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Technical Note

In-Process Exothermic Reaction in High-Velocity Oxyfuel and Plasma Spraying with SiO_2/Ni/Al-Si-Mg Composite Powder

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Reactive thermal spraying, in which thermodynamically stable compounds are formed by expected in-process reactions, has attracted considerable attention as a result of the wide availability of in situ composite coatings. Such in-process reactions occur differently in high-velocity oxyfuel (HVOF) and plasma spraying because of differences in the flame temperature and speed. In the current study, a composite powder of SiO_2/Ni/Al-Si-Mg was deposited onto an aluminum substrate to fabricate in situ composite coatings by both spraying methods. The coating hardness sprayed with Al-Si-Mg core powder increases with silicon and magnesium content, whereas the coatings by HVOF spraying show higher hardness than those by plasma spraying. In the present reactive spraying, the exothermic reaction of SiO_2 with molten Al-Si-Mg alloy leads to composite materials of $MgAl_2O_4$, Mg_2Si, and Al-Si matrix. Moreover, a rapid formation of aluminide ($NiAl_3$), which is introduced by an exothermic reaction of plated nickel with Al-Si-Mg core powder, enhances the reduction of SiO_2, especially in HVOF spraying. A series of in-process reactions proceed mainly during splat layering on a substrate instead of during droplet flight even in plasma spraying. Plasma-sprayed composite coatings become much harder because of the great progress of in-process reactions.

Keywords exothermic reactions, high-velocity oxyfuel and DC plasma, in situ composite deposits, reactive thermal spray

1. Introduction

Reactive thermal spraying offers properties superior to those of conventional coatings for various applications because it has in situ formed fine and uniformly dispersed stable hard phases within the coating, as a result of in-process reactions during flight and after impingement (Ref 1-5). Besides, for the fabrication of reliable composite coatings, instead of using expensive composite powder such as WC/Co, which has a tendency to decompose and dissolve carbide grains in cobalt, resulting in porous coatings with reduced hardness (Ref 6), reactively sprayed coatings can be achieved by using high-velocity oxyfuel (HVOF), radiofrequency (rf), and direct current (dc) plasma spray methods. Among these methods, dc plasma spraying, which utilizes the reactions of molten droplets with atmospheric gases such as nitrogen (Ref 1, 2, 7) and the mutual reactions with constituents in spray materials (Ref 7, 8), is attractive as a base in the production of reactively sprayed coatings because of its ease of fabrication with low cost, availability in various types of in situ coating, and processing flexibility. It has been shown that by utilizing reactive dc plasma spraying, in situ reinforcements such as TiN (Ref 1, 5), Ti_2AlN (Ref 7), and CrN (Ref 9) are formed during the spray process. Furthermore, by controlling spray materials and spray parameters, in situ formed phases such as carbides, silicides, oxides, borides, and nitrides dispersed within the sprayed metal matrix are formed successfully and proposed for the fabrication of composite coatings. The important limitation of the conventional dc plasma system, however, is that it allows only the use of nitrogen as a reactive plasma gas because of the optimum gap distance for the generation of discharged arc. On the contrary, in the case of reactive radio frequency (rf) plasma spraying, many reactive plasma gases such as CH_4, N_2, and O_2 can be used. It has been reported that composite coatings containing nitride (Ref 10, 11) and carbide (Ref 12) formed in situ were produced by rf plasma spraying. As for the HVOF spraying characterized by high-flame velocity and relatively low temperature, which are disadvantages in reactive thermal spraying, Lee et al. (Ref 13) studied the formation of fine NiO particles based on in-process reactions by applying HVOF reactive spraying. Although they obtained extremely fine and well-distributed oxide particles in the coating, a thermally unfavorable phase, Ni_3N, decomposed during reactive spraying, was also reported. Recently, in our previous work, which is an application of in-process reactions to the surface modification of aluminum substrates, composite coatings containing in situ formed hard phases such as $MgAl_2O_4$ (spinel), Mg_2Si was fabricated by reactive HVOF spraying, and it was also noticed that the exothermic in-process reaction proceeded mainly during splat layering rather than during flight (Ref 14). As a consequence, the in-process structure control is vital to form highly functional composite coatings.

In this study, composite powder of SiO_2/Ni/Al-Si-Mg was deposited onto an aluminum substrate to fabricate in situ com-

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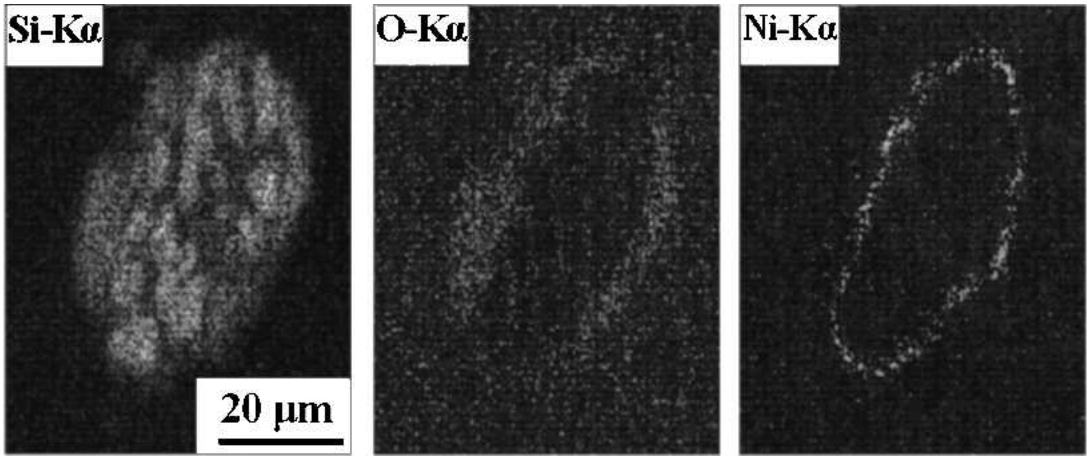

