

Resistance of Thermal Sprayed Coatings of Zn, Al and Zn-Al Alloy against Atmospheric Corrosion

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Corrosion resistance of the thermal sprayed coatings of Zn, Al, and 85Zn-15Al alloy exposed in the atmosphere for 22years at Tokyo and Sapporo were evaluated by the electrochemical anodic polarization measurements, SEM observation and EPMA, comparing with the as-sprayed specimen. These coatings showed excellent resistance against the atmospheric corrosion for over 20years. Among the 3 kinds of metals, Zn was the most superior comparing with that of Zn-Al alloy and Al. Corrosivity of the atmosphere caused by S and Cl was larger at Sapporo than at Tokyo. The fact suggests that the influence of the airborne salinity and the air pollution substances is more severe at the coast of Japan Sea rather than the coast of Pacific Ocean.

Keywords : thermal sprayed coating, Zn, Al, Zn-Al alloy, atmospheric corrosion

1. Introduction

Atmospheric corrosion behavior of thermal sprayed coatings of Zn, Al and Zn-Al alloy, and various kinds of painting on them were evaluated through the long term weathering test for over 22years at Tokyo and Sapporo. Outline of the results was reported already elsewhere.¹⁾ In this paper, the mechanism of the corrosion protection and the characterization of the sprayed films without painting are discussed based on the results of the electrochemical and surface analytical investigations for both the as-sprayed and the exposed specimens.

Thermal sprayed Zn and Al coatings have been used for the corrosion protection to steel structures, and have a history of practical use for over 80years. The technical developments were, however, based on the experiences and the improvements through the practical applications. It has been emphasized in the developments that the Zn-Al alloy spraying is superior in the performance rather than the single spraying of Zn or Al. Recently, research works for the alloy systems have been increased in many fields. In order to improve the corrosion performance against a more corrosive environment such as marine or polluted

atmosphere by making use of the characteristics and by eliminating its own defects of Zn and Al, various alloys composed of the two metals were investigated,^{2),4),5)} and the excellent property of the Zn-15Al alloy spraying was insisted.⁶⁾ Furthermore, predominance of the pseudo alloy spraying rather than the spraying with the pre-alloy wire was reported based on the tests in marine environments.⁷⁾ Detailed mechanism of the protection with the pseudo alloy was also discussed on the electrochemical and surface analytical tests.⁸⁾ On the other hand, Al single spraying was superior in the marine environments among the relative metals and alloys.⁹⁾ Considering the variety of combinations between metals and environments, it is not so easy to select the optimum materials and spraying methods in practice.

2. Experimental

2.1 Sprayed specimen

Coatings of specimen were prepared by flame spraying with wires of Zn, Zn-15Al, and Al, 3.2 mm in diameter, on a blasted carbon steel substrate, 100×50×3 mm. Spraying parameter is shown in Table 1. In the elec

Table 1. Spraying parameter

Material	Fuel gas pressure(MPa)			Wire feed rate (m/min)	Stand off distance (cm)
	O ₂	C ₂ H ₂	Air		
Zn	0.18	0.07	5	3.6	10~15
Zn-15Al	0.18~0.2	0.08~0.1	5	3.4	10~15
Al	0.2	0.07	5	3.1	10~15

trochemical polarization measurements, the detached film after spraying on a bright steel, solid wire before spraying, and the carbon steel were also tested to clarify the protection mechanism.

2.2 Long-term exposure test

The exposure tests were conducted at Ohta-ku, Tokyo and Teine-ku, Sapporo, for 22years, initiated in 1975 and finished in 1997. The test panels were set on top of buildings, the head office of Tokyo Metallikon Co. and Hokkaido Institute of Technology, respectively, faced to due south, at a horizontal angle of 35 degrees.

2.3 Electrochemical measurements

Test electrodes were cut to a rectangle from the sprayed specimen, soldered a lead wire, and mounted with an epoxy resin except the exposed area of 15×25 mm. The test electrode of the detached film was also prepared similarly using only the films detached after spraying on a bright steel. Electrodes of the solid metals and alloy were prepared using each spraying wire, 3.2 mm in diameter, mounted with a PTFE tape except an exposed length of 30 mm.

