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Technical Note

Cold Spray of SiC and Al_2O_3 With Soft Metal Incorporation: A Technical Contribution

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Al + SiC, Al + Al_2O_3 composites as well as pure Al, SiC, and Al_2O_3 coatings were prepared on Si substrates by the cold gas dynamic spray process (CGDS or cold spray). The powder composition of metal (Al) and ceramic (SiC, Al_2O_3) was varied into 1:1 and 10:1 wt.%, respectively. The propellant gas was air heated up to 330 °C and the gas pressure was fixed at 0.7 MPa. SiC and Al_2O_3 have been successfully sprayed producing coatings with more than 50 μm in thickness with the incorporation of Al as a binder. Also, hard ceramic particles showed peening effects on the coating surfaces. In the case of pure Al metal coating, there was no crater formation on hard Si substrates. However, when Al mixed with SiC and Al_2O_3, craters were observed and their quantities and sizes depended on the composition, aggregation and size of raw materials.

Keywords Al-Al_2O_3, Al-SiC, cold spray, composites, crater, peening effect

1. Introduction

Thermal spraying has been a common practice for the production of various protective coatings, such as thermal barrier, wear-resistant, and corrosion layer. There are many field-approved techniques in this category; plasma spray, high-velocity oxyfuel (HVOF), wire-arc, flame, and cold spray.[1-7] Most of spraying techniques can be categorized as high-temperature coating processes using a heat stream that melts particles and accelerates them onto the substrate to be coated.[1] Consequently, when the molten and semi-molten particles impact on the substrate, the particles are flattened and solidify to form a solid layer. During the past several years, cold spray has been introduced and has proven to have certain advantage over thermal spray. Because this technique employs a supersonic gas stream to accelerate metal-based powder particles on the order of 500-1000 m/s,[5-13] the materials do not need to be molten or semi-molten to form a coating.

When metallic powders are impinged onto the substrate, the conversion of the kinetic energy makes it possible to proceed with mechanical deformation of the particles resulting in relatively adherent coatings with low porosity. However, in the case of less-deformable materials such as SiC and Al_2O_3, cold spray coatings have not been successful so far due to the absence of flattening and/or mechanical bonding among the particles and substrate. So, at this point, producing cold spray coatings of ductile metals mixed with brittle ceramic materials would be an interesting achievement. Furthermore, in most works regarding cold spray, relatively soft, deformable substrates have been used. Consequently, crater formations at the very first stage of coating mechanism have been usually observed.[10,11] However, the mechanism of coating process of soft metal (Al) and composites (Al-SiC, Al-Al_2O_3) coatings on hard materials like Si and Al_2O_3 substrates has not been well understood. In this study, Al-SiC and Al-Al_2O_3 composite films were cold sprayed on Si substrate and the properties of the films and interfaces between the film and substrate including crater formation were investigated.

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2. Experimental Procedure

The particles were accelerated through a standard Laval type of nozzle with rectangular cross-section (aperture of 4 × 6 mm and throat gap of 1 mm). Instead of the usual He gas, air was used as the main gas. The pressure prior to entering the gas heater was fixed at 0.7 MPa (100 psi) and the temperature of gas through the nozzle was 330 °C. The standoff distance to the substrate was 5 mm and Si(100) was used as the substrate. The as-purchased Al, SiC, and Al_2O_3 particle sizes and shapes were confirmed by scanning electron microscopy (SEM; S-2400, Hitachi, Japan). The powder composition of metal (Al) and ceramic (SiC, Al_2O_3) was varied into 1:1 and 10:1 wt.%, respectively and the structure of Al-SiC, Al-Al_2O_3 composite films with various compositions was analyzed by x-ray powder diffractometer (XRD; M18XHF-SRA, McScience, Japan). The thickness and microstructure of films were measured by SEM with a field emission (ESEM; XL30 ESEM-FEG).

