Mechanical and thermal properties of HVOF sprayed Ni based alloys with carbide

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Abstract

The objective of the present study is to develop multi-functioned coating to the components, which are made of copper with electroplated Ni and are widely used for steel making industry. In this paper, we report the mechanical and thermal properties of Ni based superalloys with carbide sprayed by high velocity oxygen fuel (HVOF), and the detailed effects of sprayed material, spraying conditions, and initial powder structure on these properties. It was found that, among commercial Ni self-fluxing alloys (without fusing treatment), coating with a carbon content of 0.58 mass% had the most preferable properties, with a good balance of the hardness, strength, and thermal shock resistance. The thermal shock resistance depended not only on the strength of the coating but also on the volume contraction when tested at high temperatures. For the several developed Ni based superalloys with carbide, Ni20Cr8Mo5Fe–WC and Ni16Cr15Mo3–WC demonstrated the prominent adhesion strength and thermal shock resistance with high Galvanic corrosion resistance through optimized spraying condition. Also, 20 mass% NiCr–Cr3C2 coating sprayed by using employed relatively small primary particle succeeded in achieving the multi-superior properties; high adhesion strength, high corrosion resistance and thermal shock resistance.

Keywords: High velocity oxygen fuel; Hardness; Coating strength; Adhesion strength; Thermal shock resistance; Corrosion resistance; Primary particle size

1. Introduction

Thermal spray processes have relatively high deposition rates and capable of most materials that have a liquid phase. Therefore many researchers have been developing processes and materials for spraying. Among many advanced spray technologies, a Ni based superalloy hardened by carbide using an high velocity oxygen fuel (HVOF) is considered to be one of the most widely used techniques. A Ni based self-fluxing alloy (Ni-SFA) and a NiCr–Cr3C2 coating are typical applications to a boiler tube [1] or a continuous caster (CC) mold [2].

The CC mold, made of copper, consists of the short side mold (width of a few hundred mm) and long side mold (width of a few m). The long side CC mold is deformed by thermal stress during fusing treatment. Then, the conventional Ni-SFA technique, fused the coating after spraying, is only available to the short side. This study is aimed at development of a fusing less spraying technique, AS-spray, to the long side CC mold.

In order to apply the sprayed coating to the CC mold, it is required that coating demonstrates multi-functions; high adhesion strength (> 200 MPa), high thermal shock resistance, high abrasion resistance, and high erosion and corrosion resistance. It is, however, difficult to obtain all the functions described above because some of the properties conflict with others.

First example, it is necessary to compatibilize the adhesion strength and thermal shock resistance of coating, because the adhesion strength tends to increase with increasing hardness of sprayed material [3]. Conversely, thermal shock resistance decreases with increasing hardness of the coating. Second, the thermal shock resistance and galvanic corrosion [4] need to be consistent. The thermal shock resistance is affected by the number or size of pores and initial cracks in the coating. On the contrary, it is sure that these cracks or pores promote the corrosion or galvanic corrosion. Third, the galvanic corrosion of coated material differs from that of HCl corrosion. Seong has recommended that Ni based alloys with carbide among Ni and Co based self-fluxing alloys, iron based alloys, and Cr carbide cermet [5], despite that Co based alloys and Cr based alloys should be higher corrosion resistance to the acids [6,7].
From the points mentioned above, in order to have good balance of multi-performances at the same time, it is significant to select and develop the best material and optimize structure of the coating. The coating structure could be controlled through spray gun, gas flow rates, distance from the exit of the spray gun to the substrate, and powder structure [8,9]. This powder structure implies the primary powder size, secondary size and the forming method, because the melting process of powder, dominant of the deformation process of the particle, depends on both powder sizes.

The current study is motivated by the development of Ni based superalloy with carbide sprayed by HVOF for the CC mold made of copper with electroplated Ni. These components are widely used for steel making industry, and are required to be in order to protect the surface of them from the abrasion and corrosion.

This paper describes the development of sprayed materials and the optimization of HVOF condition to achieve good multi-performances of Ni based superalloys with carbide. These optimizations were carried out on commercial Ni-SFAs and developed 80Ni20Cr–Cr3C2, Ni20Cr8Mo5Fe–WC, Ni16Cr15Mo3WC–WC and NiCoCrAlY–WC. Knowledge of performance of these materials has guided our selection and design of coatings to an application in future.