Polarization characteristics were measured in a solution of aerated 0.1MNa₂SO₄, 30°C, which is often used for the evaluation of weathering steels. Chloride solutions, usually used for the sprayed metals and alloys,²⁻⁵⁾ were avoided because of its too much corrosivity for evaluating the atmospheric corrosion in urban environments. A saturated Ag/AgCl electrode was used as the reference electrode. Potentiodynamic anodic polarization was started with a sweep rate of 20 mV/min, after reaching a steady state potential in a prescribed condition within the electrolytic cell.

2.4 Characterization of sprayed film

SEM image and EPMA elemental mapping were observed to clarify the distribution of Zn and/or Al as the metallic components and S and Cl as the environmental pollution components in the sprayed films before and after the long-term exposure test.

3. Results and discussion

3.1 Microstructure of as-sprayed film

SEM images and EPMA elemental mappings on the cross section of the films for the as-sprayed Zn, Zn-15Al alloy and Al are shown in Fig. 1, 2, and 3, respectively. A layered fine structure is observed on the sprayed Zn film, which contains much amount of oxygen, but little defects. The film of the sprayed Zn-Al alloy has a random layer structure, which contains many defects and voids. On the other hand, the sprayed Al has a little oxygen comparing to Zn, and contains several defects in the dense and indistinct layered structure.

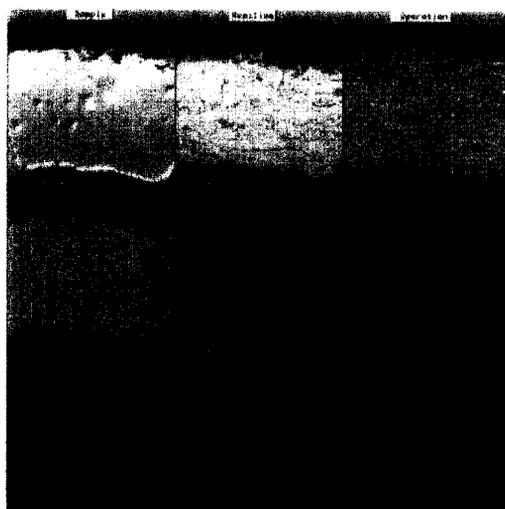


Fig. 1. SEM image and EPMA elemental mapping for as-sprayed Zn.

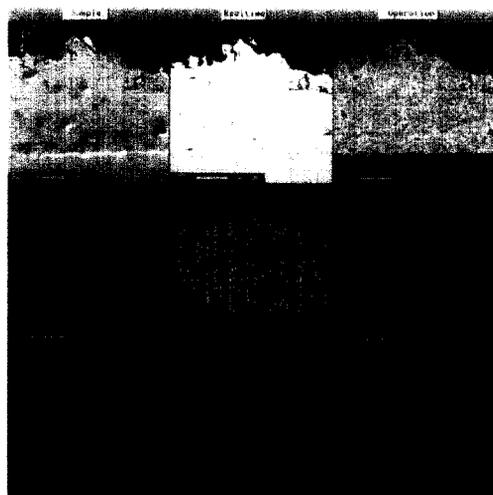


Fig. 2. SEM image and EPMA elemental mapping for as-sprayed Zn-15Al alloy.

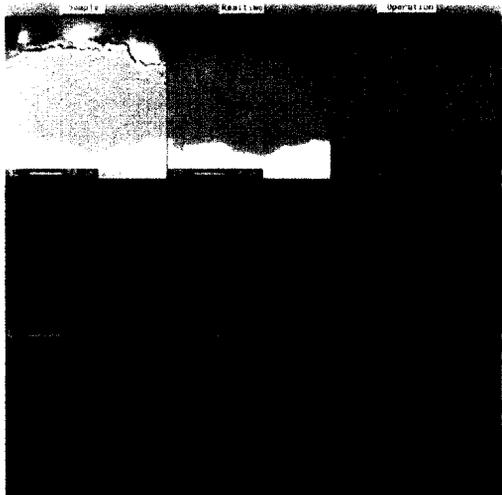


Fig. 3. SEM image and EPMA elemental mapping for as-sprayed Al.

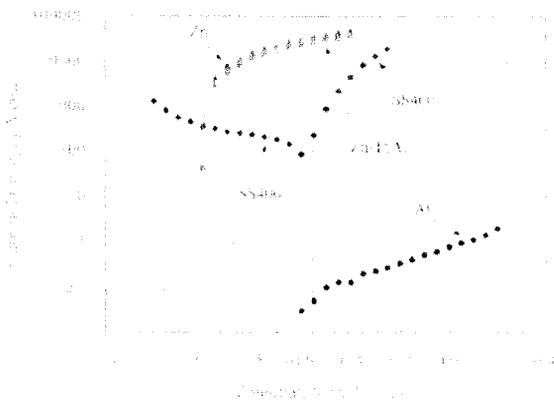


Fig. 4. Polarization characteristics of solid wire and carbon steel in aerated 0.5M Na₂SO₄ at 30°C.