Fig. 1 Characteristic x-ray images of a granulated SiO_2/Ni/Al-Si-Mg particle cross section

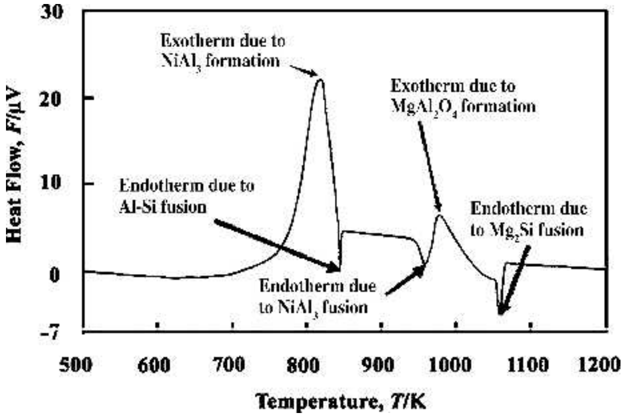

Fig. 2 DTA scan of granulated SiO_2/Ni/Al-Si-Mg particles heated to 1273 K with heating rate of 0.17 K s^{-1} in argon atmosphere

posite coatings by both plasma and HVOF spraying methods. The influence of spray method, spray parameters, and in-process reactions proceeding differently in both methods on the coating performance was studied. The in situ formed phases at each processing step, such as droplet flight, droplet impingement, and splat accumulation, were examined. Splat morphology, adhesion, microstructure, and mechanical properties such as hardness were determined.

2. Experimental Procedures

Aluminum alloy powders manufactured by gas atomization with a chemical composition of Al-37.44Si-10.71Mg (in wt.%) were supplied as core spray powder. After sieving core material with a powder size (d_p) of 32-63 µm, granulated composite powders were prepared by electroless nickel plating and finally adhesion of fine SiO_2 powder (50 nm) with water glass ($SiO_2.Na_2O$) as a binder. The granulated composite powder was sprayed onto a pure aluminum substrate (A 1050) by HVOF and the atmospheric dc plasma spraying (APS) method. Spray parameters are listed in Table 1. The substrate surface was sandblasted briefly and then cleaned ultrasonically by acetone prior to spraying. The substrate was cooled continuously by a forced airflow from the back side through a nozzle. The temperature in the central portion of the substrate was measured continuously by a thermocouple to monitor the in-process exothermic reactions and also to prevent the substrate from partially melting during the spraying.

Table 1 Spray parameters in HVOF and APS method

	HVOF	APS
Arc voltage (V)		38
Arc current (A)		500
Primary gas (L/min)	O_2: 362	Ar: 47.2
Secondary gas (L/min)	kerosene: 0.23	H_2: 2.36
Spray distance (mm)	285	150
Particle size (µm)	$32 < d_p < 63$	$32 < d_p < 63$

To confirm the in-process reactions and phases formed during spraying, a differential thermal analysis (DTA) study was performed at a temperature range of 298 to 1273 K in an argon atmosphere with a heating rate of 0.17 K s^{-1}. In addition, sprayed particles were collected at a spray distance (d_s) of 450 mm in APS and 1000 mm in HVOF droplets without impinging on a substrate to reveal that the in-process reactions occurred mainly whether during flight or on the substrate. The collection distances allow the sprayed particles to solidify completely, which is confirmed by DPV 2000 droplet temperature measurements. A stainless steel container was used to collect the sprayed particles that traveled in the plasma jet to avoid undesirable chemical reactions between the particles and collector. Different phases of sprayed particles, splats, and coatings were identified by x-ray diffraction (XRD) with Co-Kα radiation. The cross sections of sprayed particles were also examined by scanning electron microscope (SEM) and electron probe microanalyses (EPMA). For the same purpose, splats were collected on a mirror-finished pure aluminum substrate without preheating and then analyzed for elemental distribution by EPMA and their constituents by XRD. Both HVOF and APS coating cross sections were observed by SEM, and Vickers hardness of the coatings was measured with a load of 0.1 N.

