The Synthesis of Graded Thermal Barrier Coatings on Nickel Substrates by Laser Induced Thermite Reactions

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Al$_2$O$_3$ and ZrO$_2$-Al$_2$O$_3$ bearing coatings were synthesized on nickel substrates by laser induced thermite reactions. The oxide coatings were produced via thermite reactions between NiO and Al powders with and without the addition of Y$_2$O$_3$-stabilised ZrO$_2$ (YSZ), respectively. In the case where no YSZ was added, a graded coating with a top layer of Al$_2$O$_3$ was produced. Whereas, when YSZ was added, the coating essentially comprised ZrO$_2$ dendrites with the interdendritic regions filled with the ZrO$_2$-Al$_2$O$_3$ eutectic phase. The formation process of the coatings is described. [doi:10.2320/matertrans.MRP2008304]

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1. Introduction

The improved thermal barrier coatings (TBCs), which are now being developed, are playing an increasingly significant role in today’s aero engines, in engines for automobiles, as well as in power generators. In this connection, functionally graded TBCs (FG-TBCs) are being seriously explored. Currently, the two most commonly used coating techniques for commercial applications of FG-TBCs are plasma spraying and electron beam physical vapor deposition (EB-PVD). Although plasma spraying provides a flexible and economical means for producing FG-TBCs, especially in forming thick coatings, there is evidence that EB-PVD formed coatings are superior to those produced by plasma spraying.\(^1\)

On the other hand, although EB-PVD is capable of producing graded TBCs, it can be difficult to adjust the chamber conditions in such a way as to achieve the desired evaporation behaviour.\(^2\)

In considering other alternative methods for fabricating FG-TBCs, laser surface treatment is becoming a strong candidate because of its relatively simple operating principles. Indeed, it has been demonstrated that laser treatment is potentially a method for producing TBCs.\(^3,4\) With this background in mind, this research proposes a self-synthesizing laser irradiation method that is based on thermite reactions, to produce FG-TBCs on Ni substrates.

In the present research, the reaction between NiO and Al is of particular interest because the reaction products of aluminium oxide and Ni-Al intermetallics are ideal for forming FG-TBCs. Up to now, only very few publications concerning ceramic coatings formed by laser treatment through thermite reactions can be found in the literature.\(^5-7\) and to the authors’ knowledge, no published work using such an approach to produce FG-TBCs on nickel substrates can be found in the literature.

2. Experimental Method

FG-TBCs were fabricated on pure nickel (99.9 mass%) substrates by using laser deposition. In this study, Al and NiO powders were used to synthesize the TBC. Under laser irradiation, a reduction-oxidation reaction between NiO and Al occurs. The Al$_2$O$_3$ phase that is formed acts as an excellent oxidation-resistant barrier. Nickel oxide was employed because aluminium oxide has a lower level of Gibbs free energy than nickel oxide, right up to very high temperatures. In addition, the intention was to form Ni-Al intermetallics by the exothermic reactions between nickel and aluminium as the intermetallics possess high melting points and good oxidation resistance. The stoichiometry to produce Al$_2$O$_3$ and some common nickel aluminumides is given by the reactions:

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\begin{align*}
3\text{NiO} + 5\text{Al} & \rightarrow \text{Al}_2\text{O}_3 + 3\text{NiAl} (+\text{heat}) \quad (1) \\
3\text{NiO} + 2\text{Al} & \rightarrow \text{Al}_2\text{O}_3 + 3\text{Ni} (+\text{heat}) \quad (2) \\
3\text{NiO} + 3\text{Al} & \rightarrow \text{Al}_2\text{O}_3 + \text{Ni}_3\text{Al} (+\text{heat}) \quad (3)
\end{align*}
\]

It was envisaged that the heat generated by the thermite reactions between NiO and Al would raise the temperature of the product, aluminium oxide, to its melting temperature. Owing to the low density of the Al$_2$O$_3$ phase, it would form at the top surface of the reaction coating, while the Ni-Al intermetallics that are formed would likely be embedded in the Ni-based matrix. Such a graded system is ideal for resisting high temperature oxidation, but its thermal conductivity is relatively high. In order to reduce thermal conductivity, Y$_2$O$_3$-stabilised ZrO$_2$ (YSZ) powder (7 mass% Y$_2$O$_3$), an excellent thermal insulation material, was used in some of the experiments. Mixed powders of YSZ, NiO and Al powders were used in the experiment to form a composite coating. The blended powders comprised 30 mass% or 60 mass% YSZ power with balanced NiO and Al powders (in a molar ratio of 3 : 5).