3.2 Basic corrosion characteristics

Anodic polarization curves of the solid wires for Zn, Zn-15Al alloy and Al are shown in Fig. 4. Anodic and cathodic polarization curve of the carbon steel, to be protected by them, is also shown in the same fig. Zn and Zn-Al alloy had just the same corrosion potential, which was far negative than that of the carbon steel, and also showed an active anodic polarization behavior having a large anodic current controlled by the diffusion of the dissolved metal ions. From the electrochemical aspect, Zn and its alloy have a sufficient cathodic protection ability against the corrosion of the carbon steel. The effect of alloying Al is very small to decrease the anodic current slightly.

On the other hand, Al was in its passive state, and different a little in the corrosion potential to the carbon

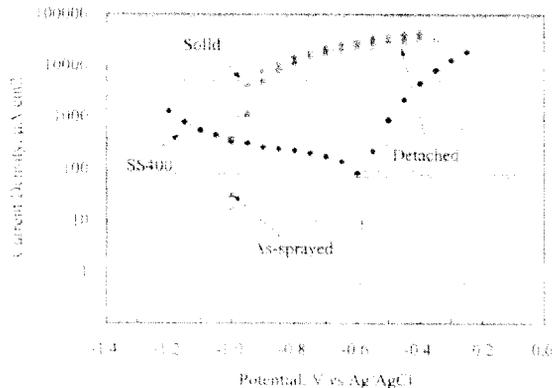


Fig. 5. Polarization characteristics of as-sprayed, detached and solid wire of Zn in aerated 0.5M Na₂SO₄ at 30°C.

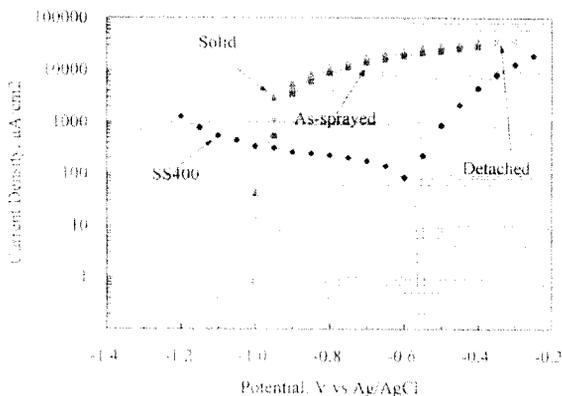


Fig. 6. Polarization characteristics of as-sprayed, detached and solid wire of Zn-15Al alloy in aerated 0.5M Na₂SO₄ at 30°C.

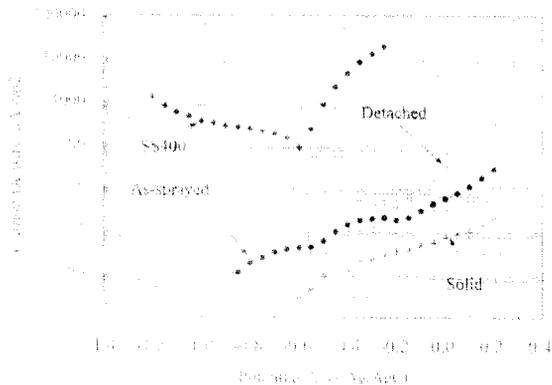


Fig. 7. Polarization characteristics of as-sprayed, detached and solid wire of Al in aerated 0.5M Na₂SO₄ at 30°C.

steel. The protection of Al should be derived from a barrier effect.

3.3 Protection behavior and mechanism by spraying

Anodic polarization curves of the as-sprayed specimen, the detached film, and the solid wire for Zn, Zn-15Al alloy and Al are shown in Fig. 5, 6 and 7, respectively. In the

anodic polarization behavior of Zn and Zn-15Al, there is no difference between the as-sprayed specimen and the solid wire. This indicates that the chemical factors such as oxidation in the spraying process, and the physical factors such as surface roughness, defects or voids, have little effect on the anodic dissolution process of the sprayed films of Zn and Zn-15Al alloy. Furthermore, no difference between the sprayed specimen and the detached film proves no effect of the substrate steel on the anodic process of the sprayed system. The fact suggests that the galvanic action between the sprayed metals and the steel substrate is negligible small, and that the protection by the spraying is based on the barrier films rather than the sacrificial anode.