3. Results and Discussion

Figure 1 shows SEM images of the as-purchased Al, SiC, and Al_2O_3 powders used in these experiments. The Al powder was sieved to −325 mesh (≤ 45 μm) and exhibited an irregular shape. The size of the SiC powder was about 45-50 μm, and it exhibited rectangular shape. And that of Al_2O_3 powder was above 50 μm due to aggregation. Metal powders like Al usually plastically deformed after collision.[10,11] As shown in Fig. 2(a), SiC powders were found to be fractured into smaller pieces without sig-

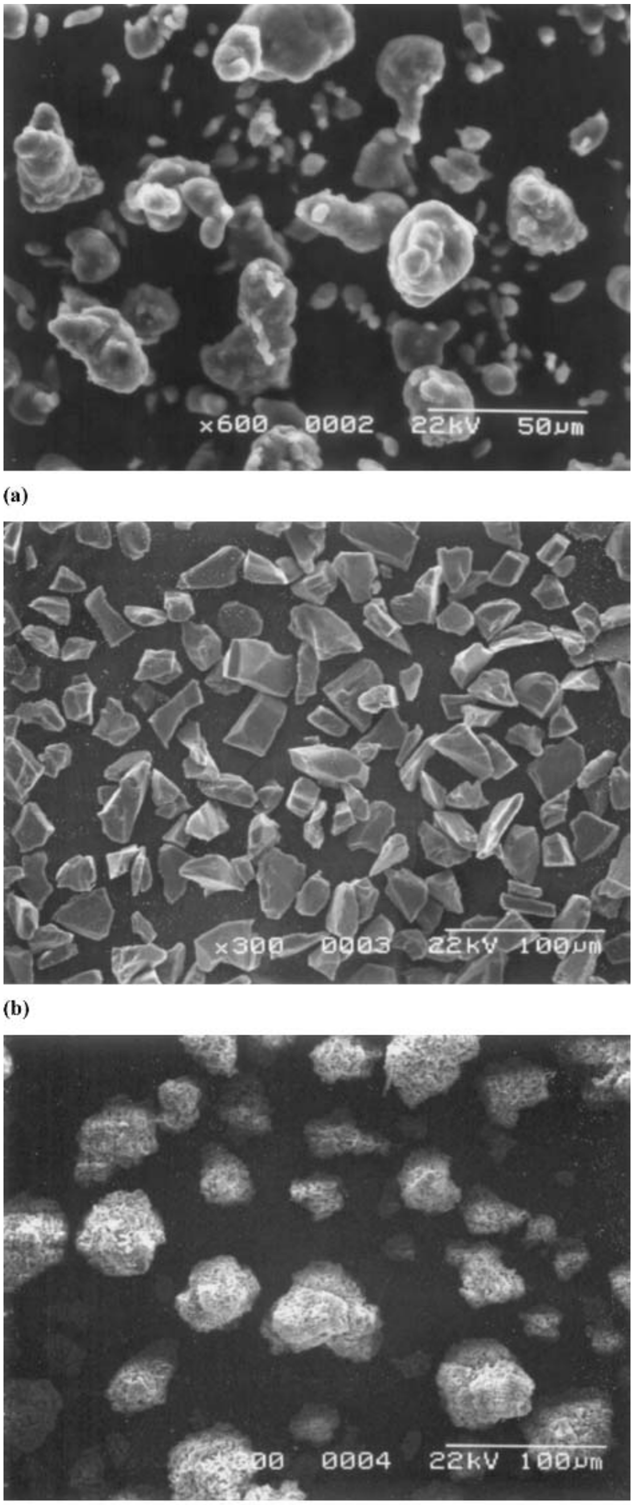

Fig. 1 SEM images of as-purchased Al, SiC, and Al_2O_3 powders: **(a)** Al powder (X600), **(b)** SiC powder (X300), and **(c)** Al_2O_3 powder (X300)

nificant shape change after collision. Also, the simple dismantling of aggregated Al_2O_3 powders occurred by high velocity impact on the substrate [Fig. 2(b)].