2. Experimental procedures

The HVOF systems employed here were DJ2600 (Sultzer Metco) and JP5000 (TATA). Table 1 shows the spraying. The effects of the combustion pressure, spray distance on the properties such as adhesion strength, coating strength, and thermal shock resistance were investigated. Also, the effects of powder material on them were evaluated.

Table 2 shows the list of sprayed materials for acid corrosion and galvanic corrosion test. The corrosion level was determined by the weight loss after soaking coatings on the copper substrate with electroplated Ni in hot HF, HCl and H2SO4, with a temperature of 353 K, a content of 1N, and a time of 8 h.

| Table 1 Spraying conditions |
|-----------------------------|
| DJ2600 | JP5000 |
| **Gas flow rate** |  |
| Oxygen | 0.22 (m3/min) | Oxygen | 0.95 (m3/min) |
| Hydrogen | 0.68 (m3/min) | Fuel | 0.00038 (m3/min) |
| Air | 0.35 (m3/min) | Pressure | 690–830 (kPa) |
| **Substrate** |  |
| Ni plated copper | Ni plated copper |
| Position | 250 (mm) | Position | 200–500 (mm) |

* Distance from the exit of spray gun to the substrate surface.

For Ni-SFA, commercial type, carbon composition rate and its powder diameter were focused (Tables 3 and 4). As-sprayed NSAs and fused NSA were used. Fusing treatment was carried out by gas burner at a temperature around 1273 K. On the other hand, 80Ni20Cr (NiCr), Ni20Cr8-Mo5Fe (Inconel 625), Ni16Cr15Mo3WC (Hastelloy–C) and NiCoCrAlY were selected as base alloys and Cr3C2 or WC is added to harden these alloys with good adhesive performance (Table 4). For NiCr–Cr3C2, the effects of carbide composition rate and the powder size on the thermal shock resistance were evaluated. Two types of NiCr–Cr3C2 powders are used in this study. One is the powder (secondary powder) consisting of several fine Cr3C2 and NiCr powders (primary powder), and the content of NiCr is determined by the volume fraction of the powder. The other is the powder (secondary powder) consisting of several fine Cr3C2 powders (primary powder) plated NiCr, and the content of NiCr is given by the thickness of NiCr layer on the fine Cr3C2 powders. In both cases, Cr3C2 primary powder is bind by NiCr.

Copper with electroplated Ni (thickness = 0.5 mm) was used as the substrate. The roughness of the substrate surface, before spraying, was 30–50 μm ($R_{\text{max}}$).

The adhesion strength, coating strength, hardness, thermal conductivity, thermal expansion coefficient, crystal structure (X-ray diffraction analyzer), and thermal shock resistance of the sprayed coatings were measured and investigated. The measurement method of interfacial strength is shown in Fig. 1. Cutting and polishing from the sprayed coating prepared the sample for this test. In this study, $t_s$ and $t_c$ were larger than 0.1 and 10 mm, respectively. An interior gap between the sample holder and the shear was 0.02–0.05 mm. This value was determined so that the difference of tensile strength and shear strength by this test, defined by fracture load/interfacial area, was less than 1% on reference material (mild steel).

The coating strength was measured by the tensile strength test by using the small sample machined from sprayed coating. The sample thickness was 0.5 mm, and other sizes were 1/5 scale of the standard JIS13B. The elongation of coatings was determined by the strain at fracture load. It was able to prepare the sample of Ni-SFA coatings for the tensile test. However, due to the hardness of Ni based superalloys with carbide, we could not measure the tensile strength of the coatings. We assumed that the tendency of effect of spraying condition on the adhesion strength was similar to that on strength of coating. The hardness was measured by the Vickers hardness test with a load of 300 g. Due to the ratio of metal to carbide at measured portion, the hardness allocation was around 200 Hv. The hardness of coating was determined to be the average value of 7-point results excluding a maximum and a minimum value.

Thermal properties of sole coating were evaluated. Thermal conductivity of the Ni-SFA coating in the direction of perpendicular to the interface between coating and
substrate was measured by a laser flash method (sample size of \(10 \times 1\) mm). The thermal expansion coefficient in the direction parallel to the interface was also measured by a vitreous silica push-rod dilatometer (sample size = \(1 \times 10\) mm). The heating rate of the sample is 5 K/min.