The sprayed Al showed a less noble corrosion potential than that of the solid wire, but the same passive behavior in the anodic polarization. No galvanic action between the sprayed Al and the steel substrate was also recognized in the same manner as the Zn and Zn-Al alloy. From the results, the protection by the sprayed Al is also not due to the sacrificial anode but to the barrier film.

3.4 Change of film after long-term exposure

No rusting was found apparently on 3 types of the sprayed specimens exposed for 22 years at Tokyo and Sapporo, proving the enough duration of the protection through the period. The results of the SEM observation and the EPMA elemental mapping for the component elements and the environmental pollution elements after the long-term exposure are shown in Fig. 8 and 9 for Zn, Fig. 10 and 11 for Zn-Al alloy, and Fig. 12 and 13 for Al, respectively.

In case of the sprayed Zn film, the corrosion products containing the pollution components of S and Cl was formed on just the outermost layer of the sprayed surface, and not penetrated inside the film. As described later, the stable outer layer should decrease the surface activity of the sprayed film and the anodic dissolution.

In the film of the sprayed Zn-15Al alloy, the pollution components were recognized to penetrate down to the substrate, and to detach the inter-spraying layers. The protection ability of the film was estimated at its final stage to the limit of the resistance.

The sprayed Al film was also deteriorated to expand the defects filled with the corrosion products. The protection of the film was also estimated at the limit of the use.

Anodic polarization curves of the exposed specimen at Tokyo and Sapporo, comparing with the as-sprayed specimen were illustrated in Fig. 14 for Zn, Fig. 15 for Zn-15Al alloy, and Fig. 16 for Al, respectively. The anodic disso

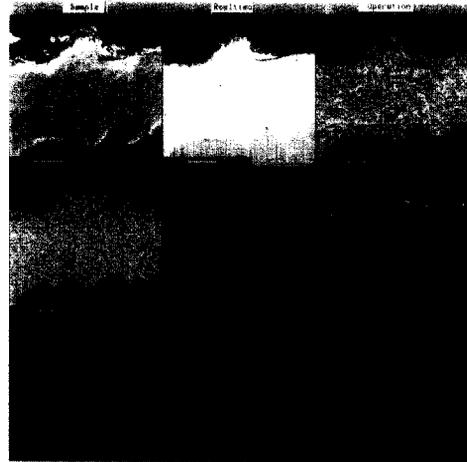


Fig. 8. SEM image and EPMA elemental mapping for sprayed Zn after 22 years exposure at Tokyo.

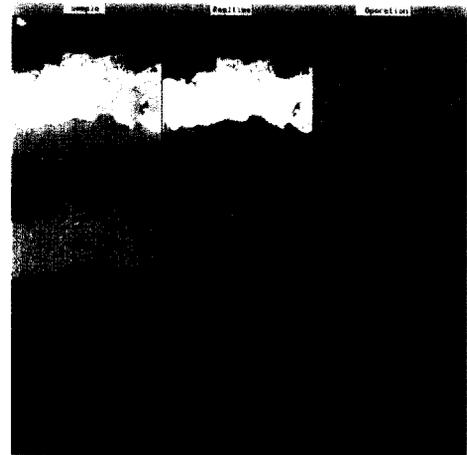


Fig. 9. SEM image and EPMA elemental mapping for sprayed Zn after 22 years exposure at Sapporo.

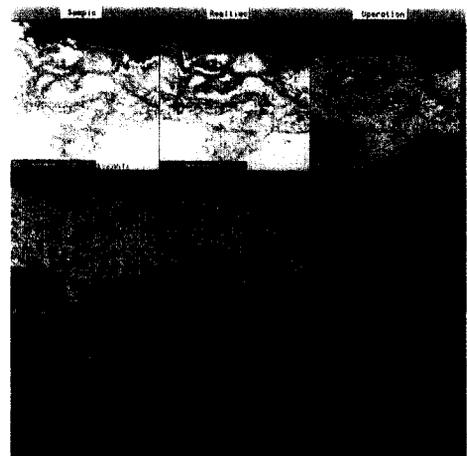


Fig. 10. SEM image and EPMA elemental mapping for sprayed Zn-15Al alloy after 22 years exposure at Tokyo.