The mixed powders of Al-NiO with and without YSZ were delivered onto the surface of the nickel substrate through a powder feeder. Laser irradiation was performed using a 5 kW CO$_2$ continuous wave laser. The laser processing parameters were: laser power between 1100 W and 2100 W, scanning velocity between 800 and 1000 mm/min. To determine the thermite reaction temperature, a DSC experiment was performed using the mixed powders of Al and NiO (molar ratio 3 : 5) in argon gas at a heating rate of 20 K/min.

3. Results and Discussion

Figure 1 shows a cross-section of the coating, without
the addition of YSZ, which consists of two distinct layers. The results of an XRD analysis show that Al$_2$O$_3$, NiAl and Ni$_3$Al are present in the reaction coating (Fig. 2), moreover the X-ray distribution maps of elements show that the top layer basically consists of Al and O. The results thus show that the top layer is composed essentially of the $\alpha$-Al$_2$O$_3$ phase with a trace of $\gamma$-Al$_2$O$_3$. While a relatively dense layer of Al$_2$O$_3$ was obtained, cracks were found in the coating, this was likely due to thermal stresses developed during rapid solidification. It is obvious that these nickel aluminides are by-products of the thermite reactions.

The formation process of the top surface layer of Al$_2$O$_3$ is considered to be as follows. At the start of laser irradiation, a shallow molten pool was created in the substrate and subsequently Al and NiO powders were fed into the pool, while the workpiece was moving at a constant speed. Since Al has a lower melting point than NiO, it started melting once it reached the melting point which is about 933 K. When the temperature was raised to a certain temperature, the thermite reaction between NiO and Al started. According to the results of the DSC curve for the mixed powders of Al and NiO, an endothermic peak and an exothermic peak occurred at the temperatures 935 K and 1350 K respectively (Fig. 3). The endothermic peak corresponds to the melting of Al while the exothermic peak represents the thermite reaction. These results suggest that when the temperature of the molten pool reached 1350 K, the exothermic chemical reaction between molten Al and NiO started and the reactants, Al$_2$O$_3$ and NiAl were produced. Some variation in composition is expected in the melt. In fact not only NiAl was produced, other nickel aluminides, such as those according to reaction (3), were formed.

Since all the three reactions (1), (2) and (3) are exothermic, the temperature of the entire reaction layer could be increased and exceeds the melting point of alumina and forms liquid Al$_2$O$_3$. Assuming that the temperature of the reaction layer was at 1350 K when the reactions (1)–(3) occurred, the exothermic heat generated by the three reactions can be calculated as 1402 kJ, 987 kJ, 1162 kJ, respectively. It can be calculated that heat energies of 636 kJ, 422 kJ, and 388 kJ are sufficient to raise the temperature of the reaction products of reactions (1)–(3) respectively from 1173 to 2327 K, i.e. the melting point of alumina. It is therefore considered that the exothermic heat generated by the reactions was high enough to cause the melting of the Al$_2$O$_3$ phase. Comparing the density of liquid alumina and those of the other reaction products, the former was lighter, therefore it floated to the top of the reaction layer, whilst the rest of the other phases sank and mixed with the already molten substrate and formed the graded reaction coating as shown in (Fig. 1). The presence of a small amount of $\gamma$-Al$_2$O$_3$ phase indicated by the two small peaks at 2θ of 51.001° and 74.548° in Fig. 2, which were not marked in the figure, is believed to be due to the rapid cooling rate of the laser processing condition (10$^2$–10$^3$ K/s). It is known that $\gamma$-Al$_2$O$_3$ is a transitional phase that usually forms by rapid cooling below 1200 K.$^6$ Cao$^8$ reported that laser-melted $\alpha$-Al$_2$O$_3$ re-solidified as a transitional $\gamma$-Al$_2$O$_3$ phase after excimer laser irradiation. He suggested that the high cooling rate during solidification after the pulsed laser irradiation had prevented the ordering of aluminium atoms required for the formation of the stable $\alpha$-Al$_2$O$_3$. The $\gamma$-Al$_2$O$_3$ can form by changing the stacking sequence of the closed-packed oxygen sub-lattice from hcp to fcc and the occupying of aluminium cations from two-thirds of the total octahedral sites available in $\alpha$-Al$_2$O$_3$ to both octahedral and tetrahedral sites in $\gamma$-Al$_2$O$_3$.