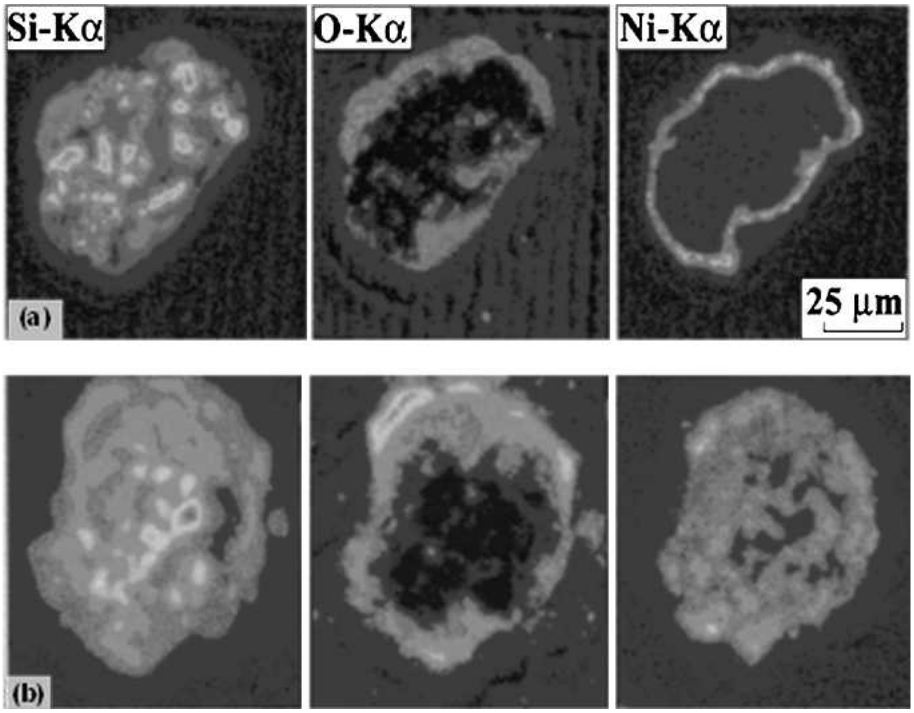

Fig. 3 Characteristic x-ray images showing elemental distribution on the cross section of sprayed particles in (a) HVOF and (b) APS conditions

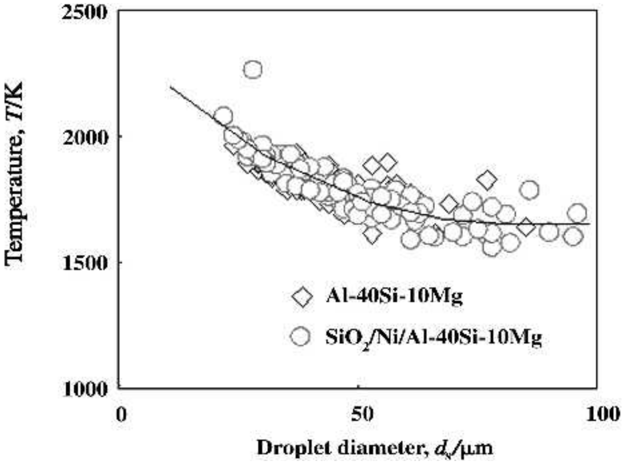

Fig. 4 Droplet temperature measurements performed using DPV 2000 (d_s = 230 mm)

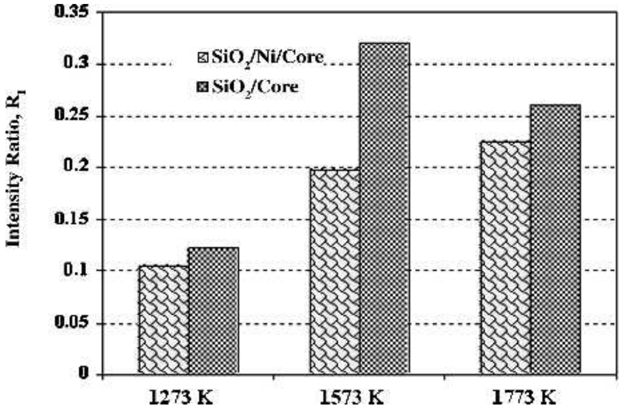

Fig. 5 Effect of composite material system on the formation of spinel phase as a function of temperature

3. Results and Discussion

3.1 *In Process Reaction during HVOF and APS Spraying*

Figure 1 shows the characteristic x-ray images and elemental distribution of granulated particles composed of plated nickel, fine SiO_2 particulates, and Al-Si-Mg core particle with a water glass binder. It appears from the images that SiO_2 particulates adhered on an Al-Si-Mg particle, and nickel at the periphery was present in the composite powder. Even though a mass of SiO_2 particulates in the granulated particle is not well distributed and tends to be situated in some regions, it is detected on all core Al-Mg-Si particles.

In our granulated composite powder system, SiO_2/Ni/Al-Si-Mg, in which premixing ratios in weight were selected as 0.126/0.032/1, respectively, the SiO_2 particulates act as an oxygen source for proceeding of the exothermic reactions and also rapid formation of aluminide ($NiAl_3$) as indicated (Eq 2) and promote the reduction of SiO_2 with molten aluminum alloy. As a consequence, the synthesis in-process reactions expected in granulated powders can be summarized by:

$$2SiO_2 + 2Al + Mg = MgAl_2O_4 + 2Si \text{ (in Al)} \tag{Eq 1}$$

$$Ni + 3Al = NiAl_3 \tag{Eq 2}$$

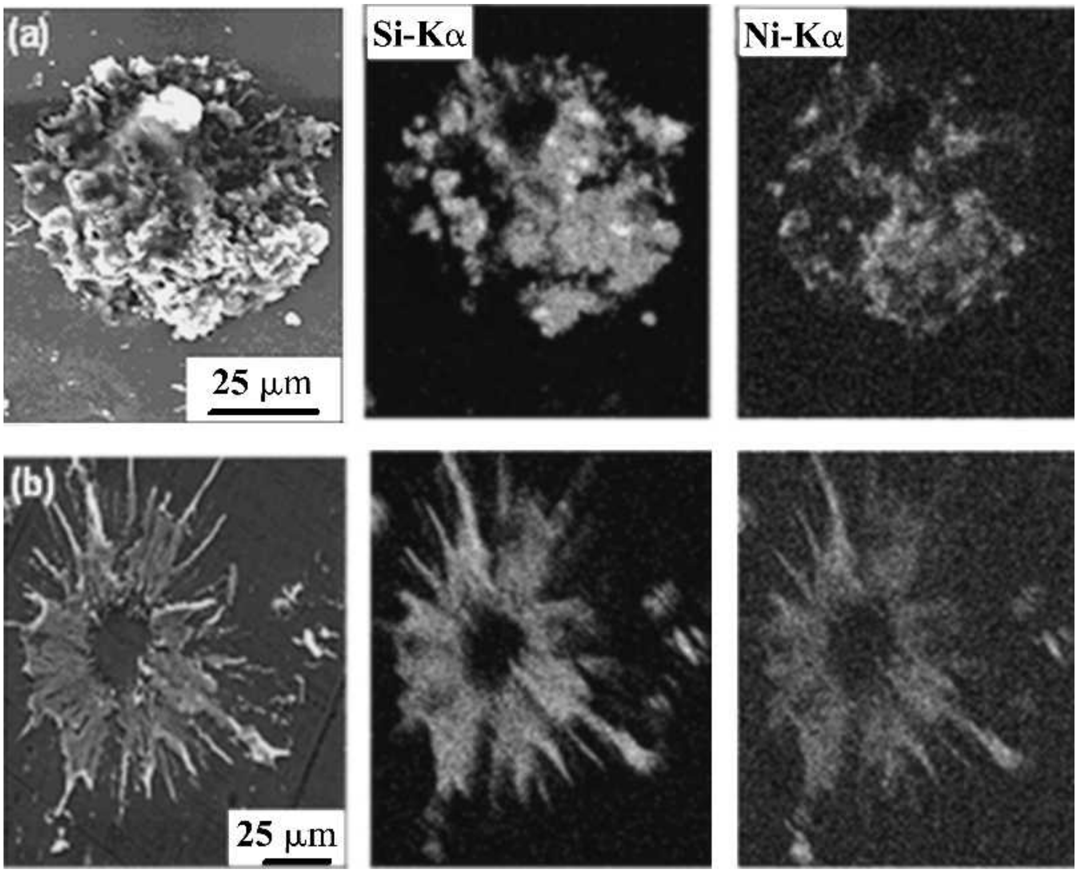

Fig. 6 SEM and characteristic x-ray images of splat surface in (a) HVOF and (b) APS conditions

$$3/2\ SiO_2 + 2Al = Al_2O_3 + 3/2\ Si\ (in\ Al) \qquad (Eq\ 3)$$

These exothermic reactions take place during flight, and splats layering on the substrate release a significant amount of energy, resulting in a rise in temperature in the reacted particles and substrate. As a matter of fact, the heat quantity of −575 kJ/mol was calculated based on the in-process reactions (Eq 1, 2) and corresponded to the rise in temperature of 620 K in the reacted particle.

The resulting curves, obtained from a DTA scan on granulated powders as shown in Fig. 2, confirmed that strong exothermic peaks are noticeable at about 810 and 980 K, corresponding to aluminide and spinel formation, respectively. An endotherm of Al-Si and Mg_2Si fusion was also determined after the DTA scan. An XRD pattern of composite powder scanned for DTA up to 1273 K in an argon atmosphere consisted mainly of $MgAl_2O_4$, $NiAl_3$, and Al-Si as can be estimated from Eq 1 and 2. However, there are no diffraction peaks of metastable Mg_2Si on the XRD pattern. This is because only stable phases formed, and all reactions were completed as a result of full reduction of SiO_2 by molten Al-Si-Mg alloy under the ideal DTA scan conditions. It is noted that there is a significant difference in the heating and cooling rate between DTA and thermal spraying. To make a comparison and clarify that the reactions occurred during flight, the cross section of sprayed granulated particles collected at d_s of 450 mm in APS and 1000 mm in HVOF was observed by SEM and EPMA, as illustrated in Fig. 3. The O-Kα image points out the existence of oxygen even inside the sprayed particle in both spray conditions, which means that SiO_2 on a granulated particle surface reacted with molten Al-Si-Mg alloy during flight. The segregated intensity of images detected on particles also confirms that incomplete and limited reactions occurred on granulated particle centers during flight. Now that a relatively uniform elemental distribution of nickel was observed in APS spraying, which produces a rise in temperature and a longer in-flight period of droplets, the progress of in-process reactions is expected to be much better than that of HVOF. Moreover, there is no major difference in droplet temperature when the core and granulated particles are sprayed by HVOF, as shown in Fig. 4. In addition, molten droplets are solidified completely, and the cooling rate is found still to be rather fast, which is based on the mean temperature of the particles monitored by the DPV 2000 system. Thus the HVOF spraying does not exhibit appreciable in-process reaction during the droplet flight.

3.2 Synthesis of Reaction Rate and Magnesium Evaporation

Reactively sprayed coatings containing dispersed hard phases can be formed in situ by either reactions between the injected powder and reactive gases or mutual reactions with constituents in spray materials. In both cases, it is well established