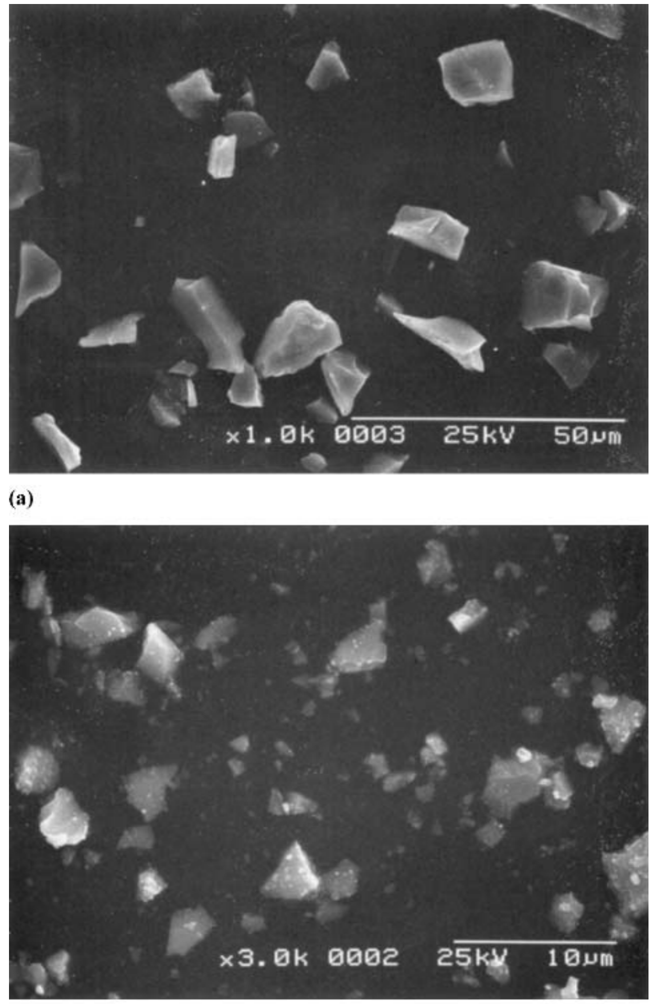

Fig. 2 SEM images of SiC, and Al_2O_3 powders after collision: **(a)** SiC powder (X1k) and **(b)** Al_2O_3 powder (X3k)

Figure 3 shows XRD patterns of the Al-SiC and Al-Al_2O_3 composite films. The diffraction peaks of the films were the same as those of the raw materials; Al, SiC, and Al_2O_3. Therefore, it seemed that the chemical interactions among particles and substrate were absent.

According to an Steenkiste,[10,11] it was suggested that the process consisted of several stages of coating formation in the cold spray process for Al powders on metal substrates:

Region 1, Substrate Cratering & First Layer Build-Up of Particles: initial cratering and deformation of substrate, and first layer build-up of particles

Region 2, Particle Deformation & Realignment: particle rotation and void reduction

Region 3, Metallurgical Bond Formation Between Particles: formation of particle-particle bonds

Region 4: Bulk Deformation

Figure 4 shows SEM images of pure Al film by cold spray at the same condition with composites coatings. Similar to the cases of coatings on the metallic substrates, the “splat” phenomena of Al particles were observed and the dense film on Si substrate was obtained, accompanied by severe plastic deformations and the metallic bonding (Fig. 4b). However, for the most interesting point, the craters between Al film and Si substrate were not observed (Fig. 4c). It is likely that incident soft Alparticles could only be "splatted" rather than making craters on the relatively hard Si surface. To clarify the crater formation at the interface between Al film and Si substrate, cold-sprayed Al films were completely removed form Si substrate by chemical etching using NaOH stock solution. As shown in Fig. 4(d), it was confirmed that the craters were not observed on the surface.

