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EFFECT OF ISOTHERMAL TREATMENT ON Ni₃Al COATINGS DEPOSITED BY AIR PLASMA SPRAYING SYSTEM

Ni$_3$Al coatings were obtained on AISI 321 steel samples by air plasma spraying system. The behavior of heat treatment on intermetallic coatings were evaluated after exposure at various temperatures i.e. 500ºC to 800ºC. The stay time in this regard was varied from 10 to 100 hours. The coatings were then characterized by X-Ray diffraction analysis, optical and scanning electron microscopy, eddy current measurements and stress analysis. It was observed that the formation of NiO increases drastically with time and temperature. The hardness of the coating increases with the formation of NiO. It was noted that the residual stresses can be correlated with the formation of NiO. Further, the development of residual stresses can be monitored by a non-destructive technique i.e. eddy current method.

Keywords: Air plasma Spraying, Ni-20Al, Residual Stresses, Intermetallic coating, Nickel aluminide

1. Introduction

Metallurgy of ordered intermetallics has been developed rapidly, in parallel with other new materials. The new developments can cater the needs of industry and power generation, such as coal-burning boilers, fluidized beds, gas turbines, combustion of heavy oils [1], synthetic fuels, and pulverized coal. In such environments, protective coatings can help to protect the surface of hardware [2]. Nickel aluminide coatings can be used in industrial applications having high temperature corrosive environments. Recently many researchers showed great interest in intermetallic compounds such as Ni$_3$Al. This compound demonstrates good 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 aluminide [8].

There are many coating techniques such as pack cementation, plasma spraying and chemical vapour deposition for the deposition of Ni$_3$Al. However, plasma spraying is proved to be the best technique due to its versatility in depositing metallic, ceramic, cermets and intermetallics powders [9]. This technique can deposit thick coatings i.e. more than 100 micrometers. Further, the freedom of size and shape is available without degrading the substrate material.

Degradation of hot sections by high-temperature oxidation is one of the problem in gas turbines. Stainless steels and superalloys 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, isothermal oxidation behavior of Ni$_3$Al coating, sprayed by air plasma technique, was studied along with the feasibility of non-destructive evaluation.

2. Experimental

2.1. Deposition of coating

Irregular shaped nickel aluminide (Fig. 1) powder, AM-DRY-404, having 45-125 µm size was used in these experiments. Air plasma spraying system was utilized to deposit the coating on the stainless steel (AISI-321) substrate. For this purpose 80KW plasma gun was utilized. Before coating the surface of the substrates were grit blasted with alumina particles. During grit blasting the air pressure was kept at 90 psi and the angle between the substrate surface and nozzle was about 90º. After grit blasting the substrate surface roughness was ranged from 3 to 5 µm (Ra). For plasma spraying 25 mm diameter samples were screwed in a steel fixture. The fixture was then rotated at 120 rpm while the plasma torch move in to and fro manner along the rotation axis of the samples. Freshly grit blasted samples were coated by utilizing the spraying parameters shown in Table 1. The spraying gun (80 KW) 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. During plasma spraying the temperature of the substrate was kept below 100°C by using compressed air at 1 MPa.

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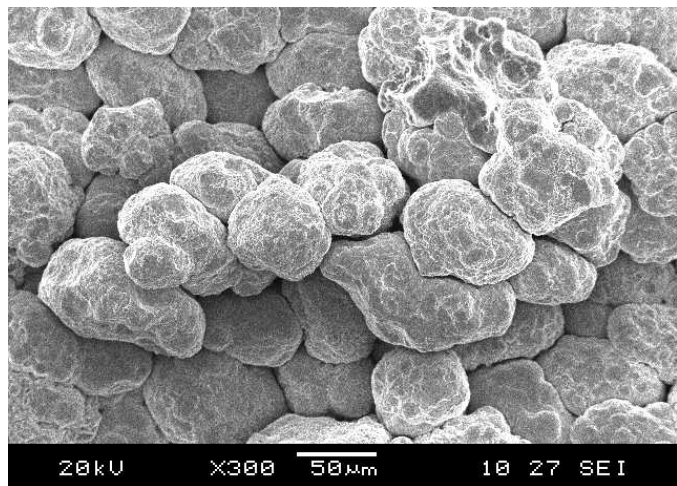\#   Corresponding author: engrkhalid80@yahoo.com

Fig. 1. SEM image showing the morphology of spraying powder

TABLE 1

Parameters used in plasma spraying

Parameters	
Current, A	500
Voltage, V	70
Plasma gas (Ar) flow rate, dm^3/min	75.5
Secondary gas (H$_2$) flow rate, dm^3/min	4.72
Powder feed rate, g/min	113.6
Carrier gas (Ar) flow rate, dm^3/min	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 spraying parameters showing minimum porosity level were selected to spray the final coating.