Thermal shock and fatigue resistance was evaluated by using a modified high temperature difference thermal shock test [10]. Fig. 2 represents the schematic diagram of the thermal shock resistance test. During continuous cooling from the under surface of the substrate, the sample is heated from the surface of coating by a Xe lamp with a focus diameter of 2 mm. An electric power supply (Panasonic, Model Light beam 150, maximum power of a 150 A, 5 kW) was used as the lamp source. The coating surface was polished with 1 \(\mu\)m \(Al_2O_3\) powder, and the thermocouple was set at 2 mm away from the center of surface coating.

The lamp current was 150 A and the cooling water flow rate was 1.5 l/min. In this condition, this apparatus irradiated onto the sample up to 6 MW/m\(^2\) heat flux and the center surface temperature of the sample was estimated to be 943–1003 K. The heat flux, \(Q\), could be expressed by

\[
Q = \frac{\lambda_{Cu} \Delta t}{r_2}
\]

\(\lambda_{Cu}\) is the substrate thermal conductivity, \(\Delta t\), the temperature difference between the two measured points, \(r_2\) is the distance between two measured points (0.5 mm). The substrate with a diameter of 30 mm and a thickness of 5 mm had two side holes to measure the temperature along the positions on the substrate centerline. Also, the center temperature was calculated from the surface temperature distribution that was assumed to follow the lamp power distribution that commonly indicates a Gaussian profile.

The thermal shock resistance was defined by the number of heat cycles that crack could, firstly, be observed by an optical microscope with a magnitude of 50.

### 3. Result and discussion

#### 3.1. Corrosion resistance

In order to develop the coating with multi-functions: high adhesion strength, corrosion resistance and high thermal shock resistance, firstly, it was necessary to select a base metal with good corrosion resistance. Fig. 3 is the result of the corrosion test of the coating. The corrosion resistance of Ni based alloys, Mo, and oxides tend to be superior to that of Co based or Cr based alloys due to that the result of this test is extensively affected by galvanic corrosion, electrical potential difference between coating and electroplated Ni through pores in the coating.

The adhesion strength of Mo and oxide was less than 100 MPa, thus, we selected Ni-SFAs and Ni based superalloys as base metals, and developed a novel material by adding carbide or optimizing powder structure.
3.2. Mechanical and thermal properties of Ni based self-fluxing alloy coatings

Ni-SFAs, without fusing treatment (AS), were sprayed by DJ2600 under the conditions shown in Tables 1, 3, and 4. Fig. 4 shows the relationship between [C] and the peak intensity of Cr$_3$C$_2$ and M$_{23}$C$_6$ by XRD. The intensity of Cr$_3$C$_2$ gradually increases with [C], and at [C] $> 0.58$ mass% M$_{23}$C$_6$, is observed. It is well known that the hardness of NSF is determined by the amount of CrB, Cr$_3$C$_2$, M$_{23}$C$_6$ and other borides and carbides. Cr$_3$C$_2$ and M$_{23}$C$_6$ are only observed by our XRD result. Thus in this study, assuming that carbides are dominant in the hardness, the effect of [C] on the mechanical properties are focused.

Fig. 5 shows the effect of carbon content, [C], on the hardness of the coating ($d = 10–90$ μm). For a higher [C], the coating is effectively hardened, especially, around [C] $< 0.58$ mass%, the hardness tends to change with the change of [C]. This data identifies the primary reason of the tendency that the increase in hardness of coating with [C] is caused by a formation of M$_{23}$C$_6$.

Fig. 6 shows the effect of [C] on the strength and elongation of coating. It is found that the strength of coating decreases with increasing [C]. Conversely, the elongation decreases with [C], and drastically at [C] of 0.59 mass%. In order to compatibilize the hardness, strength and elongation, it is concluded that NiSFA-C, [C] $= 0.58$ mass%, is the most preferable material.

The temperature difference test mentioned that the thermal shock resistance of coating decreased with increasing of [C]. The thermal shock resistance should depend on the mechanical properties and thermal properties of coating. Fig. 6 inferred that for a higher [C], the coating indicates the lower strength and elongation. Thus, investigation of the influence of thermal properties on the thermal shock resistance will be discussed below.