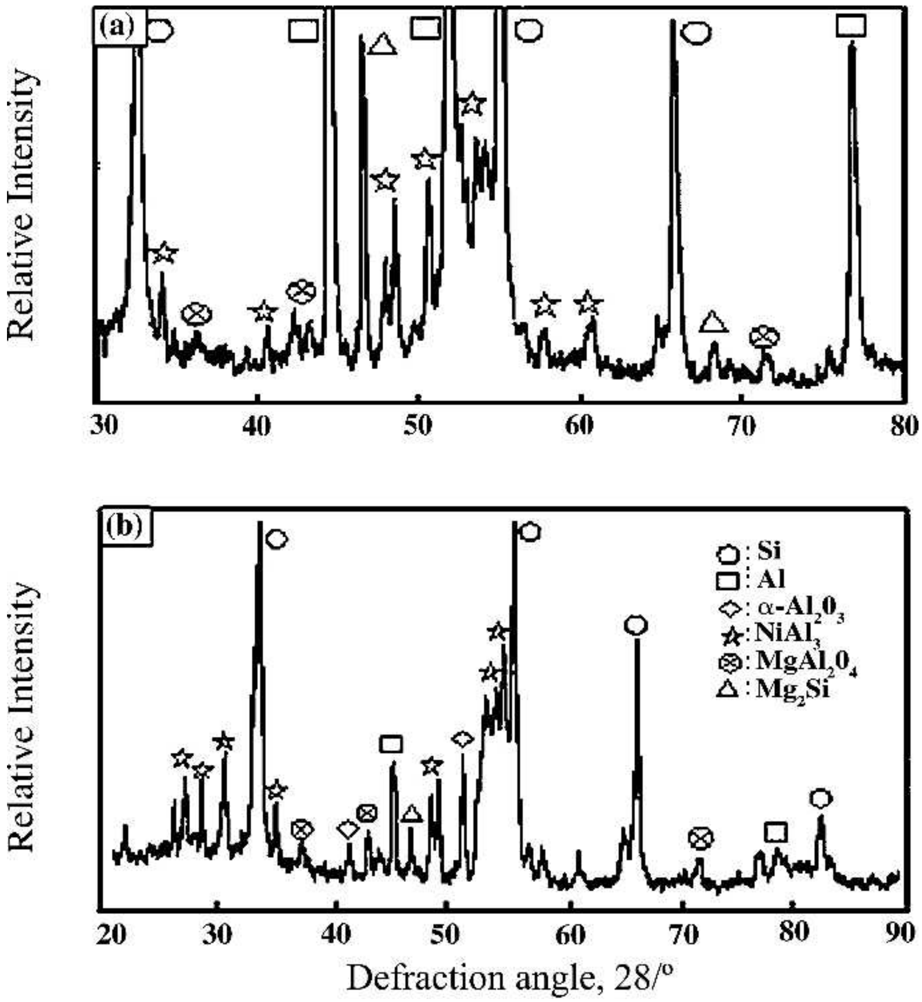

Fig. 7 XRD patterns of coating surfaces sprayed by (a) HVOF and (b) APS

that the higher degree of in-process reactions can be achieved by selecting proper raw materials and optimal spray parameters (Ref 3, 15, 16). Moreover, it is claimed that the in situ phases promise to have better cohesion with matrices from which they are formed and result in high wear resistance of the coatings (Ref 16). Therefore, considering the short residence time of composite powders in the high-temperature environment of the thermal spray jet, to obtain highly functional composite structure it is essential to realize the degree of the expected in-process reactions and ideal phase compositions in our granulated composite system. For this purpose, green compact samples prepared from granulated composite powders of SiO_2/Ni/core and SiO_2/core were used for this study. At first, to achieve a high degree of ideal phase combination, composite samples were heated in an argon atmosphere up to 1473 K and kept constant at this temperature for 2 h and finally cooled down slowly at room temperature, at which time both the heating and cooling period were maintained as 323 K/h. XRD results revealed that $MgAl_2O_4$, $NiAl_3$, and α-Al_2O_3 were present in the structure because the sample was exposed to high temperature for a long time. However, there are no diffraction peaks of metastable Mg_2Si on the XRD pattern. This is because only stable phases formed, and all reactions completed as a result of full reduction of SiO_2 by the molten Al-Si-Mg alloy. Consequently, green compact samples were composed of stable and thermodynamically favorable phases. On the other hand, when the test temperature was raised and relatively rapid heating and cooling rates (283 K/s) were applied, according to Eq 4, which is based on the intensity ratio, SiO_2/core powder up to 1573 K showed higher amounts of spinel phase formation compared with the SiO_2/Ni/core composite system, in which nickel prevents core powder from high temperature exposure, resulting in low reaction rate.

$$R_I = \left[I_{MgAl_2O_4\{311\}} / I_{MgAl_2O_4\{311\}} + I_{Si\{111\}}\right] \qquad \text{(Eq 4)}$$

However, above this temperature, it is evident from Fig. 5 that composite powder without nickel showed a marked decrease in the amount of spinel, which may be attributed to magnesium depletion. Because the core particles contain a large amount of magnesium (10 wt.%) there is a tendency toward magnesium evaporation with increasing temperature, especially when considering powders in the high-temperature environment of the plasma flame. For this reason, sprayed particles and composite deposits were subjected to chemical analysis to determine

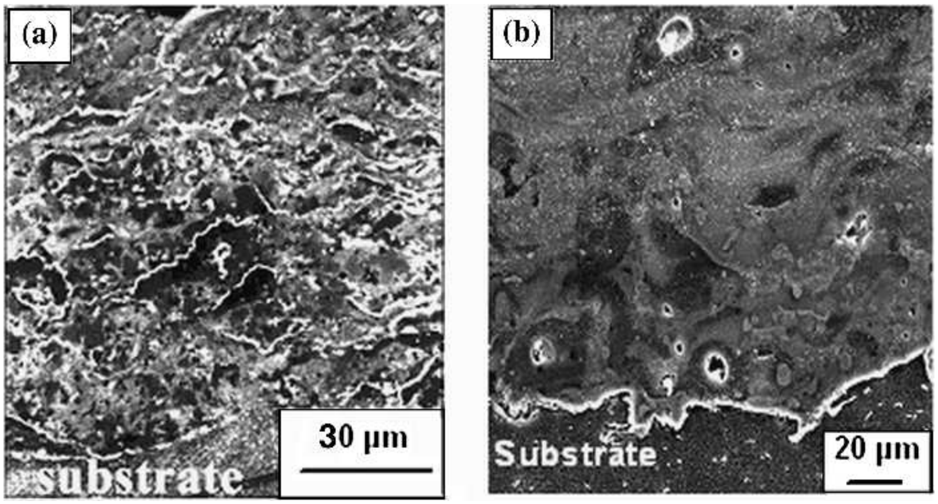

Fig. 8 SEMs showing cross-section microstructure of coatings sprayed by (a) HVOF and (b) APS methods