2.2. Isothermal treatment of coating and characterization

After coating the samples were subjected to isothermal heat treatment cycles. In this regard, the 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. During heat treatment the heating rate was 10°C per minute. 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-Ka 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.

2.3. Simulated experimentation for non-destructive evaluation

In order to simulate the interaction of eddy current and the stresses, present within the coating, a series of experiments were done. In this regard, tensile test steel samples were selected in fully annealed condition. The samples were then subjected under a known stress by utilizing a universal testing machine. At each stress condition, the values of eddy current were noted and a curve was drawn against the applied stress and the eddy current values. In this regard, a standard eddy current defectoscope was utilized to measure the eddy current values for different heat treated samples.

3. Results and discussions

3.1. Metallography

The cross section of the as received sample revealed that about 250-270 micrometer thick coating was deposited on the steel substrates, Fig. 2. The coating consists of well developed
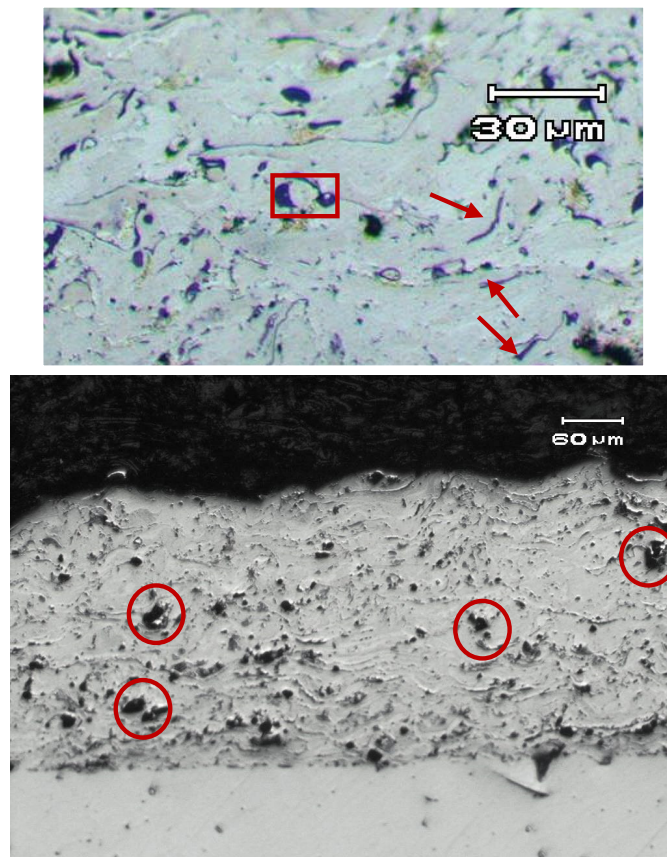

Fig. 2. As sprayed Nickel Aluminide coating showing different features of the coating i.e. porosity (encircled), oxide layers (arrows) and unmelted particles (dotted box)

splats with good interface between the substrate and the coating. It was observed that few porosity sites were also present in the coating, Fig. 2. Further, un-molten particles were also present randomly within the coating, Fig. 2A thin grayish oxide film was observed between the splats, which was probably formed due to oxidation of powder, during the spraying process.

