Formation of Fe-Based Amorphous Coating Films by Thermal Spraying Technique

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Some amorphous Fe-Cr-P-C coating films having high hardness and high corrosion resistance have been produced by a newly developed thermal spraying technique. In order to control the temperatures of the powder particles in the flame spray and the substrate, a newly developed cylindrical nozzle, with external cooling nitrogen gas, was mounted to the front end of the thermal spraying gun. Fe\(_{70}\)Cr\(_{10}\)P\(_{13}\)C\(_7\) films with various external cooling gas velocities between 20 m/s and 40 m/s exhibited entire amorphous structure without oxides and/or unmelted particles. Corrosion-resistance of the films was observed in immersion tests using various corrosive liquids. An amorphous film was formed on the surface of the shaft sleeve of the slurry pump by using the cylindrical nozzle. This shaft sleeve was installed in the slurry pump of chemical fertilizer maker’s production line and the life test was done under the real operation condition for two months.

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1. Introduction

Thermal spraying is a superior technique for producing amorphous alloy coating films with large area on various industrial materials.\(^{1-4}\) Especially, Fe-Cr based amorphous alloys have high hardness and high corrosion resistance.\(^{5-8}\) However, the Fe-Cr based amorphous alloys having high melting temperatures of about 1000°C have not yet been well produced by previous thermal spraying methods. The important problems in these methods may be due to the contamination of oxide and the density of pores in the thermal sprayed films.\(^{1,2,9-13}\) Recently, there are some research papers that were able to inhibit the oxide formation by the shield nozzle installed at the front end of the atmospheric plasma spray gun or the high velocity oxygen fuel gun.\(^{14,15}\)

In the present study, formation of some amorphous Fe-Cr-P-C coating films having high hardness and high corrosion resistance have been demonstrated by a newly developed thermal spraying technique. In order to control the temperatures of the powder particles in the flame spray and the substrate, a newly developed cylindrical nozzle with external cooling nitrogen gas was mounted at the front end of the thermal spraying gun. Cooling rates of the sprayed samples on SUS316L substrates were estimated to attain about 10\(^6\)°C/s by measuring the temperature gradient of the spraying flame.

2. Experimental Procedures

The thermal spraying equipment used in this study was composed of a gas flame spraying gun and a newly developed cylindrical nozzle. The thermal spraying material was gas-atomized powder (grain size: 38–63 μm) of Fe\(_{70}\)Cr\(_{10}\)P\(_{13}\)C\(_7\) (at%) with a melting temperature of 997°C. A SUS316L (100 mm × 50 mm × 3.2 mm) substrate, shot blasted by alumina powder, was used. In order to keep a reduction atmosphere in the flame, an acetylene-rich gas fuel mixture was used. Nitrogen gas was introduced into the cylindrical nozzle to prevent the formation of oxides in the coating film. The thermal spray gun was mounted on a robot arm, scanned at the rate of 300 mm/s in feed rate and 10 mm in spraying pitch, and an alloy layer of up to 300 μm in film thickness was produced. Structural analysis of the coating films was done by X-ray diffraction (Cu Ka radiation with a graphite monochromator, 40 kV-200 mA) and transmission electron microscope (TEM:HF2000-200 kV). The amorphous alloy coating films, separated from the substrate, were immersed in various kinds of corrosive liquid for the maximum period of 4-weeks. For comparison, standard specimens of Hastelloy C and commercially produced pure titanium were used. An amorphous film was formed on the surface of the shaft sleeve of the slurry pump by using the cylindrical nozzle. This shaft sleeve was installed in the slurry pump of chemical fertilizer maker’s production line and the life test was done under the real operation condition for two months.

Figure 1 shows a schematic illustration of cylindrical-nozzle type thermal spray gun. In order to control the temperatures of the powder particles in the sprayed flame and the substrate, and to prevent the formation of oxides in the coating film, a newly developed cylindrical nozzle with external cooling nitrogen gas was mounted at the front end of the thermal spraying gun.