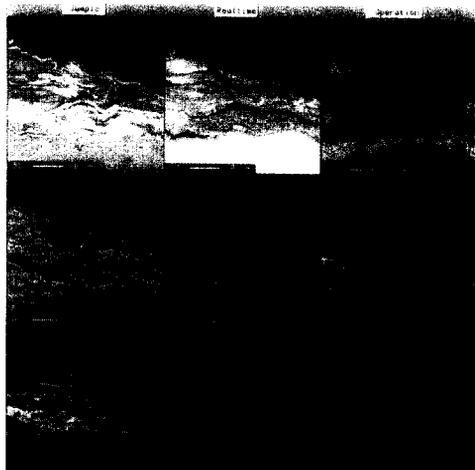


Fig. 11. SEM image and EPMA elemental mapping for sprayed Zn-15Al alloy after 22 years exposure at Sapporo.

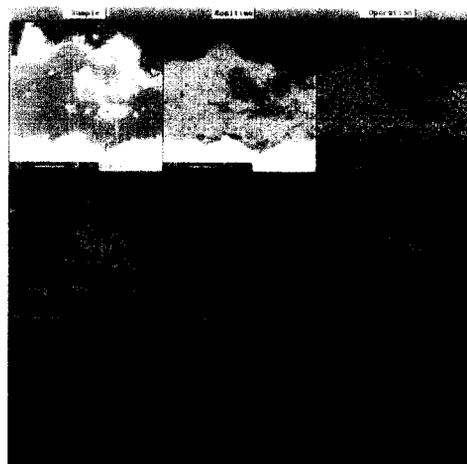


Fig. 12. SEM image and EPMA elemental mapping for sprayed Al after 22 years exposure at Tokyo.

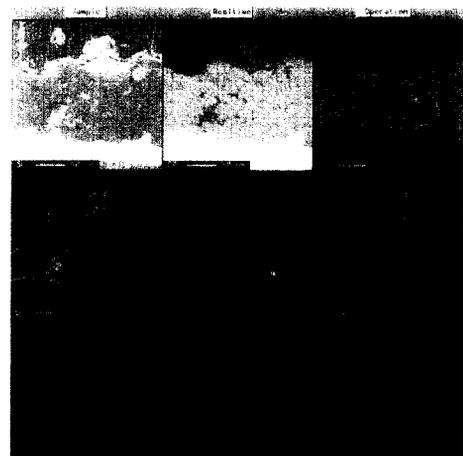


Fig. 13. SEM image and EPMA elemental mapping for sprayed Al after 22 years exposure at Sapporo.

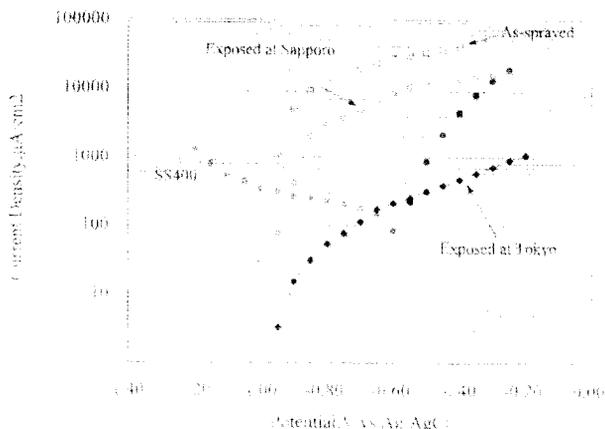


Fig. 14. Change of polarization characteristics of sprayed Zn after 22 years exposure at Tokyo and Sapporo.

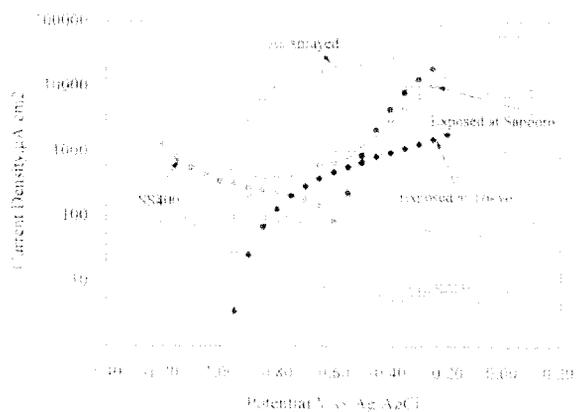


Fig. 15. Change of polarization characteristics of sprayed Zn-Al alloy after 22 years exposure at Tokyo and Sapporo.