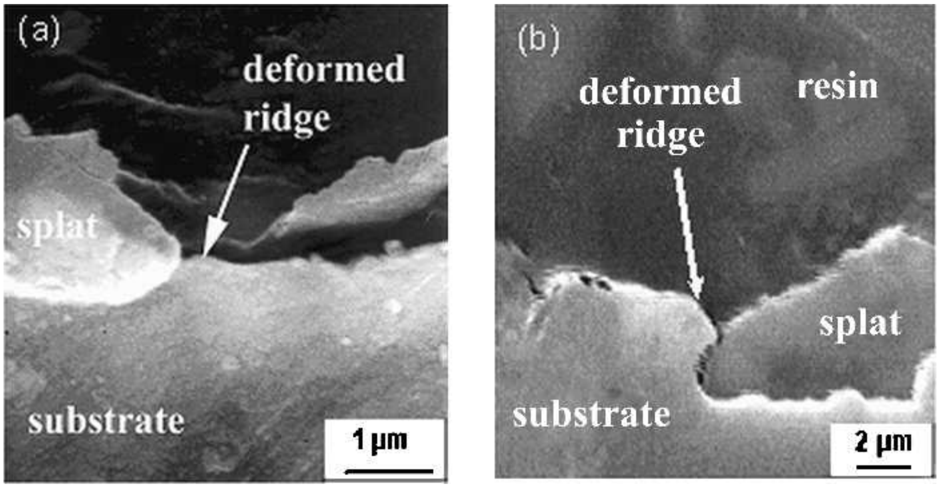

Fig. 9 SEMs showing a splat cross section and formation of deformed ridge on an aluminium substrate by (a) HVOF and (b) APS methods

the degree of evaporation. As a matter of fact, the depletion of magnesium took place almost entirely during droplet flight instead of splat layering, and as a result even lower hardness was observed for the granulated powders without plated nickel. According to the XRD results, the coatings sprayed with SiO_2/Ni/core particles in APS conditions resulted in an increase in the spinel amount of nearly 50% compared with the coatings produced by composite powder without plated nickel. Therefore, it can be deduced that the best compromise between starting materials and resultant composite deposits was achieved spraying with SiO_2/Ni/core granulated particles because they have denser, much harder, and well-distributed hard phases within the coatings.

3.3 Splat Morphologies in HVOF and APS

It is known that thermal spray coatings are produced by a piling up of the splats (Ref 17). Therefore, splat morphology and deposition are very important to obtain highly functional coatings. Main morphologies of splat sprayed by HVOF and APS are shown in Fig. 6. When composite powders are sprayed onto an aluminum substrate, circular and star-shaped splats with long radial streaks are formed mainly in HVOF and APS conditions, respectively. Morks et al. (Ref 18) noted that star-shaped splats provide good adhesion as a result of a high collision force at their center, which promotes a firm contact between a splat and its substrate. The Si-Kα, Ni-Kα, as observed in the APS splat, had a widespread distribution compared with that of the HVOF splat. This is because high-velocity and low-flame temperature were obtained in the case of HVOF spraying, which are disadvantages in reactive thermal spraying. Therefore, in HVOF spraying, the expected in-process reactions are not well propagated, and further reactions are hindered because the molten droplets are rapidly solidified and flattened on a substrate.

3.4 Microstructure and Properties of Coatings

Typical XRD patterns of the coating surfaces fabricated by HVOF and APS are demonstrated in Fig. 7. Whereas plasma