Figure 2 shows the cooling-gas flow rate, over the distance from the cylindrical nozzle head to the substrate, measured by a pitot tube. The cooling-gas flow rate can be controlled up to 60 m/s by adjusting the gas pressure in the cylindrical nozzle. To keep the optimal temperature and flow states of the spraying flame, the flow rate of the cooling gas was set to the nearly equal to that of the spraying flame. In this study, optimal flow rate of the sprayed flame was 30~40 m/s.\(^{16}\)}
Figure 3 shows the thermal gradients of the spraying flame, over the distance from the cylindrical nozzle head to the substrate, measured by a thermocouple. In this diagram, the 0 mm gradient curve indicates the thermal gradient at the flame center, while the 5 mm and 10 mm gradient curves indicate the thermal gradient at the positions outlying from the center of flame. Although the center of flame hits the substrate at a temperature of approximately 1000°C, the flame temperature decreased sharply to about 300 to 500°C for the 10 mm and the 5 mm respectively positions.

Figure 4 shows the compositions of the thermal spraying flame, over the distance from the cylindrical nozzle head to 20 mm and 70 mm, measured by the orsat apparatus. In this experiment, nitrogen gas or compression air were used as a cooling gas. In order to keep a reduction atmosphere in the spraying flame, an acetylene-rich gas fuel mixture was used. When nitrogen gas was used, oxygen was contained in the spraying frame, 0.2% and 0.8% at positions of 20 mm and 70 mm away from the cylindrical nozzle head, respectively. On the other hand, when compression air was used, oxygen was contained 8% and 14% in the spraying frame at same positions.

3. Results

3.1 Structure of the coating films

Figure 5 shows the optical micrographs in cross-section of the thermal spray coating films with and without the newly developed cylindrical nozzle. When the thermal spray gun without the cylindrical nozzle was used, many inclusions of oxides have been observed in the coating film as shown in
On the other hand, shown in Fig. 5(b), when the thermal spray gun with the cylindrical nozzle was used, high-quality amorphous sprayed film without the inclusion of oxides can be produced.

Figure 6 shows the X-ray diffraction patterns of the thermal spray coating films with and without the cylindrical nozzle. When the thermal spray gun without the cylindrical nozzle was used, crystalline peaks from many kinds of oxides were observed. On the other hand, when the thermal spray gun with the cylindrical nozzle was used, X-ray diffraction peaks are well-broadened, indicating structure of the film is the amorphous.

Figure 7 shows a TEM image and a selected area diffraction pattern (SADP) of the sprayed coating film fabricated by using the cylindrical nozzle. It consists of amorphous phase in general. The SADP with halo rings also supports that the coating film has an amorphous structure. Compositions of the coating film obtained by EDX analysis are as follows; Fe: bal, Cr: 11.6 at%, P: 13.7 at%, indicating a similar composition to that of the gas-atomized powder.

3.2 Corrosion tests

The amorphous alloy coating films separated from the substrates were immersed in various kinds of corrosive liquid. For comparison, standard specimens of Hastelloy C and commercially produced pure titanium were used. Table 1 shows the results of the corrosion tests. In the corrosion standard for chemical plant materials, a corrosion rate in the weight variation of between \( \frac{0.5}{C_24} \) g/m\(^2\) day is considered good.\(^{17}\) Corrosion of the amorphous sprayed film scarcely progressed after an initial increase arising from the generation of an oxide layer. On the other hand, both Hastelloy C and titanium slightly corroded. Accordingly, the corrosion tests have clarified that the sprayed amorphous film exhibited a high corrosion resistance, equal to that of Hastelloy C and commercially produced pure titanium, under most conditions. However, the corrosion resistance test in hydrochloric acid did not show a favorable result for the Fe\(_{70}\)Cr\(_{10}\)P\(_{13}\)C\(_7\) film. The corrosion liquids containing strong oxidizers such as nitric acid and sulfuric acid etc. usually exhibit the high formability of the passive films on the sample surface. On the contrast, the hydrochloric acid is the nonoxidizing acid.
indicating the formation speed of the passive film may be slower than that of the other liquids.