The microstructure of the heat treated samples revealed that the oxidation of the coating increases with time and temperature. At low temperatures i.e. upto 700°C, it was observed that the oxidation of the coating was almost uniform throughout the coating (Fig. 3), however, at higher temperature 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, Fig. 3. Further, it was noticed that the samples exposed at 600°C for 60 hours, had a formation of new grains at the periphery of the splats, Fig. 4. As these grains were grown at the peripheral
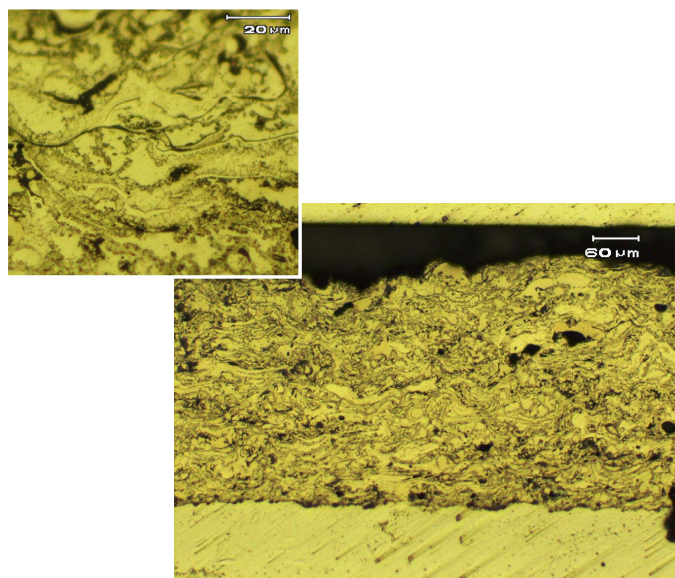

Fig. 3. NiAl coating exposed at 700°C for 60 hours showing uniform distribution of oxides throughout the coating
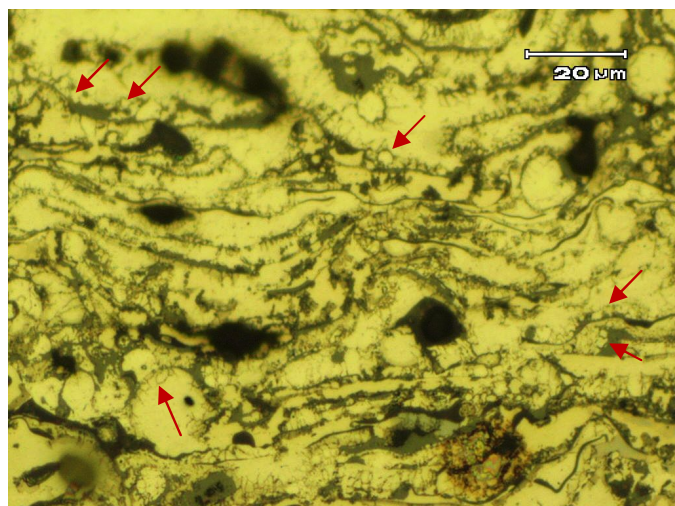

Fig. 4. Growth of new grains (arrow) on the surface of the splats. The sample exposed at 600°C for 60 hours

surface of the splats, it can be inferred that the formation is probably due to the oxidation process.

It was noted that the oxygen was pre dominantly attacked on the top surface of the coating; this was more prominently visible in the samples heat treated at 800°C, Fig. 5. Further, in the same samples, it was observed that the level of porosity also increased closed to the top surface of the samples, Fig. 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. Yes, as heating timing is increased, more NiO oxides are formed on surfaces than smaller heating times.
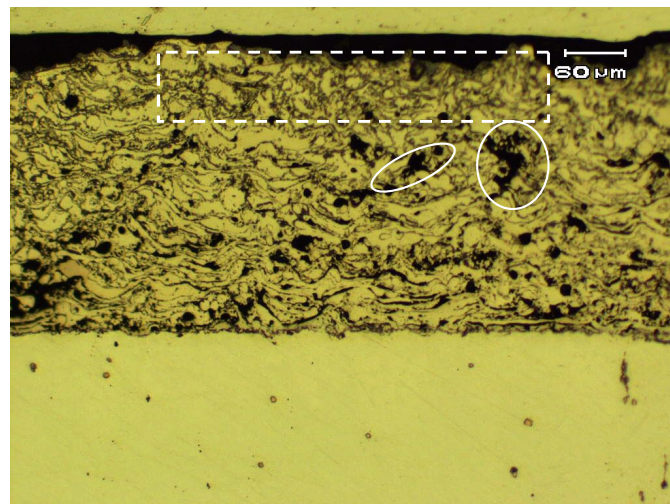

Fig. 5. Sample exposed at 800°C for 60 hours showing more attack of oxygen at the surface (marked with box) and the formation of porosity (encircled)