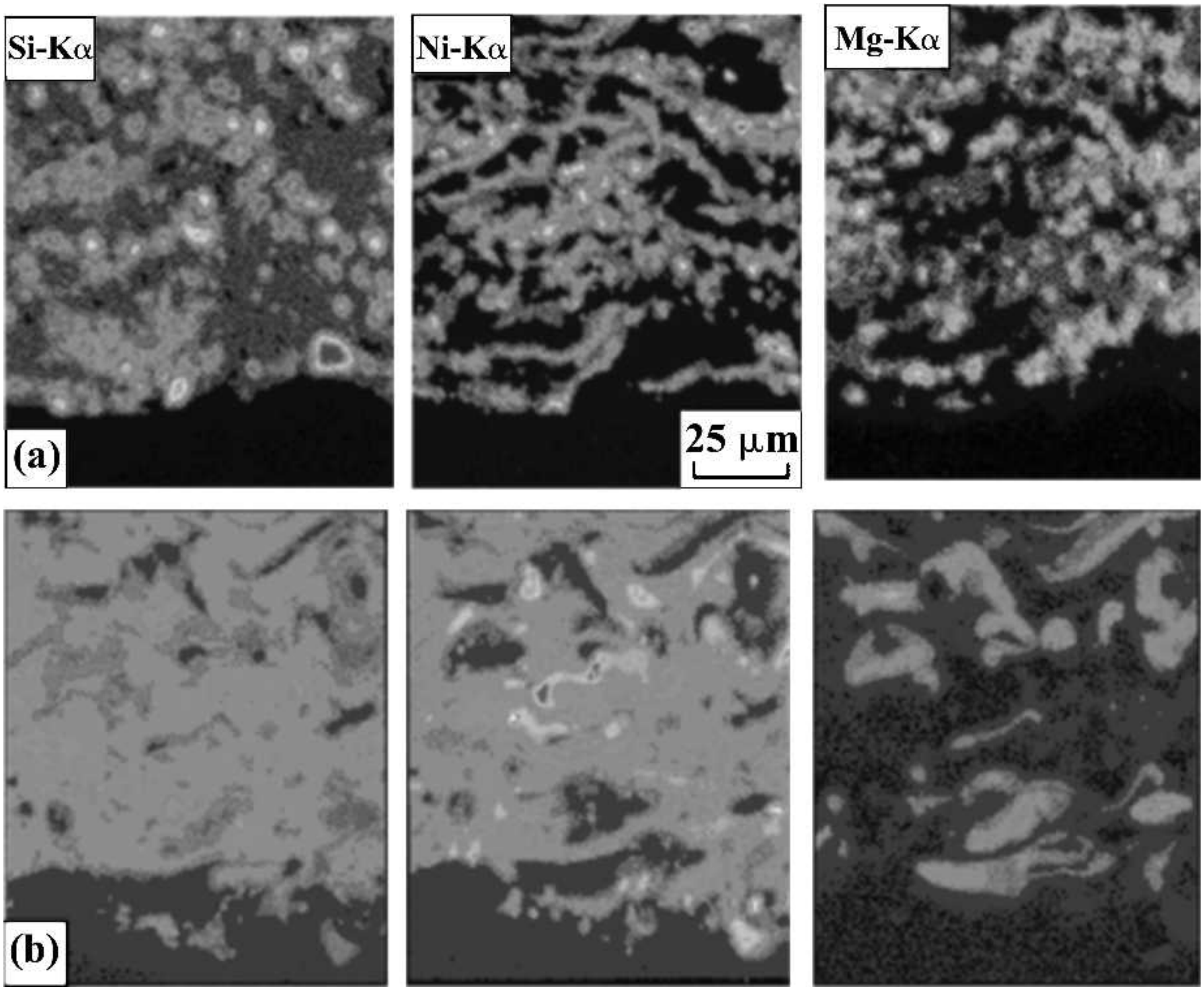

Fig. 10 Elements distribution on a cross section of coatings sprayed by (a) HVOF and (b) APS conditions

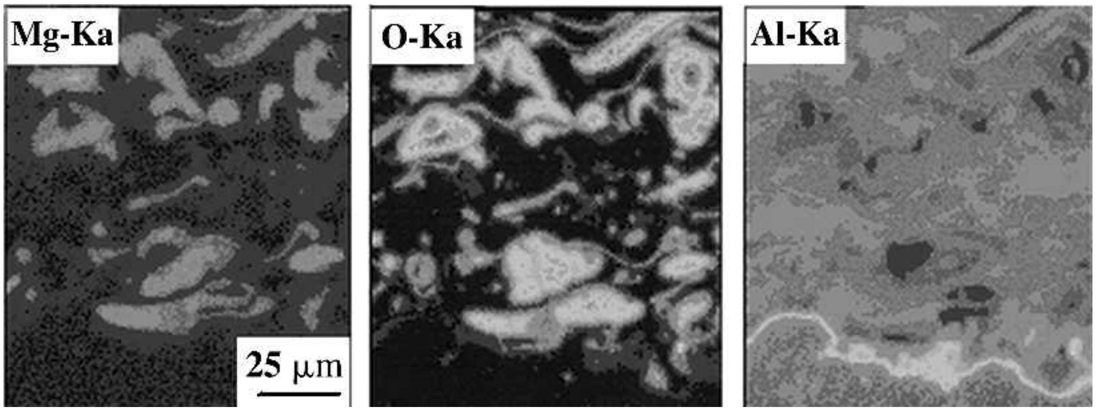

Fig. 11 Mg-, O-, and Al-Kα images on a cross section of the APS coating

sprayed composite coating consisted of Al_2O_3, Mg_2Si, $MgAl_2O_4$, $NiAl_3$, and Al-Si matrix, no formation of aluminum oxide was observed in the HVOF-sprayed coating. Hence, in situ composite coatings can be fabricated successfully both by HVOF and APS spraying accompanied by the in-process reaction of SiO_2 reduction. Figure 8 shows the typical appearance of microstructures on the coating cross-section after etching with 5 wt.% NaOH aqueous solution. It seems that the HVOF-sprayed

Table 2 Change in substrate temperature as a function of the spray method and powder composition

Spray materials	Spray method	Substrate temperature, T_{max} (K)
Al-40Si-10Mg	APS	462
Al-40Si-10Mg	HVOF	619
SiO_2/Ni/Al-40Si-10Mg	APS	839
SiO_2/Ni/Al-40Si-10Mg	HVOF	692

sample exhibited a wavy layered structure. This is confirmed by the observation of the sinking splat outer periphery in a substrate, which is called a deformed ridge, as seen in Fig. 9. As a result, HVOF-sprayed samples had adhesion strength values superior to those of their APS counterparts because of the formation of slightly deformed substrate ridges, which create a kind of mechanical bond between the impinging particle and substrate surface. On the other hand, the observation of plastic deformation on the substrate surface of the APS sample can be attributed to the partial melting of the upper surface rather than heavy collision and kinetic energy of droplets. This is because the highest substrate temperature (839 K) was measured in APS conditions compared with the HVOF spraying. To reveal the role of substrate melting on the formation of deformed ridges, based on thermal analysis (for further details, see Ref 14), substrate surface temperature, T_i, is estimated by Eq 5, which is only true when the latent heat of aluminum is negligible, and there is perfect contact between splat and substrate:

$$(T - T_i)/(T_s - T_i) = \mathrm{erf}\,[-x/\{2(kt/\rho C_p)\,1/2\}] \qquad \text{(Eq 5)}$$

where, T_i, T_s, and T are interfacial, substrate initial, and calculated temperature, k is the thermal conductivity, ρ is the density, and C_p is the specific heat. In HVOF spraying, the maximum temperature of 1190 K is calculated at the interface between the substrate and splat, which exceeded the melting point of aluminum (933 K) and caused a slight surface melting on the substrate. This means that the quality of the contact between piled-up splats and substrate is a function of interdiffusion and chemical reactions (metallurgical bonding). In the microstructure of the APS coating of some occasional pores, which degrades the mechanical properties and adhesive strength resolvable with SEM microscope, was seen, but no extremely thin wavy layered structure was noticeable. The progress of in-process reactions on the cross sections of the coatings was examined by EPMA, as shown in Fig. 10.

