Microstructural study of as sprayed and heat treated Ni\textsubscript{3}Al coatings deposited by air plasma spraying technique

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Abstract. Air plasma spraying system was utilized to deposit Ni\textsubscript{3}Al coatings on AISI 321 steel samples. After plasma spraying the coatings were heat treated at different temperatures i.e. 500 \degree C to 800 \degree C for 10 to 100 hours. The characterization tools such as, X-Ray diffraction analysis, optical and scanning electron microscopy were used. By comparing the XRD scan data of as sprayed and heat treated coating, it was observed that the formation of NiO increases drastically with time and temperature. Due to the formation of NiO, hardness was also enhanced. The oxidation behavior was observed by using optical microscope and when it was studied that the oxidation was increasing with time and temperature. Further, the SEM tool was utilized to study the detail microstructural behavior such as shrinkage cavity and oxide particles. The other phases like alumina and spinel phases were determined by using Energy dispersive spectrometer method.

1. Introduction

The intermetallic compounds have been established speedily, in matching with other new materials. These materials have best applications to fulfil the requirement of industry such as power generation, coal-burning boilers, fluidized beds, gas turbines and combustion of heavy oils [1], synthetic fuels, and pulverized coal. To protect the components used in area, protective coatings play a vital role to protect the surface of hardware [2]. This complex validates decent structural properties such as low density, increase in yield strength with temperature, high strength in relation to the specific mass, oxidation resistance and excellent creep properties [3-7]. Nickel aluminide is comparatively less utilized, in industry, as compared to iron and chromium aluminde [8].

The coating techniques such as pack cementation, plasma spraying and chemical vapour deposition are utilized to deposit the metallic, ceramic, cermets and intermetallic powders on different substrates, but plasma spraying is showed to be the best technique due to its flexibility in depositing [9]. This technique can deposit thick coatings up to 1000 micrometers. More, this technique is useful for each size and shape of the substrate material.

The hot sections of components being used at high-temperature, oxidation is one of the problem in boiler tubes and gas turbines. Superalloys and Stainless steels are difficult to sustain both high-strength and oxidation at high temperature [10]. Thus, at high temperature oxidation behavior of aluminide coatings is important [11]. In this work, the as sprayed coatings were isothermal heat treated and oxidation behavior of Ni\textsubscript{3}Al coating was studied.
2. Experimental

2.1. Deposition of coating

Nickel aluminide intermetallic powder of irregular shaped (Figure 1) AMDRY-404, needing 45-125 µm size was used in these experiments. Air plasma spraying system of 80KW was utilized to deposit the coating on the stainless steel (AISI-321) substrates. The surface of the substrates were grit blasted with alumina particles before the coating. The grit blasting parameters are mentioned in the Table 1. The substrate surface roughness was ranged from 3 to 5 µm (Ra) after grit blasting. For plasma spraying 25 mm diameter samples were screwed in a steel fixture and the fixture was rotated at 120 rpm while the plasma torch move in to and fro manner along the rotation axis of the samples. The parameters used during spraying are mentioned in the Table 2. The spraying gun (80KW) having 7.5 mm anode internal diameter. The powder injector was fixed at 90° with respect to the spraying gun, whereas, the internal diameter of the powder injector was 1.5 mm.

| Table 1. Parameters used in grit blasting |
|------------------------------------------|
| Parameters                                |
| Air Pressure, psi                         | 90 |
| Angle between the substrate surface and nozzle, degree | 90 |
| Time, min                                | 05 |
| Grit size, mesh                           | 46 |

| Table 2. Parameters used in plasma spraying |
|---------------------------------------------|
| Parameters                                  |
| Current, A                                 | 500 |
| Voltage, V                                 | 70 |
| Plasma gas (Ar) flow rate, liter/minute    | 75.5 |
| Secondary gas (H₂) flow rate, liter/minute | 4.72 |
| Powder feed rate, g/min                    | 113.6 |
| Carrier gas (Ar) flow rate, liter/minute   | 16.5 |
| Standoff distance, mm                      | 125 |

The powder feed rate and the spray conditions were optimized by doing different experiments. After each experiment, the interface and the porosity of the coating was measured. The optimized spraying parameters showing minimum porosity level were finalized to spray the final coating. The temperature of the substrate was kept below 150°C by using compressed air at 100 MPa during plasma spraying.

2.2. Heat treatment of coating and characterization

The as sprayed samples were exposed at 500 to 800°C with 100°C increments, whereas, the holding time at each temperature was 10, 30, 60 and 100 hours. The heating rate was kept at 10°C per minute during heat treatment. As sprayed and heat treated samples were then characterized with the help of X-Ray Diffractometer (XRD), Scanning Electron Microscope (SEM), optical microscope and hardness tester. Density of the coating was calculated by utilizing the Archimedes method. For this purpose the coating sample was delaminated from the surface of the substrate and then weighed in air and water.