With regard to the coating produced with the addition of YSZ (Fig. 4), the microstructure is rather different from that of the coating without YSZ (Fig. 1). In the case with YSZ, a graded coating with a top layer of Al$_2$O$_3$ was not obtained. The XRD results show that beside Al$_2$O$_3$ and the various Ni-Al intermetallics, t-ZrO$_2$ phase and a small amount of m-

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**Fig. 1** A cross-section of the coating formed without the addition of YSZ.

**Fig. 2** X-ray diffraction pattern of the coating without YSZ.

**Fig. 3** DSC curve of the mixed powders of Al and NiO.
ZrO$_2$ phase were present in the coatings. Moreover, as YSZ increased from 30 to 60%, the amount of ZrO$_2$ increased. A TEM study was conducted to examine the microstructure of the coating. The results revealed the presence of a well-defined lamellar eutectic structure of Al$_2$O$_3$-ZrO$_2$ in the interdendritic regions (Fig. 5).

In the case where the YSZ powder was added to NiO and Al powders, the main reaction is considered to have occurred between NiO and Al, since a large free energy of reaction ($\Delta G < 0$) is obtained from the reactions (1)–(3). Therefore spontaneous reactions are expected to occur between NiO and Al. On the other hand, the free energy of the reaction between ZrO$_2$ and Al, i.e. $4\text{Al} + 3\text{ZrO}_2 = 3\text{Zr} + 2\text{Al}_2\text{O}_3$, at elevated temperatures is positive ($\Delta G > 0$), this indicates that it is a non-spontaneous reaction. Assuming this is the case, then a simple calculation shows that a heat energy of 1072 kJ will be sufficient to raise the temperature of the reaction products of NiO and Al (1 mol $\text{Al}_2\text{O}_3$ and 3 mol NiAl) and the extra 1 mol ZrO$_2$ from 1350 to 2950 K, i.e., the melting point of ZrO$_2$. Given that the exothermic heat generated by reaction (1) is 1402 kJ which is higher than the calculated value of 1072 kJ, therefore Al$_2$O$_3$, NiAl and ZrO$_2$ phases would be in liquid form. In considering the solidification process, it is believed that the high melting point ZrO$_2$ phase will solidify first and form dendrites. As the results of the EDX analysis showed that the constituents of the dendrite were primarily Zr and O with a few percent Al present, it is therefore believed that Al$_2$O$_3$ exists in solid solution form in the ZrO$_2$ dendrite. This is in agreement with the ZrO$_2$–Al$_2$O$_3$ phase diagram. As the temperature continuously decreased, the eutectic structure of ZrO$_2$–Al$_2$O$_3$ formed in the interdendritic regions together with some nickel aluminides. Under the experimental conditions where 30 mass% or 60 mass% YSZ was employed, a graded coating was not formed. It is considered that if the amount of YSZ is much reduced, a graded coating can be produced and further studies on this will follow shortly.

It is worth noting that unlike the coating formed without YSZ, which contained horizontal cracks at the interface between the top Al$_2$O$_3$ layer and the underneath reaction coating, such cracks were not observed in the coating when YSZ was added. This suggests that the introduction of the ZrO$_2$ phase into the TBC helps to alleviate stresses arising from the thermal expansion mismatch between the Al$_2$O$_3$ phase the metal phase. Actually, the thermal expansion coefficient of ZrO$_2$ is between that of the Al$_2$O$_3$ phase and nickel.

### 4. Conclusions

The study showed that laser treatment is a promising method for coating nickel with an Al$_2$O$_3$ or a ZrO$_2$–Al$_2$O$_3$ bearing thermal barrier coating. Without the addition of YSZ, a top layer of Al$_2$O$_3$ was obtained and a graded coating was produced, while when YSZ was added, the entire coating was composed essentially of ZrO$_2$ dendrites with the ZrO$_2$–Al$_2$O$_3$ eutectic structure. Further work is required to optimise the parameters of the process. This may include adjusting the composition of the mixed powders, in order to obtain coatings of good integrity.

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### REFERENCES