Fig. 7 shows thermal conductivity of AS-sprayed and fused NiSFA-A coating. The thermal conductivity of AS-sprayed coating is smaller than that of the fused coating whose temperature range, due to the lower density of AS-sprayed coating measured by Archimedes method, was found to be less than 99% of that of fused coating. This
result suggested that there are enough pores to contract the volume of the coating during the measurement.

Also, the thermal expansion coefficient of each coating is shown in Fig. 8. The expansion coefficient of AS-sprayed coating was measured at temperature range of room temperature to 1073 K (1st), and after cooling to room temperature, the coefficient of the same sample was measured again (2nd). The thermal expansion coefficient of fused coating slightly increases with temperature and this tendency is consistent with common bulk materials. Conversely, that of AS-sprayed, 1st coating diminishes at a temperature of 673 K. Also that of 2nd does around 927 K. According to the result of XRD, the phase of NiSFA-A transferred from amorphous like structure to crystal structure at around 673 K.

Thus, this crystallization and the reduction of pore volume cause the volume contraction of the coating. Thus, even though temperature increased, the measured expansion coefficient decreased over 673 K. Also, the melting of B$_2$O$_3$ (> 700 K) and the sintering of the coating are capable of affecting the result. The possible reason for the coefficient diminishing in 2nd was the incompleteness of the melting and the sintering. Detailed analysis was not carried out in this work.

It is considerable that the volume contraction of coating derives a higher tensile stress during the thermal shock test. Therefore, not only the mechanical properties, but also thermal properties should affect the relationship between [C] and thermal shock resistance of AS-sprayed NiSFA coating. From the previous results, in order to compatibilize the properties, [C] of around 0.58 mass% is the most preferable and it is concluded that this material is most useful for the CC mold that is hard to fusing treatment by its too large size.

3.3. Mechanical and thermal properties Ni based superalloys with carbide

The hardness of NSAs is not beyond 700 Hv and it was
required to develop the harder material for spraying. The corrosion test inferred that Ni based alloys indicate relatively higher corrosion resistance than other metal based alloys. However, the hardness of Ni based superalloys are less than that 700 Hv. Hence Ni superalloys were used as the base metals and developed harder materials by adding carbide. Inconel, Hastelloy–C, NiCoCrAlY, and NiCr were selected as base metal. Inconel, Hastelloy–C, NiCoCrAlY with carbide have not yet been developed. On the other hand, NiCr, although NiCr–Cr$_3$C$_2$ has been widely used for industry, the adhesion strength of NiCr–Cr$_3$C$_2$ was 60 MPa and this value is less than half value of our purpose. Thus, the optimization of spray distance, one of the most important parameter for spraying, for Inconel-WC, Hastelloy–C–WC and NiCoCrAlY–WC coating by JP5000 and that of component content or powder structure for NiCr–Cr$_3$C$_2$ were carried out.

For a higher combustion pressure, the hardness of Inconel-WC and Hastelloy–WC slightly increases. On the other hand, the hardness of NiCoCrAlY decreases. The latter result is not unexpected as the anchoring effect is high due to the higher combustion pressure spray condition. Detailed analysis was the following.

The choice of spray distance significantly influences the hardness and the strength of the coating. Fig. 9 shows the effect of spray distance on the hardness. Under the constant pressure value of 827 kPa, the hardness decreases with increasing distance.

There are several possible reasons for these results. According to Thorpe’s velocity measurement of JP5000 [11], the higher particle velocity could be attained at relatively higher-pressure conditions and the shorter spray distance. With increasing particle velocity, particles have higher kinetic energy. When particles impinge on the substrate, this kinetic energy converts to thermal energy. Thus, for a higher velocity particle, amount of precipitated carbide might increase and hardness increases. Another possible reason is based on the density of dislocations in the coating. In the case of higher velocity, the large kinetic energy can induce the higher dislocation density and hardness.
On the other hand, the relationship between the spray distance and adhesion strength is shown in Fig. 10. At a distance of 350 mm of Inconel-WC and Hastelloy–C–WC coating, the maximum interfacial strength is achieved. On the other hand, the strength of NiCoCrAlY–WC is not significantly dependent on the distance.