3.2. Micro hardness testing

Micro-hardness testing was performed on all the samples i.e. before and after heat treatment process. For this purpose the hardness was made on the cross section as well on the surface of the samples, Fig. 6. All the hardness tests were performed on 100 gram load with 10 seconds dwell time. Indentation type and geometry was pyramid and indentation depth depends upon hardness values. At least five to ten hardness values were taken from different portions of a sample. The results demonstrate that the hardness, from the surface of the samples, constantly increases with temperature. The higher hardness values at higher temperature are attributed to the formation of nickel oxides. The % of NiO is increased and oxide layer was made denser. 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. 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.
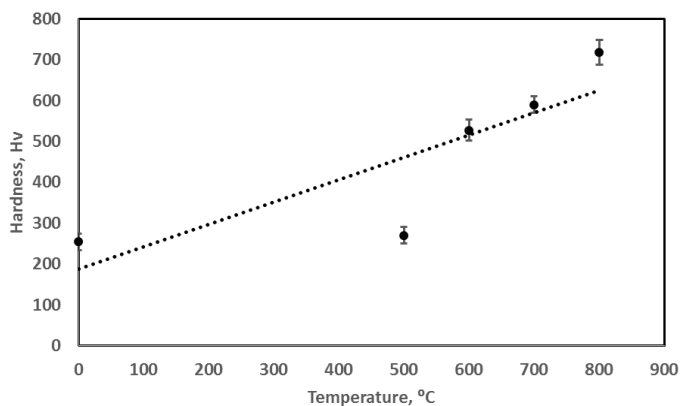
Fig. 6. Effect of temperature on hardness of the coating exposed for 100 hours

3.3. Chemical composition profile

The chemical composition profile of one of sample exposed at high temperature was performed to observe the percentage variation of chemical species. In this regard, the sample exposed at 700°C for 100 hours was selected. It was noted that the elements both from substrate and coating were diffused in each other, Fig. 7. It was demonstrated that the chemical species present in higher concentration diffused from higher to the lower side. For instant chromium and iron diffused in to the coating and nickel diffused out towards the underlying substrate. However, no change in aluminum concentration was observed due to the formation of intermetallic with nickel matrix. This diffusion activity may create the voids at the interface and deteriorate the adhesion between the substrate and the coating.
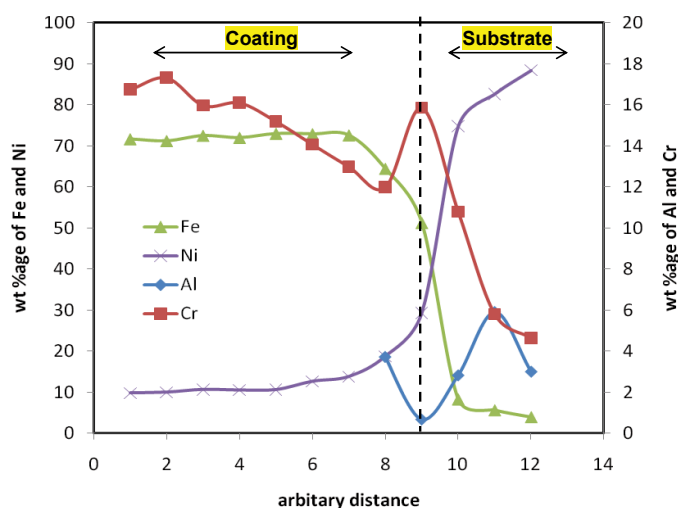

Fig. 7. Chemical composition profile for the samples exposed at 700°C for 100 hr

3.4. Porosity measurement

The density of the 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 observed that the porosity of the sprayed Aluminide was about 5.35%.

3.5. Phase analysis

Phase analysis of as-deposited coating revealed that Ni$_3$Al was predominately formed. XRD pattern of samples exposed at different temperature and exposure time are compared in Figures 8-11. 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. 600, 700 and 800°C), Fig. 9. However, it was observed that the slope of the curves was increased with increase in temperature. In Fig. 12, it was noted that at 600°C the formation of NiO varied from 20% to 25% for 10 to 100 hours, similarly, this variation increased from 30 to 55% and 55 to 85% for the samples exposed at 700°C and 800°C respectively. Intensities of XRD plots were utilized to measure the NiO content.
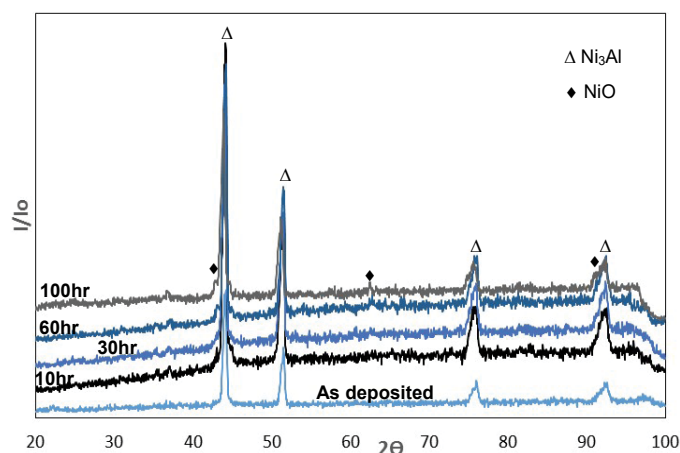

