating density in Fig. 6. The spraying conditions for the results shown here are the same as those of Fig. 4. The values in bracket indicate the surface maximum temperature measured by thermal video during this test. The profile with a type A demonstrated the highest thermal shock resistance, with crack forming thermal cycle in excess of 30. One of the possible primary reasons for this result was that, in the case of type C, the higher thermal stress was loaded on YSZ coating due to the higher YSZ content. Another possible reason is that because the lower surface temperature in the case of type A yielded the higher strength of YSZ coating during the test, the higher strength contributed to the higher thermal shock resistance.

As expected, use of the higher density coating resulted in overall higher thermal shock resistance. In general, it is observed that the sprayed coating strength increases with increasing of its density. Thus, the tolerance of dense coating was superior to that of porous coating.

As described, the coating density was controlled by the chamber pressure, therefore, this result implied not only the effect of YSZ coating density but also NiCr
density. One must consider the possibility that the NiCr density affects the thermal shock resistance. For this experiment, to distinguish the effect of both coating densities, the dependence of NiCr density was evaluated and results are shown in Fig. 7. We illustrate this effect for type A and type C profile with YSZ density of 5.70 and 5.79 g/cm$^3$. The spraying condition for an YSZ density of 5.70 g/cm$^3$ was chamber pressure of 13 kPa, while that of 5.79 g/cm$^3$ was 27 kPa. For both cases, YSZ particle size was 27 $\mu$m and NiCr particle size was 39 or 57 $\mu$m determining NiCr density. It was clear from this figure that the choice of NiCr density significantly influences the thermal shock resistance in all cases. It is considered that the density should affect the coating strength and the result is shown in Fig. 8.

Fig. 8 shows the NiCr content on the mixture coating strength measured by MSP test in the cases of using 39 and 57 $\mu$m NiCr particles with a chamber pressure of 13 kPa. It was found that strength increased with NiCr content in this study range. Also, compared with a NiCr particle size of 39 $\mu$m, the strength of mixture coating with a NiCr particle size of 57 $\mu$m was higher. Furthermore, as unexpected in Fig. 7, the optimum thermal shock resistance was seemed to obtain at the YSZ density of 5.70 g/cm$^3$ and NiCr density of 8.02 g/cm$^3$ in a composition profile of type A which was not highest density coating, due possibly to a balance between strength of coating increase and thermal stress decrease. Most importantly, if the density decreases, the thermal conductivity increases, then thermal temperature decreases under a constant heat flux heating. The relevant criterion was not coincident with the result that, even though the optimum FGM has not the lowest density, its surface temperature in the test was the lowest among type A FGMs. Hence, we could not conclude that the intermediate density was the best coating.

### 3.3. Cracking and spalling process

In order to investigate the cracking and spalling process of the coating during the test, cross-section (Fig. 9) of the sample after the 30 heat cycle test was observed. Fig. 9(a) is a part of no-damage cross section. In Fig. 9(b), it was seen a small and narrow crack in YSZ coating. A crack in Fig. 9(c) penetrated from YSZ coating into FGM coating. Additionally, it could be seen, in Fig. 9(d), two cracks coupled in FGM coating. Although those features were not an exactly temporal series of a crack, it was considerable that those were a successive series of crack propagation from the point of the depth of cracks. Fig. 10 presents, also, cross-sectional photograph of the FGM after the test. It looks like that a crack takes a roundabout flattened NiCr particles and propagates through the YSZ particles or interface between NiCr and YSZ.

In order to observe detail of the crack path, especially in the direction of parallel to the coating, a plane section TEM

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**Fig. 7.** Effect of NiCr coating density on the thermal shock resistance. NiCr particle size = 39 $\mu$m at NiCr coating density of 7.96 and 8.04 g/cm$^3$, and 57 $\mu$m at that of 8.02 and 8.09 g/cm$^3$.

**Fig. 8.** Effect of NiCr content on the coating strength. Chamber pressure is 13 kPa. NiCr coating density at a particle size of 39 $\mu$m is 7.96 g/cm$^3$ and that of 57 $\mu$m is 8.02 g/cm$^3$.

**Fig. 9.** Typical cross-sectional photographs of FGM after 30-heat cycle temperature difference test. A type of the composition profile is A, YSZ density is 5.79 g/cm$^3$ and NiCr density is 8.04 g/cm$^3$. 

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photograph around a crack is shown in Fig. 11. This figure mentioned that the crack occurred along grain boundaries of YSZ and the interface between YSZ and NiCr particles. Also, the part of the residual surface after spallation was analyzed by X-ray Diffraction. Fig. 12 carried information that the surface was covered by mostly Ni composites, NiCr and NiCr$_2$O$_4$. These results could suggest that the crack, in the direction of parallel to the coating, mainly propagates through the interface and the coating spallation from the interface.

Summing up these results, it was considered that, first, an initial crack was formed in the YSZ coating and then the crack propagated into YSZ particles in FGM coating in a direction of perpendicular to the coating. Second, because crack could not spread into YSZ particles where the amount of NiCr surrounding YSZ was enough to keep from its propagation in a perpendicular direction, the crack did in the direction of parallel to the coating through the interface between NiCr and YSZ, and more than two cracks connected with each other. Finally, the coupled cracks caused the spallation of the surface part of coating.

4. Summary and conclusions

The investigation on the effect of the composition profile and coating density of FGM, consisting of YSZ and NiCr on copper substrate, was carried out using a modified temperature difference test under the constant heat flux, 5 kW. The density was controlled by the spraying conditions such as the chamber pressure and initial particle size. The density of YSZ coating and NiCr coating could be controlled in the range from 5.43 to 5.79 g/cm$^3$, and from 7.89 to 8.09 g/cm$^3$, respectively. The profile such that the increasing rate of YSZ content in FGM coating above the NiCr coating was gentle and that below YSZ coating was acute (Type A) and then the total amount of YSZ was minimized, sustained the highest thermal shock resistance. Also, the higher density coatings tended to perform the higher thermal shock resistance. The possible reasons of these results were that the higher density coating implied the higher coating strength and/or its higher thermal conductivity reduced the surface temperature and thermal stress during the test.

For a cracking and spalling process, an initial crack was formed in the YSZ top coating and then the crack propagated into YSZ regions of FGM coating in a direction of perpendicular to the coating. Additionally, because the amount of NiCr was enough high, the crack could not propagate in the depth direction; the crack did in a direction...
parallel to the coating through the grain boundary of YSZ and/or interface between NiCr and YSZ. Moreover, more than two cracks connected with each other, then the coupled cracks caused the coating spallation.

Although it should be noted that, the maximum thermal shock tolerance was achieved by the FGM with an intermediate density, our most data suggested that use of the higher density YSZ was prominent in the thermal shock resistance. Furthermore, from the standpoint of crack propagation path in the coating, it was determined that type A with higher strength of YSZ and higher interface strength between flattened YSZ and NiCr particles was the best coating for the thermal shock resistance resistance. The cracking process must therefore be strongly dependent on the strength of YSZ strength. On other hand, the interface affected the spallation. It was considered that increasing the interface strength would improve the spallation.

The coating sprayed using the higher substrate pre-heat temperature to enhance heat transfer and diffusion at the interface of particles is one of the solutions of this problem. This consideration is especially critical in LPPS because the exclusion of air from the vacuum chamber prevents the oxidation of the particle at elevated temperature.

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