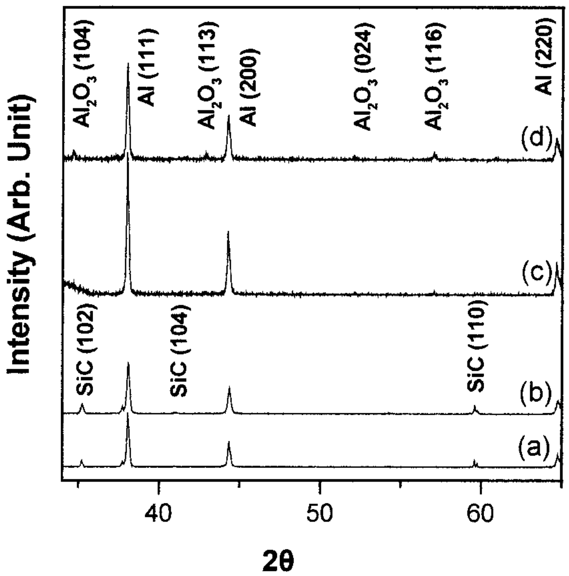

Fig. 3 XRD patterns of composite films: **(a)** Al-SiC composite films (10:1), **(b)** Al-SiC composite films (1:1), **(c)** $Al\text{-}Al_2O_3$ composite films (10:1), and **(d)** $Al\text{-}Al_2O_3$ composite films (1:1)

The SEM morphologies of SiC coating are shown in Fig. 5. As stated earlier, it was found that the cold spray coating of hard particles such as SiC, has inherent limitation of coating thickness (~2-3 μm) and consist of just-fractured particles without "splatting." Also, considerably large portion of impact particles merely bounced off the substrate.

However, Al-SiC composite films on Si substrates looked different (Fig. 6). First of all, when Al-SiC powders with the ratio of 10:1 and 1:1 wt.% were cold-sprayed on Si substrates, the thickness of the coating could reach as much as 50 μm, and SiC particles were embedded in splatted Al (Fig. 6a and b). Secondly, the surfaces of the films became rougher with increase of Al contents (Fig. 6c and d). It was observed that the surface of the composite coating (Al:SiC = 1:1) was relatively smoother than any other surface. It seemed that large amount of SiC particles in the mixed powders were bounced off rather than embedding in the Al matrix and in turn, these hard particles offered effective additional bombardments on surface; so called "peening effect" of the SiC powders,[11] which bounced off.

It seemed that Al_2O_3 particles formed so many craters that the polished Si surface became dimpled. Some of small Al_2O_3 par-