3.3 Life test of the sprayed coated slurry pump shaft sleeve

An amorphous film was formed on the surface of the shaft sleeve of the slurry pump by using the cylindrical nozzle. This shaft sleeve was installed in the slurry pump of chemical fertilizer maker’s production line and the life test was done under the real operation condition for two months.

Figure 8 shows the diagrammatic illustration of the slurry pump. The shaft sleeve of the slurry pump was worn easily because of the grinding effects of slurry that sandwiched between the driving shaft and the seal. Therefore, the development of the material of high hardness and high corrosion resistance has been demanded.

Table 2 shows the life test conditions for the shaft sleeve of the slurry pump. Surface of the SUS304 shaft sleeve was shot blasted by alumina powder, and then NiCr undercoat layer with about 50 μm thickness was formed. The Fe-Cr-P-C amorphous film of 300 μm thickness was coated on the NiCr layer. Finally the surface of the coated shaft sleeve was ground with a diamond grindstone and finished up. As a result, the thickness of the remained Fe-Cr-P-C coating film was about 150 μm.

Figure 9 shows the wear track of the shaft sleeve after life test for two months. There is no wear track in the amorphous thermal spraying shaft sleeve though wear track of 4 μm is admitted in conventional SCS23 product (Fe: bal, Cr: 20 mass%, Ni: 30 mass%, Mo: 3 mass%, Cu: 3 mass%). The amorphous thermal spraying shaft sleeve indicated high corrosion resistance and high abrasion resistance (HV700~900).

4. Discussion

Figure 10 shows a schematic diagram explaining the temperature distribution of the flame just prior impact on the the substrate: (a) Without the cylindrical nozzle; (b) With the cylindrical nozzle.

Cr: 20 mass%, Ni: 30 mass%, Mo: 3 mass%, Cu: 3 mass%).
Figure 11 shows the changes of the substrate temperature as a function of the thermal spraying time with and without the cylindrical nozzle. The thermal spray gun was mounted on a robot arm, scanned at the rate of 300 mm/s in feed rate and 10 mm in spraying pitch. Temperature of the substrate at the surface center point was measured by radiation thermometer. When the thermal spray gun without the cylindrical nozzle was used, a hot area expands over all the flame, thus causing a rapid increase of substrate temperature beyond the vitrification point (493°C) and, accordingly, crystallization of the coating occurred easily. In contrast, when the thermal spray gun with the cylindrical nozzle was used, the substrate temperature saturated gradually under the vitrification temperature (400°C), indicating the high formability of the amorphous film. Therefore, the high scanning speed of 300 mm/s is very effective for rapid cooling of the coating films, preventing the crystallization of the former coated amorphous layer.

5. Summary

Some amorphous Fe-Cr-P-C coating films having high hardness and high corrosion resistance have been produced by a newly developed thermal spraying technique. In order to control the temperatures of the powder particles in the flame spray and the substrate, a newly developed cylindrical nozzle with external cooling nitrogen gas was mounted to the front end of the thermal spray gun. When the thermal spray gun with the cylindrical nozzle was used, the substrate temperature increased gradually because of the lower temperature area surrounding the high temperature area of about 1000°C. Cooling rates of the sprayed samples on SUS316L substrates were estimated to attain about 10^6°C/s by measuring the temperature gradient of the spraying flame. Fe_70Cr_10P_13C_7 films with various external cooling gas velocities between 20 m/s and 40 m/s exhibited an entirely amorphous structure without oxides and/or unmelted particles. Corrosion testing has clarified that the sprayed amorphous films exhibited a high corrosion resistance equal to that of Hastelloy C and commercially produced pure titanium. An amorphous film was formed on the surface of the shaft sleeve of the slurry pump by using the cylindrical nozzle. This shaft sleeve was installed in the slurry pump of chemical fertilizer maker’s production line and the life test was done under the real operation condition for two months. The amorphous thermal spraying shaft sleeve indicated high corrosion resistance and high abrasion resistance.

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