It is evident from elemental distributions that the Si-Kα and Ni-Kα displayed better widespread dispersion in APS coating compared with that of the HVOF sample, indicating that a series of in-process reactions propagated well during splat layering. However, in some splats a weak intensity of Ni-Kα and Mg-Kα was noticeable, which implies that insufficient in-process reactions occurred in these splats. On the other hand, high-intensity areas of Mg-Kα coincided with O-Kα as observed in Fig. 11 and allowed formation of spinel in the plasma-sprayed coating. To determine the exothermic in-process reactions that occurred on a large scale during splat layering, substrate temperature changes of the coatings sprayed with core and composite powder were measured as presented in Table 2. When granulated particles were sprayed by the APS method, a significant rise in temperature was seen, which means that the expected in-process reactions occurred intensively compared with HVOF. Evaluation of coatings hardness is a good indicator of the performance of the composite coatings. The effect of alloying elements and spray method on the hardness behavior of the coatings sprayed with core materials is shown in Fig. 12. It is noticeable on the figure that the coating hardness sprayed with Al-40Si-10Mg core powder increases with magnesium content, whereas the coatings by HVOF spraying show higher hardness than those by plasma spraying. It is expected that the higher hardness in HVOF spraying arises from the refinement of microstructure and work hardening. The average values of hardness measured on coatings sprayed by HVOF and APS with Al-40Si-10Mg core and composite powders are illustrated in Fig. 13. It is clear that by spraying with composite powder a moderate improvement in hardness for the HVOF sample was obtained, but in the case of APS, a substantial increase in hardness was observed as a result of a higher amount of hard phase formation in the coating.

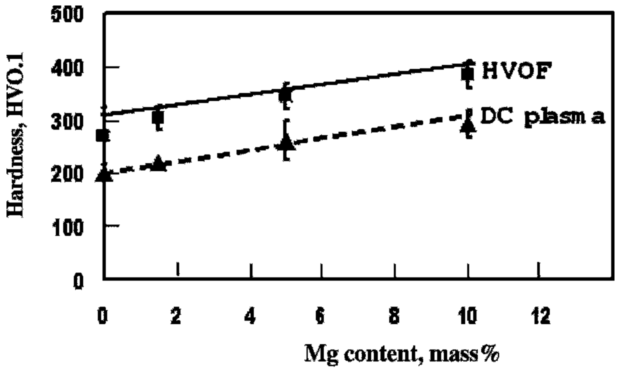

Fig. 12 Hardness results of HVOF and APS coatings sprayed with different core powder compositions

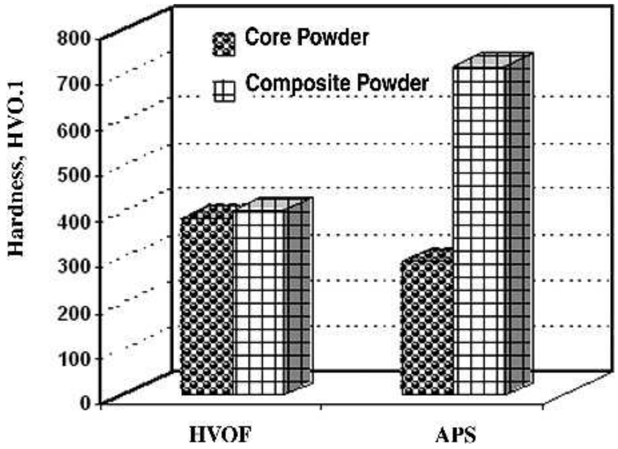

Fig. 13 Effect of powder composition and spray methods on the hardness behavior of the coatings

4. Conclusions

In the present work, granulated SiO_2/Ni/Al-Si-Mg particles were deposited onto an aluminum substrate to fabricate the composite coatings using reactive HVOF and dc plasma spraying methods. After the evaluation of experimental observations the following are concluded:

- Based on the reaction of SiO_2 and molten Al-Si-Mg in a spray material, reactively sprayed coatings consisting of Mg_2Si, $MgAl_2O_4$, and $NiAl_3$ in an Al-Si matrix are formed by HVOF and dc plasma spraying. Reaction of molten droplets with atmospheric gases in the case of APS resulted in the formation of aluminum oxide in the coating as well.
- A series of in-process reactions occurs mainly during splat accumulation on a substrate instead of during droplet flight even in dc plasma spraying.
- The highest substrate temperature (839 K) was observed when the granulated particles were sprayed by APS in contrast to spraying with core particles, which implies the possibility of great progress of in-process exothermic reactions.
- HVOF samples sprayed with core particles showed higher improvement in hardness. In contrast, when sprayed with granulated particles, plasma-sprayed coatings become much harder because of the higher amount of formed in situ compounds in the coating.
- For the HVOF-sprayed samples, slightly deformed substrate ridges create a kind of mechanical bond between the impinging particle and substrate surface, which allows well-adhered and a dense composite deposit.

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