Effects of heat treatments on the microstructure and hardness of thermally sprayed Ni-Cr-Mo-Al alloy coating

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Abstract. Thermal spray coating is one of the technologies used to prevent corrosion and wear by creating a protective layer on the substrate. From previous research, the microstructure of arc-sprayed nickel-chromium-molybdenum-aluminium (Ni-Cr-Mo-Al) after heat treatment at 1100°C was investigated. It was found that the corrosion rate of this coating under 20vol%H\textsubscript{2}SO\textsubscript{4} was reduced by 97%. However, the heat treatment at high temperatures is still limited to industrial applications. Therefore, this research will focus on studying microstructure and properties after heat treatment at moderately high temperatures, which are in a range of service temperature. Specimens were arc sprayed and heat treated at 300, 400, 500, 600 and 700°C and characterized by Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) technique. Phases were analyzed by X-ray diffraction (XRD). There was no significant change of \(\gamma\)-Ni grains after heat treated at 600°C for 10 days from the Electron Backscattered Diffraction (EBSD) study. The hardness of the coatings increased after heat treatments due to a reduction in porosity, an increase of oxides and the formation of MoSi\textsubscript{2}.

1. Introduction
Thermal spray coating is a corrosion and wear-resistant technologies that creates high quality coatings in a short time, which is suitable for use in conditions of wear and corrosion protection of materials. This technology is gaining popularity due to the following advantages: convenience, speed, flexibility, and deposition rate. The cooling rate of arc spraying is moderately high, which makes the structure and properties of the substrate unaltered due to heat. The process also enables recoating [1]. The technology can be used in various industries, such as repairing conveyor rollers in sheet metal production, repairing parts in agricultural machinery and boiler maintenance [2].

One of the thermal spray technologies is arc spraying, which uses the arc between two electrodes as the heat source. This process has the distinctive feature of being applicable for use on site [3].

A previous study studied the microstructural evolution of an arc-sprayed Ni-Cr-Mo-Al coating using cored wire as a raw material in detail [4]. The cored wire is composed of two components: a sheath and a filler. In the arc spraying process, the tip of the cored wire was melted and formed molten droplets and randomly combined with molten particles inside the cored wire at high temperatures before being spread out and crushed on the substrate. After spraying, oxides form via oxidation. It was found that the coating
after spraying consisted mainly of Ni, Cr and Mo elements covering the surface of the spray coating. Moreover, it was found that the microstructure contained (1) $\gamma$-Ni phase, (2) (Mo, Si)-rich in $\gamma$-Ni at splat regions, (3) Mo splat, (4) $\text{Cr}_2\text{O}_3$, (5) $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ at intersplat and (6) small/spherical $\text{Al}_2\text{O}_3$ particles [4]. In addition, heat treatment at 1100°C for 60 min resulted in better corrosion resistance for the Ni-Cr-Mo-Al alloy coating. After studying the factors that affected corrosion, it was found that a reduction in porosity improved corrosion resistance of the Ni-Cr-Mo-Al alloy coating after post thermal treatments [5]. However, there is no in-depth characterization of the microstructure of the coating after thermal treatment at various temperatures.

Therefore, this research aimed to study the microstructure of thermally sprayed Ni-Cr-Mo-Al alloy coating after heat treatment at temperatures from 300-700°C.

2. Experimental procedures

2.1. Coating preparation

Thermal spraying was done by electric arc method (Thermach Inc. AT-400; USA) using cored wire (PMet 866). The cored wire contains the following elements: 20wt.% Cr, 13wt.% Mo, 6wt.% Si, <2wt.% Al and <1wt.% Ti and Ni. It was used to produce the coating on a low carbon steel substrate the parameters for the electric arc spray are shown in table 1. Thermal treatment was done at 300, 400, 500, 600 and 700°C with an electric furnace for 10 days.

Table 1. Arc spray processing parameters.

| Parameters             | Value      |
|------------------------|------------|
| Current (A)            | 200        |
| Arc load (V)           | 35         |
| Air pressure $\times 10^5$ (Pa) | 4.13      |
| Spraying distance (mm) | 120        |
| Wire feed rate (g/s)   | 3          |

2.2. Characterization of coatings

The microstructure of heat-treated coating was characterized by Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) with operating voltage at 15.0 kV and the Electron Back-Scattered Diffraction (EBSD) technique operation voltage at 20.0 kV and a step size of 0.6 μm in a JSM-IT300. The phases in the coating were characterized by X-ray diffraction using a SmartLab X-Ray Diffractometer with Cu Kα radiation ($\lambda = 1.54060 \text{ Å}$) with a step size of 0.01°.