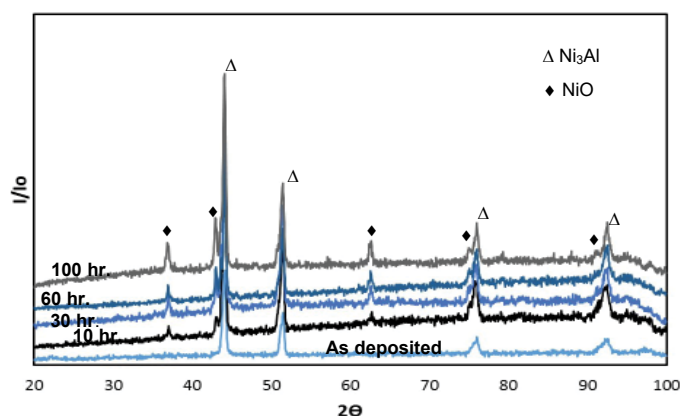Fig. 8. Comparison of XRD results of Ni$_3$Al coating treated at 500°C for different times

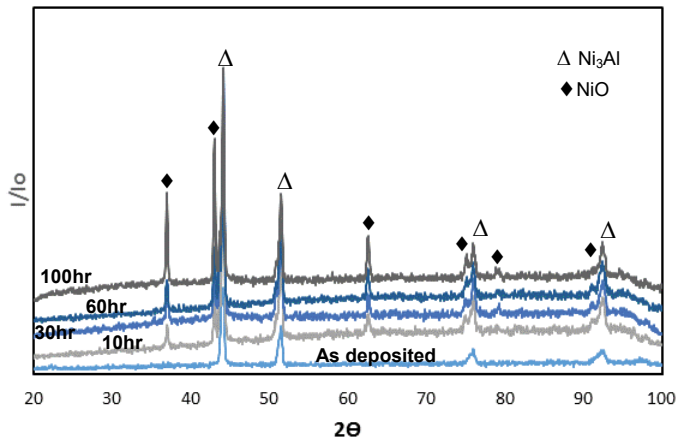Fig. 9. Comparison of XRD results of Ni$_3$Al coating treated at 600°C for different times

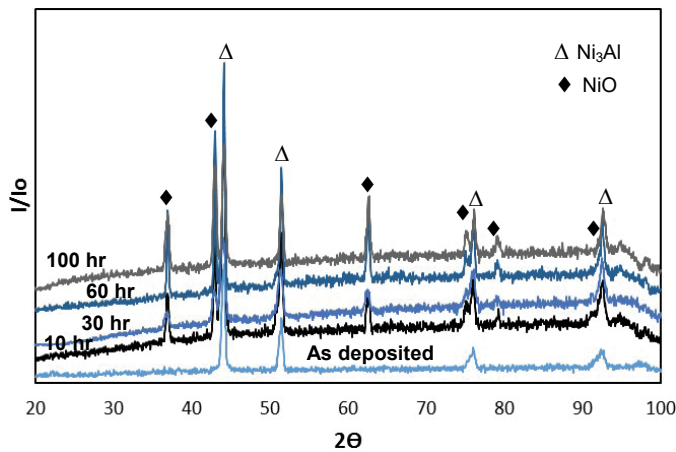Fig. 10. Comparison of XRD results of Ni₃Al coating treated at 700°C for different times