For X-ray diffraction (XRD) analysis, the samples were scanned with JEOL JDX-99C, using Ni-filtered Cu-Kα radiation. The microstructures of the top and cross sectional coatings were studied using optical and scanning electron microscope, before and after heat treatment process. The chemical composition profiles and analysis of some important phases of as - sprayed and heat treated samples were estimated by Energy Dispersive Spectroscopy (EDS) technique.
3. Results and discussions

3.1. Metallography

To determine the thickness of coating, as sprayed sample was cross sectional mounted and it was revealed that about 250-270 micrometer thick coating was deposited on the steel substrates, Figure 2. The interface between the substrate and the coating was also studied and found satisfactory. It was observed that few porosity sites were also present in the coating, Figure 2. Further, un-molten particles were also present randomly within the coating, Figure 2. A thin grayish oxide film was observed between the splats, which was probably formed due to oxidation of powder, during the spraying process.

The detail microstructural study of the heat treated samples treated for 100 hours at different temperatures revealed that the oxidation of the coating increases with time and temperature. At low temperatures i.e. at 500°C for 100 hours, it was observed that the oxidation just started along the grain boundaries of splats as shown in the Figure 3. This coating can be utilized at 500°C up to 60 hours satisfactory and after treated for long time, it will dissociated in to new phase like NiO. After 600°C for 100 hours the oxidation of coating was gradually increased with time and temperature Figure 4. When the temperature was increased up to 700°C, it was observed that the oxidation of the coating was almost uniform throughout the coating Figure 5, however, at higher temperature as at 800°C this was more prominent at the top surface. This is because of the initial attack of oxygen which almost reached uniformly throughout the coating and formed a thin grayish layer around the splats, Figure 6.

It was noted that the oxygen was predominantly attacked on the top surface of the coating; this was more prominently visible in the samples heat treated at 800°C, Figure 6. Further, in the same samples, it was observed that the level of porosity also increased closed to the top surface of the samples, Figure 5. This is probably due to the formation of more oxides at the top surface which upon cutting and grinding broke away due to brittleness. , as heating timing is increased, more NiO oxides are formed on surfaces than smaller heating times.

Figure 1. SEM image showing the morphology of spraying powder

Figure 2. As sprayed nickel aluminide coating showing different features of the coating i.e. porosity (encircled), oxide layers (arrows) and un-melted particles (dotted box)
3.2. Micro hardness testing

The as sprayed and heat treated samples were subjected to micro-hardness testing which was performed on all the samples. For this purpose the hardness was made on the cross section as well on the surface of the samples. All the hardness tests were performed on 100 gram load with 10 seconds dwell time. At least five to ten hardness values were taken from different portions of a sample. The results demonstrate that the hardness on the surface of the samples, continually increases with increasing temperature as shown in Figure 7. The increasing in hardness values are due to the formation of NiO phase. This nickel oxide phase is more dense and hard as compare to intermetallic phase. As heating time is increased, more hardness on surface is achieved than lesser heating time. The hardness data taken from the cross section of the samples, however, demonstrated a constant increase till 600°C and then a decreasing trend in the same as shown in Figure 8. The decrease in hardness values is maybe due to the cracking phenomenon observed at higher temperatures which caused relaxation of stresses. The decreasing hardness trend can be explained by the fact that the formation of NiO at the boundaries of the splats may weakened the overall structure, while the force was acting from the cross-section side.
3.3. Porosity measurement

After plasma spraying, density of the as sprayed coating was measured by taking the ideal density of Ni$_3$Al i.e. 7.29 g/cm$^3$ [12], and porosity was calculated from the measured value of the chipped off coating, which was 6.9 g/cm$^3$. It was detected that the porosity of the sprayed Aluminide was about 5.35%.

3.4. Phase analysis

For phase analysis of as-received powder for coating purpose it was revealed that Ni$_3$Al was predominately formed. XRD pattern of samples exposed at different temperature for different times are observed but here only two XRD scans of samples treated at 100 hours for 500°C to 800°C were discussed for comparison in Figures 9-10. X-Ray diffraction analysis demonstrates that small percentage of NiO formed after 100 hours exposure at 500°C. It was observed that by increasing the temperature above 500°C, the formation of NiO became relatively faster and even noted after 10 hours exposure at 600°C. It was noticed that the formation of NiO phase was linear at all the exposed temperatures (i.e. 500 and 800°C), Figures 9-10. However, it was observed that the slope of the curves was increased with increase in temperature.

4. Conclusion

Nickel aluminide coating when subjected to different temperature for different times revealed the formation of nickel oxide phase. This NiO phase frequently increases at different temperatures with time. It was also observed that due to the formation of NiO phase the hardness of the coating constantly increasing. The porosity level was also controlled by optimizing the spraying parameters. The percentage of other phases such as alumina and spinels were 1-2 % which were not detected by XRD scans due to less amount, only observed by EDS.
5. References

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