2.3. Hardness test

The hardness of the coating was examined by a Vickers microhardness tester (SMV-1000) with an applied load of 200 g and a 15 second dwell time. The hardness was randomly measured and averaged from 10 points across the cross-section of the coating value.
3. Results and discussion

3.1. The effect of post-treatment on the microstructure of Ni-Cr-Mo-Al alloy

Figure 1 shows the microstructure of the Ni-Cr-Mo-Al alloy coating. Both the as-sprayed and thermally treated coatings were characterized by Scanning Electron Microscopy (SEM) with electron backscattering mode. It was found that the coating thickness is in a range of 400-600 µm. The appearance of the coating is not homogeneous. When comparing the image of the coating surface after spraying and after heat treatments at various conditions, it was found that the microstructure characteristics were not significantly different. The coating after heat treatment consist of splat particles, intersplats, porosity, Mo elemental splats (white phase) and oxides (gray and black phases), as confirmed by the Energy Dispersive X-ray Spectroscopy (EDS). The EDS maps are shown in figure 2. It was found that the as-sprayed coating consisted mainly of Ni, Cr and Mo elements. There are some elements concentrated in the white phase, namely the Mo phase (due to the non-melting of Mo particles) and the black phases (the junction between the coating and pore) containing Cr, Si, Al, O and Ti. The black phases were indicated as oxides of Cr, Si, Al and Ti as confirmed by EDS. They are oxides as Cr$_2$O$_3$, SiO$_2$, Al$_2$O$_3$ and TiO$_2$, respectively. In addition, it was found that the surface coating which was thermally treated under various conditions also showed the characteristic distribution map of the element from the EDS technique. From the EBSD analysis of γ-Ni phase by EBSD technique as shown in figure 3, it was found that there was no significant change of the γ-Ni phase with no preferred orientation after heat treatment of as-sprayed coating at 600°C for 10 days. From the XRD patterns of each coating condition (figure 4), it was found that all coatings consist of the γ-Ni phase. After heat treatment at 600°C for 10 days, MoSi$_2$, Mo-Ni-Si and Mo$_6$ (Ni$_{0.75}$Si$_{0.75}$) phases are formed. The as-sprayed coating consisted of solute (Mo, Si)-rich splats due to a moderately high cooling rate of the arc spraying. The intermetallic phases detected in XRD were formed during the heat treatments, mainly in the former solute-rich splats, similar to that which was observed in the literature [6-7].

![Figure 1. Back scattered electron (BSE) images of the Ni-Cr-Mo-Al coatings at 200X (a) as-sprayed and heat-treated at (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C and (f) 700°C for 10 days.](image-url)
3.2. Hardness value of Ni-Cr-Mo-Al alloy

It is found that the hardness value tends to increase with heat treatment up to 500°C with a constant temperature due to the reduction of porosities and a slight increase in oxides. The average hardness of the as-sprayed coating was 243.86 ± 79.48 HV. The hardness of the coatings heat treated for 10 days at 300, 400, 500, 600, and 700°C was 317.38 ± 80.47, 318.25 ± 77.65, 483.48 ± 88.72, 483.04 ± 56.73, and 511.46 ± 82.35 HV, respectively. Even though, it was not seen in the SEM images, it was presumed that some MoSi₂ was formed during the heat treatments due to an excessive amount of Mo and Si that segregated in the γ-Ni splats [4-5], causing an increase in the hardness of the coating, especially when heat-treated at higher temperatures. This could lead to the application of a Ni-Cr-Mo-Al alloy coating at elevated temperatures, where the coating will improve the mechanical property after being subjected to heat for a period of time.
4. Conclusion
The heat treatment of arc sprayed Ni-Cr-Mo-Al alloy coatings was carried out at various temperatures. Lower porosity, more oxides, and the formation of MoSi$_2$ caused an increase in hardness. There is therefore the potential to use this coating for elevated temperatures with improved mechanical properties after heating for a long period.

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*Figure 4.* X-ray diffraction pattern of the as-sprayed and heat-treated coating at 600°C for 10 days.