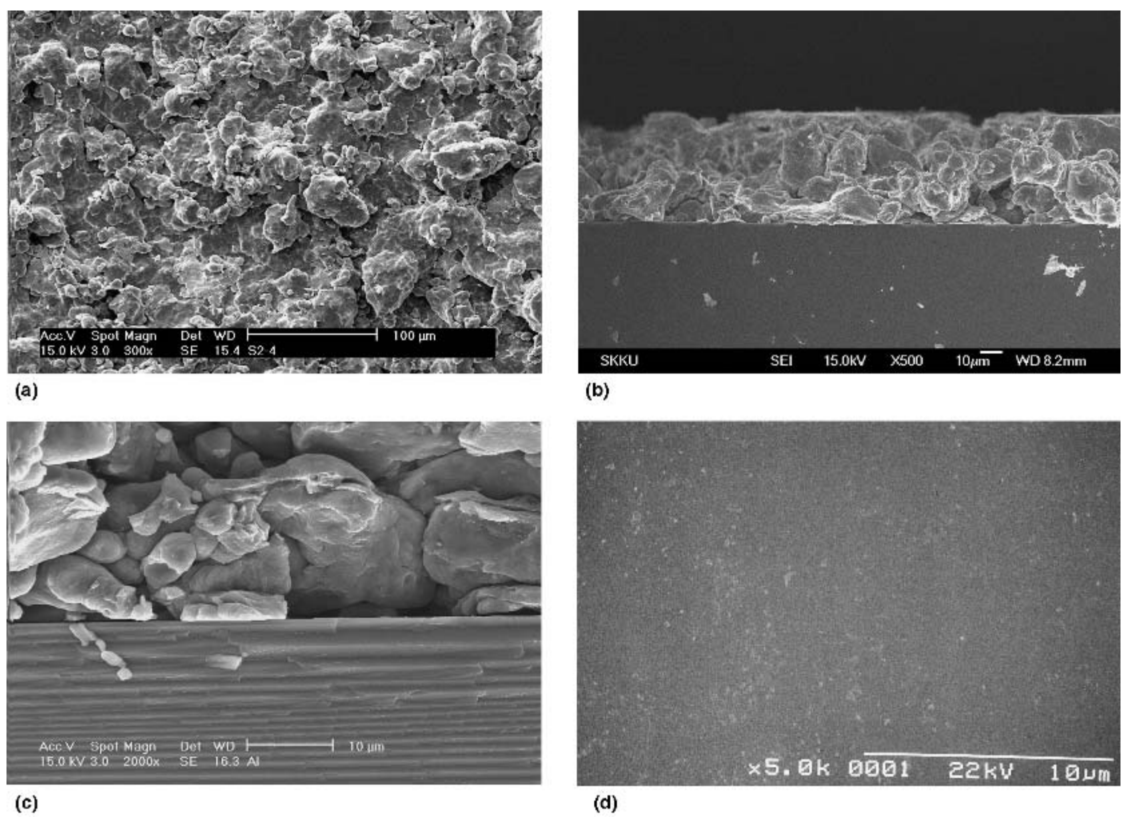

Fig. 4 SEM images of pure Al film by cold spray: **(a)** surface (X300), **(b)** cross-section (X500), **(c)** cross-section (X2k), and **(d)** the surface of Si substrate after etching Al film (X5k)

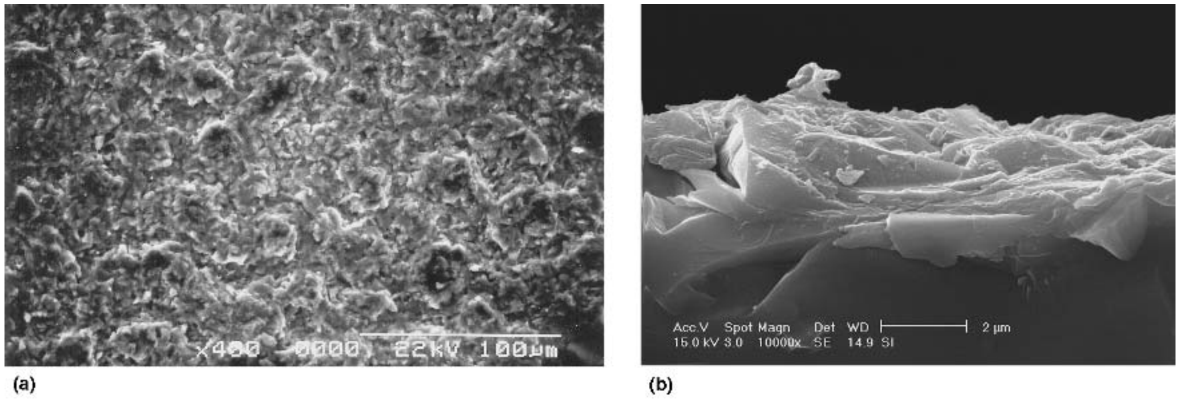

Fig. 5 SEM images of pure SiC film by cold spray: **(a)** surface (X400) and **(b)** cross-section (X10k)