The adhesion strength of HVOF depends on the hardness of impinged particles which is dominant of the anchoring effect on the substrate surface and the kinetic energy of the particle. At the distance of 250 mm, even though particle velocity is superior to other distance, the temperature of particle is higher, and then the hardness of it might be lower. Therefore, the adhesion strength at the distance is lower than that at the distance of 350 mm.

Fig. 11 shows the effect of NiCr content ([NiCr]), particle size, and the structure of particle of NiCr–Cr$_3$C$_2$ on the interfacial strength (JP5000, combustion pressure = 827 kPa, secondary powder size = 40 μm). It can be seen that the maximum adhesion strength is achieved with [NiCr] of 20 mass%. In the case of [NiCr] < 20 mass%, due to the high carbide rate, the strength of coating declines. On the other hand, [NiCr] > 20 mass%, the softer particle could derive the decreasing of the adhesion strength.

It is also clear from this figure that, there is a substantial effect of primary particle size on the adhesion strength, at a secondary powder size of 40 μm. The powder with a primary particle size of 2–3 μm has elevated adhesion strength than that with larger size of 8–25 μm. In the case of using smaller particle, the relatively extensive surface area, causing effective kinetic momentum and heat transfer from gas flame to the particle attributes superior acceleration and heat. Furthermore, this figure implies another powder structure influence. The strength employed coated NiCr on Cr$_3$C$_2$ powder is prominent at a [NiCr] of 20 mass%. Metallurgical bonding seems to act on the interfacial bonding, though detailed analysis has not been carried out.

Fracture stress, $\sigma$, is given by [13]

$$\sigma = \frac{E\alpha\delta\gamma}{3.25AT(1 - \nu)}$$

$E$ is the Young’s Modulus, $\alpha$, the thermal expansion coefficient, $\delta$, the thickness, $\gamma$, the heat transfer coefficient, $T$, the maximum tolerance shock temperature, $\nu$, the Poisson’s ratio, and $\lambda$ is the thermal conductivity.

Also, thermal shock resistance coefficient, $P_1$, is determined as [13]

$$P_1 = \frac{\lambda\sigma}{E\alpha}$$

This equation infers that in order to enhance the thermal shock resistance; it is significant to increase not only the strength of coating, but also thermal conductivity.

By optimizing the spray condition of Inconel-WC, Hastelloy–C–WC and NiCoCrAlY–WC coating, and the component content or powder structure of NiCr–Cr$_3$C$_2$, we
could succeed the harder coating than NSAs with good adhesion strength and thermal shock resistance.

4. Summary and conclusions

The result of the acids corrosion test of the coating inferred that, as for base metal, Ni based self-fluxing alloys (Ni-SFAs) and Ni based superalloys were selected and adding carbide or optimizing powder structure developed novel materials.

The optimizations of the composition of commercial Ni-SFAs without fusing treatment were carried out through the measurement of the hardness, elongation, strength and thermal shock resistance of coating. It was found that coating with a carbon content of 0.58 mass% had the most preferable properties, with a good balance of the hardness, strength, and thermal shock resistance. The thermal shock resistance of Ni-SFA depends not only on the strength of coating, but also on the volume contraction.

The effect of spray distance on the hardness and adhesion strength of the developed 80Ni13Cr–WC, 53Ni19Mo17Cr–WC, NiCoCrAlY–WC and 80Ni20Cr–Cr3C2 coatings were also investigated. Under the optimum spray distance, the coating with a hardness of 1150 (300 Hv) and adhesion strength of 200 MPa could be obtained. However, the optimum spray distance for the hardness differed from that for adhesion strength. The optimum impinged particle state for hardness is mainly the higher velocity. On the contrary, for adhesion strength is not only the higher velocity but also the moderate temperature due to the anchoring effect based on the hardness of impinged particle.

The adhesion strength of 25(NiCr)–Cr3C2, is inferior to other coatings. The investigation from the viewpoint of initial particle composition rate and structure were carried out. It was found that by using smaller primary powder size and coated powder, it was successful to improve the adhesion strength up 250 MPa with a NiCr content rate of 20 mass%. In this study, improvement of the adhesion strength attributes to enhance the thermal shock resistance of them.

HVOF is a promising method of applying to surfaces for thermal, chemical, and mechanical protection. These results have guided our selection of materials and configurations needed to extend this process to the CC mold and more challenging structural materials.

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