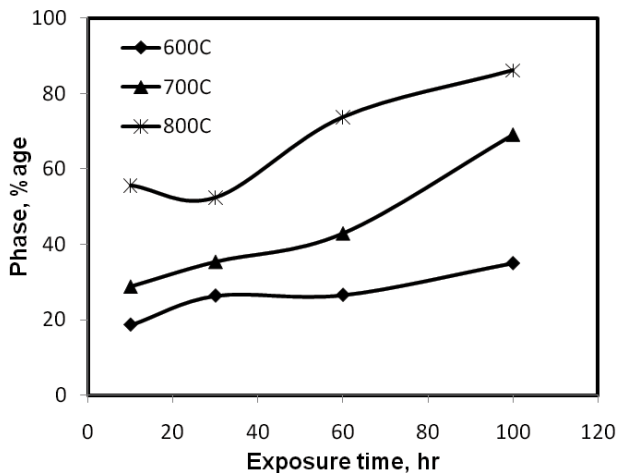Fig. 11. Comparison of XRD results of Ni₃Al coating treated at 800°C for different times

Fig. 12. Phase percentage of NiO phase at different temperatures and times

3.6. Stress analysis

The residual stresses of the as-sprayed coating and the change in induced stresses due to phase transformation can be calculated by using the XRD plots. In this regard, number of

models are being utilized by different researches [13-14]. In this work N. Choudhury et al. [15] model was utilized and the stresses were calculated after the long thermal treatment. According to this model:

$$\delta = \left(\frac{a-a_0}{a_0}\right)\left(\frac{E}{2v}\right) \qquad (1)$$

where:
- δ – residual stress,
- a – lattice parameter after Thermal Treatment,
- a_0 – lattice parameter of as spray coating,
- E – young's modulus,
- v – poison's ratio.

Since the formation of NiO at higher temperatures contributes towards the development of stresses in the coating, therefore, (111) plane of NiO phase was considered to calculate the residual stresses. In this regard, the value of E and v for NiO are taken as 171.8 GPa and 0.384 respectively [16]. After plotting the values of the stresses against the thermal treatment, it was observed that the behaviors of stresses are different at different temperatures as shown in the Fig. 13. It can be observed in Fig. 13 that at 600°C the level of overall stresses was in compression. After 10 hours exposure at 600°C, a compressive stress was observed within the coating which seemed relaxed after 30 and 100 hours exposure at the same temperature, as shown in Fig. 13. However, after 60 hours similar level of compressive stresses, as were after 10 hours, were observed. The relaxation of the stresses after 30 and 100 can be co-related with the micro cracking of the nearby Ni₃Al or NiO phase. Apparently, when the volume of the NiO increased with time at the same temperature, it exerted more stresses which caused micro cracking within the matrix.
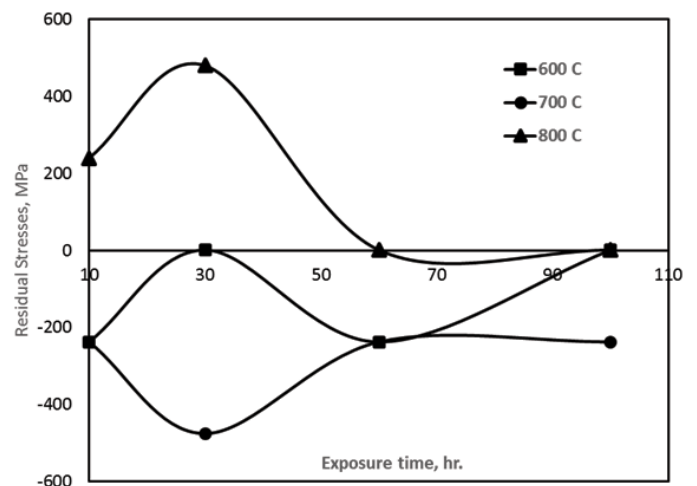

Fig. 13. Variation in stresses with different exposure times and temperatures

At low temperature i.e. 600°C and 700°C, the residual stress curves are in compression region; this is due to the formation of NiO phase. Since the lattice parameter of NiO is greater than Ni₃Al, therefore, it can be expected that the NiO will exert tensile stresses on the matrix of Ni₃Al and as a reaction Ni₃Al matrix will exert the compressive stresses, Fig. 14, to balance the sys-