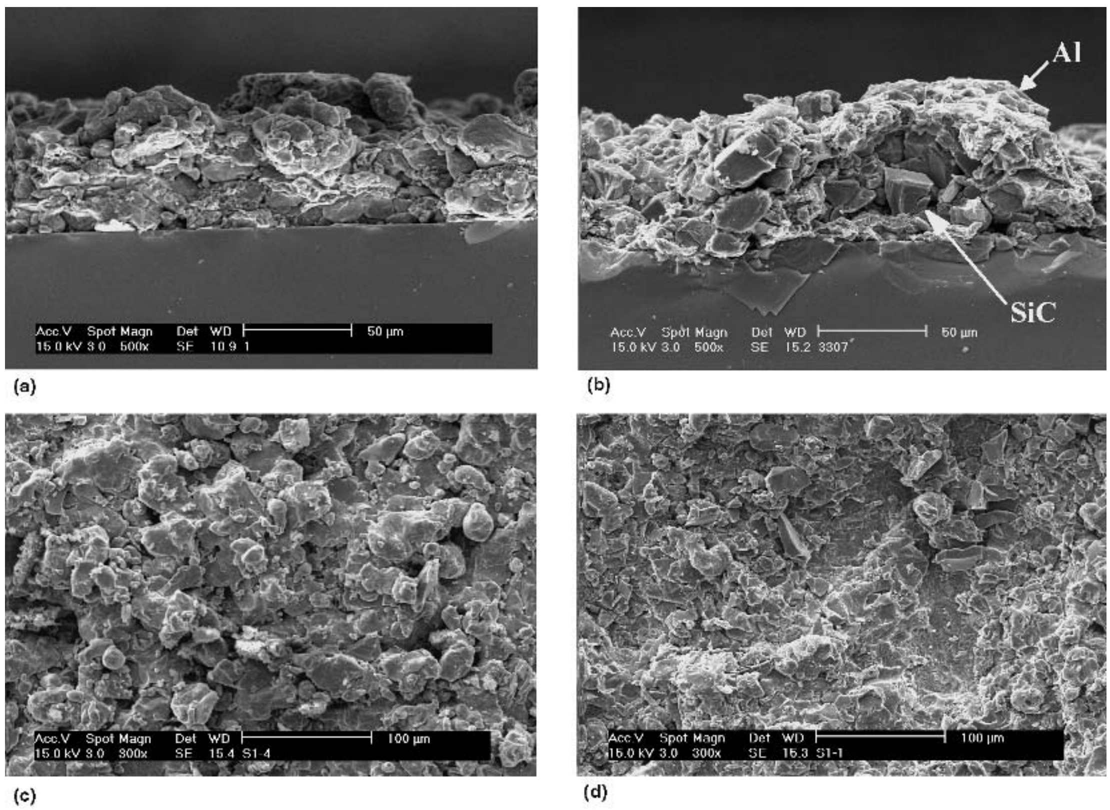

Fig. 6 SEM images of Al-SiC composite films: **(a)** cross-section (10:1, X500), **(b)** cross-section (1:1, X500), **(c)** surface (10:1, X300), and **(d)** surface (1:1, X300), respectively

ticles may be trapped inside the crater, but there was no accumulation above them to build the thickness of coating. Al-Al_2O_3 composite films exhibited similar features to that of Al-SiC composites even though the effect of the Al contents seems to be different. From the cross-sectional SEM photograph (Fig. 7a and 7b), apparently only very fine Al_2O_3 particles were embedded in the Al matrix. And as same as the treatment of pure Al films, Al-Al_2O_3 composite film was chemically etched to confirm the crater formation at the interface (Fig. 7c). By impacting Al_2O_3 particles onto Si substrate, the crater formation on the surface of Si substrate was clearly confirmed.

As shown in Fig. 7(d) and (e), the fine Al_2O_3 particles were observed on the surfaces of all compositions. Because the aggregation of fine-sized primary particles collapsed at the time of arrival on the surface (Fig. 1c and 2b), the peening effects of fine bounced Al_2O_3 particles could not be large as Al-SiC coating even though Al contents were reduced. On the contrary, encapsulating trends of larger Al particle persisted so that smoothness of all surfaces looked like coating of pure Al (Fig. 7f and g).

For adhesion of coatings, the formation of crater is of interest. It was observed that the craters were absent when Al-SiC composite coatings have 10:1 wt.% composition just like pure Al