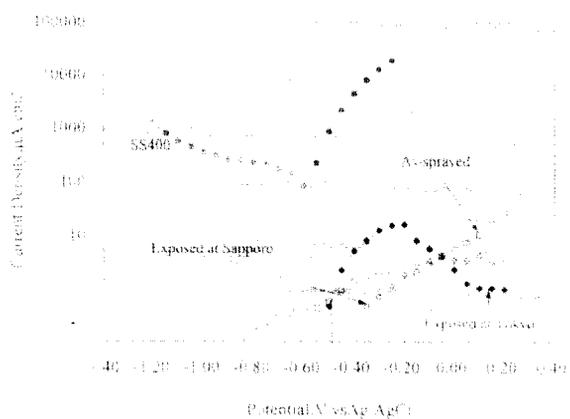


Fig. 16. Change of polarization characteristics of sprayed Al after 22 years exposure at Tokyo and Sapporo.

lution current for Zn increased 1~2 orders of multitude by the long-term exposure, suggesting an effect of the corrosion inhibition by the outer surface layer consisting

of the corrosion products. The degree of the inhibition was larger at Tokyo than at Sapporo. On the other hand, the corrosion potential of Al shifted to a more noble potential than that of the carbon steel, so as to diminish the sacrificial ability for the cathodic protection. The passive behavior still remained in the anodic polarization. The facts suggest the protection of Al for the steel substrate be derived from the coating as a barrier film. An increased passive current in the exposed specimen comparing with that of the as-sprayed specimen substantiates the deterioration of the sprayed Al film mentioned above.

4. Conclusions

1) Corrosion prevention by the thermal sprayed Zn, Zn-Al alloy and Al coatings was due to a barrier effect rather than an effect of the electrochemical cathodic protection.

2) All of three kinds of the coatings showed a sufficient protection against the atmospheric corrosion for over 22years.

3) A thin protective layer containing the corrosion products formed on the outermost layer of the sprayed Zn decreased the surface activity and the anodic dissolution. The pollution components of S and Cl were not found to penetrate inside the film.

4) The sprayed Zn-15Al alloy showed a similar polarization characteristic to the sprayed Zn, but the pollution components were found to penetrate down to the substrate, and to detach the inter-spraying layers. The protection ability was at its final stage to the limit of the resistance.

5) Passive behavior of the sprayed Al continued still

for 22years, but the film deteriorated to expand the defects filled with the corrosion products. The protection of the film was also at the limit of the use.

6) Corrosivity of the atmosphere caused by S and Cl was larger at Sapporo than at Tokyo. The influence of the airborne salinity and the air pollution substances is more severe at the coast of Japan Sea rather than the coast of Pacific Ocean.

References

1. Y. Kitamura, H. Nuriya, M. Seki, K. Ishikawa, and S. Yoshida, in *Proceedings of the 30th Scientific Lectures Meeting, College of Industrial Technology, Nihon University*, 25 (1997).
2. H. Nagasaka and K. Kato, *J. Japan Thermal Spray Soc.*, **2**, 41 (1965).
3. S. Miyase, N. Fukami, K. Toyoda, and M. Tagaya, *J. Japan Thermal Spray Soc.*, **4**, 144 (1967).
4. R. Suzuki, T. Shibata and H. Nagasaka, *Keikinzoku*, **30**, 679 (1980).
5. R. Suzuki, H. Nagasaka, Z. K. Ming, and N. Onuki, *J. Japan Thermal Spray Soc.*, **23**, 1057 (1986).
6. M. Leclercq and R. Bensimon: in *Proceedings of the 8th International Thermal Spray Conference*, Miami Beach, FL, 417 (1976).
7. B. A. Shaw and P. J. Moran, *Materials Performance*, **24**(11), 22 (1985).
8. Z. Zhongli, G. Weisheng, and W. Jinlin: in *Proceedings of the 13th International Thermal Spray Conference*, Orlando, FL, 399 (1992).
9. B. A. Shaw and A. G. S. Morton, in *Proceedings of 2nd National Thermal Spray Conference*, Cincinnati, OH, 385 (1988).