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tem. However, the variation in stresses at 700°C demonstrated that the compressive stresses increases for the first 30 hours and then decreased. Similarly, the stress variation for the coatings exposed at 800°C was similar but the nature of stresses was opposite. (Fig. 13). The change in nature of stress from compressive to tensile, in samples exposed 800°C, is due to the fact that the volume percentage of NiO became increased to 55-85% i.e. the matrix became dominated in NiO phase which, as discussed above, is already in tensile state.
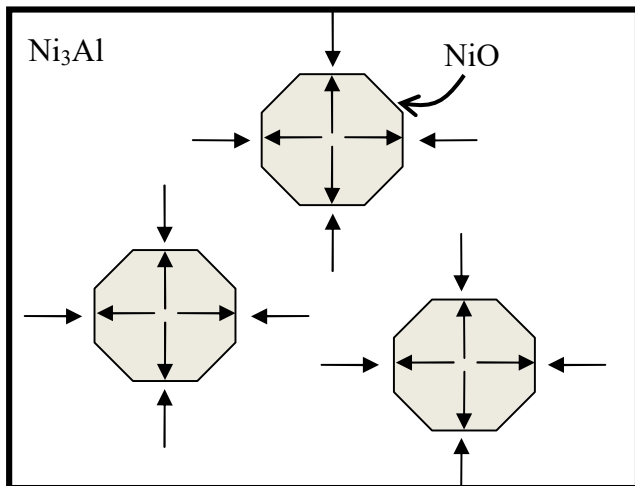

Fig. 14. Schematic demonstrates that NiO phase exerted tensile stresses due to which the matrix (Ni$_3$Al) becomes in compressive stress

Similarly, when the samples exposed at 700°C for 30 hours, about 35% NiO formed which consequently exerted more stress on Ni$_3$Al matrix i.e. 500 MPa (Fig. 13). This high magnitude stress, after 30 hours, in both the samples (i.e. exposed at 700°C and 800°C) forced the coating to crack and consequently relaxing the stresses.

3.7. Non destructive evaluation

Eddy currents induced in the material based on the principal of electromagnetic induction and are thus sensitive to electrical conductivity and the magnetic permeability of the material. In case of Ni$_3$Al coating there must be a certain values of electrical conductivity in as sprayed condition which compromised or varied with time at high temperatures due to the formation of Nickel oxide in the coating system. Metallurgical phase analysis, of different samples exposed at high temperature, demonstrates that the percentage of NiO grew with time at high temperature.

The percentage of NiO phase increases linearly with time at any particular temperature. Since NiO has a magnetic permeability greater than one [17], therefore, it can be expected that the eddy current values will also increase linearly. However, it was observed that the eddy currents followed almost the same curve as in case of stresses measured after different intervals, Fig. 15. This demonstrates that the residual stresses present within the system had dominantly dictated the induced eddy currents.
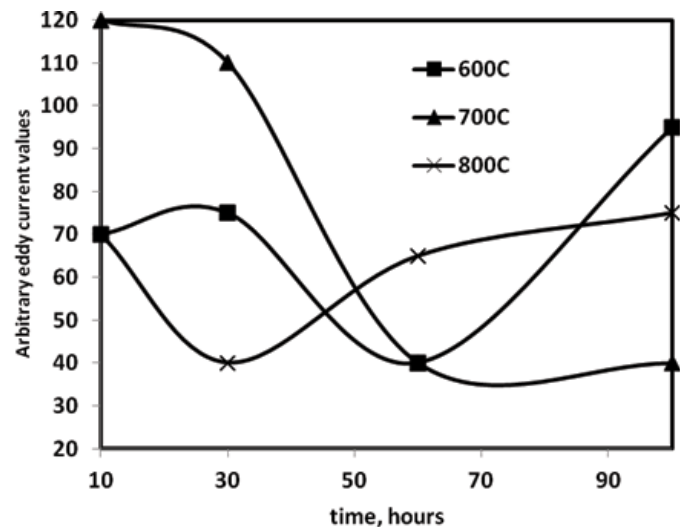

Fig. 15. Variation in Eddy current values for different times and temperature

The effect of stresses on eddy current values were also confirmed by a laboratory simulated experiments. The simulated experiments performed on the tensile specimens demonstrated that there exists a linear relationship between the stress and the eddy current values.

4. Conclusion

Nickel aluminide coating exposed at different time and temperature demonstrated the formation of nickel oxide phase. This phase constantly increases at different temperatures with time. It was observed that due to the formation of NiO phase the hardness of the coating constantly increasing. Further, the development of residual stresses within the coating were correlated with the formation of NiO phase. It was noted that the non-destructive evaluation i.e. eddy current technique, can be effectively utilized to monitor the stresses within the coating during the service at high temperature.

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