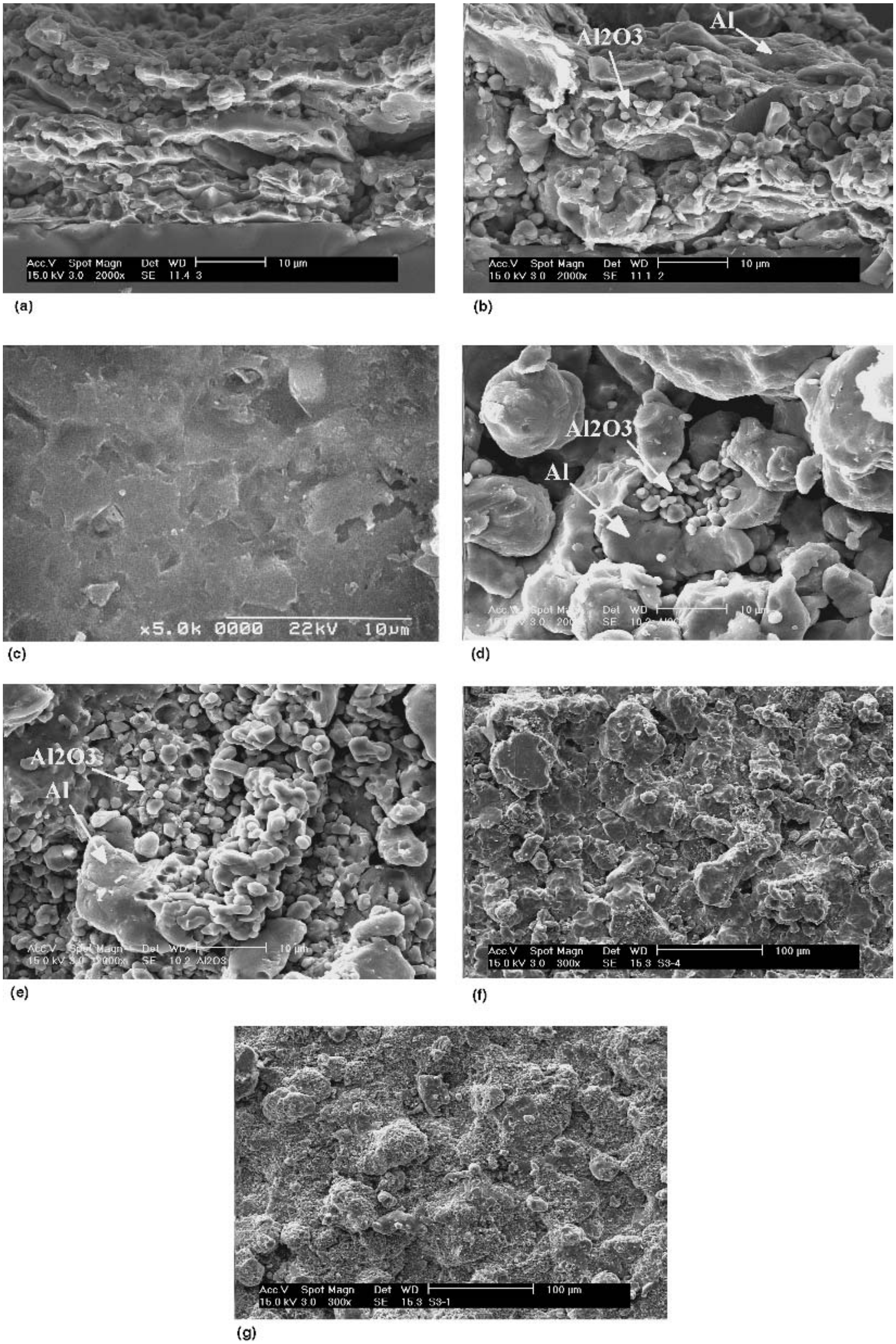

Fig. 7 SEM images of Al-Al_2O_3 composite films: **(a)** cross-section (10:1, X2000), **(b)** cross-section (1:1, X2k), **(c)** the surface of Si substrate after etching Al-Al_2O_3 film (X5k), **(d)** surface (10:1, X2k), **(e)** surface (1:1, X2k), **(f)** surface (10:1, X300), and **(g)** surface (1:1, X300)

film on Si substrate. Meanwhile, many craters were formed in the coatings of 1:1 wt.% composition owing to increased bombardments of hard SiC particles at the very first stage of coating. Compared with the cross sections of Al-SiC films, there were not so many craters at the interface even though amount of Al_2O_3 powder were increased in the Al-Al_2O_3 coatings. Also, the sizes of craters were smaller than those found in Al-SiC coatings due to fine size of fragmented incoming Al_2O_3 particles.

4. Conclusions

The cold spray processing of hard materials such as SiC and Al_2O_3 can be successfully performed with meaningful thickness by the incorporation of soft materials. The adhesion and compactness depends on the quantities and size of raw materials.

Acknowledgment

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