REACTIVE PLASMA NITRIDING OF Al_2O_3 POWDER IN THERMAL SPRAY

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Among advanced ceramics, aluminum nitride (AlN) had attracted much attention in the field of electrical and structural applications due to its outstanding properties. However, it is difficult to fabricate AlN coating by conventional thermal spray processes directly. Due to the thermal decomposition of feedstock AlN powder during spraying without a stable melting phase (which is required for deposition in thermal spray). Reactive plasma spraying (RPS) has been considered as a promising technology for in-situ formation of AlN thermally sprayed coatings. In this study the possibility of fabrication of AlN coating by reactive plasma nitriding of alumina (Al_2O_3) powder using N_2/H_2 plasma was investigated. It was possible to fabricate a cubic-AlN (c-AlN) based coating and the fabricated coating consists of c-AlN, $\alpha\text{-Al}_2\text{O}_3$, $\text{Al}_5\text{O}_6\text{N}$ and $\gamma\text{-Al}_2\text{O}_3$. It was difficult to understand the nitriding process from the fabricated coatings. Therefore, the Al_2O_3 powders were sprayed and collected in water. The microstructure observation of the collected powder and its cross section indicate that the reaction started from the surface. Thus, the sprayed particles were melted and reacted in high temperature reactive plasma and formed aluminum oxynitride which has cubic structure and easily nitride to c-AlN. During the coatings process the particles collide, flatten, and rapidly solidified on a substrate surface. The rapid solidification on the substrate surface due to the high quenching rate of the plasma flame prevents AlN crystal growth to form the hexagonal phase. Therefore, it was possible to fabricate c-AlN/ Al_2O_3 based coatings through reactive plasma nitriding reaction of Al_2O_3 powder in thermal spray.

Keywords: Reactive plasma nitriding; Aluminum Nitride; Thermal Spray.

1. Introduction

Thermal spraying is a technique of coating manufacturing implementing a wide variety of processes which offers a large choice of processes (plasma spraying, flame spraying, electric arc spraying, etc.) and materials (metallic, ceramic, polymer and composite materials). In this process, the powder particles are injected in a plasma jet created by the passage of a gas through an electric arc under high current conditions. The particles are heated, melted or semi-melted and accelerated towards the substrate where they collide, flatten and solidify rapidly. Therefore, deposition of the aluminum nitride (AlN) particles in the thermal spray process directly has been impossible due to the particle decomposition under high temperature without a stable melting phase. Aluminum nitride is an attractive material due to its outstanding properties¹, and it has been expected to contribute several applications. Furthermore, fabrication of thermal sprayed AlN coatings will enable cost-effective solutions for a number of applications². Especially for structural parts and power devices which require thick coatings coating (about 100 μm or more). Reactive plasma spraying (RPS) is considered to be an ideal solution to fabricate AlN thermally sprayed coatings. The principle of RPS is based on the reaction between the feedstock powder and the surrounding reactive gaseous species present in the plasma. In our previous studies^{3,4}, it was possible to fabricate AlN based coatings through reactive plasma nitriding of aluminum (Al) powders in Atmospheric DC Plasma Spray (APS) system. In our study, small feedstock Al particles were supplied to high temperature N_2/H_2 plasma. However, the fabricated coating contains remaining metallic Al. Thus, it was difficult to reach complete nitriding due to the coagulation and aggregation of Al particles with each other due to its low melting point. Furthermore, aluminum oxide (Al_2O_3) coatings are one of the most applied materials to improve both wear and corrosion resistance of metallic components. While the low thermal conductivity of Al_2O_3 limits its application in heat exchange applications. Therefore, the feasibility of using alumina (Al_2O_3) for feedstock powder in RPS process to avoid the presence of the metallic phases in the coating was investigated. And the nitriding process of Al_2O_3 particles in the N_2/H_2 plasma was estimated.

2. Experimental procedures

Commercial Al_2O_3 powder (Fujimi Incorporated, Aichi, Japan), with average particle size 26.6 μm was used as feedstock material. All experiments were carried out by atmospheric plasma spray system (APS: 9MB, Sulzer Metco, Switzerland), using primary gas of N_2 (pressure: 330.9 kPa) and secondary gas of H_2 (pressure: 344.7 kPa). The feedstock powder was supplied to the plasma stream with carrier gas of N_2 , towards the substrate (Grid mild blasted steel). However, it was difficult to understand the nitriding process of the particles from the coatings because the particles lose their shape and characteristics after deposition. Therefore, to clarify the nitriding process of the Al_2O_3 particles, the powders were directly sprayed and collected in water without using substrate. The phase composition of the coating was verified by X-ray diffraction (XRD: RINT-2500, Rigaku,

Japan) with CuK α radiation. The Fourier transform infrared (FTIR) spectroscopy (JEOL: JIR-7000) was used to observe the Al-O and Al-N bonds of the collected particles (20 wt. % of the powder was thoroughly mixed with KBr powder). The powders microstructure and cross sections were observed by scanning electron microscope (SEM: JSM-6390, JEOL, Japan). The surface morphology of as sprayed powder was observed by the field-emission scanning electron microscope (FE-SEM; SU8000, Japan).

3. Results and Discussion

It was possible to fabricate AlN/Al₂O₃ coating with thickness about 120 μ m (porous structure) as shown in Fig. 2. It is clear from the XRD spectra that, after spraying the feedstock powder (α -Al₂O₃), the cubic-AlN (*c*-AlN) phase appeared in the fabricated coating. The XRD diffraction peak at 44° of 2 θ value is corresponding to *c*-AlN with JCPDS No. 046-1200 (rock salt AlN). Moreover, transient γ -Al₂O₃ and aluminum oxynitride (Al₅O₆N) phases appeared in the coatings. It indicates that with spraying the Al₂O₃ powder, some of particles reacted with the surrounding N₂/H₂ plasma and formed *c*-AlN phase. The formation of meta-stable cubic phase in plasma spray process is related to the rapid cooling and solidification of sprayed particles at the collision to the substrate surface. As it is well known in plasma spraying process, the powder particles are quickly melt in the plasma stream and accelerated to the substrate where they spread upon impact and rapidly solidify^{5, 6}. These results agree with the previous report about plasma spraying processing of Al₂O₃/AlN composite powders⁷. Furthermore, it also agrees with the formation of the *c*-AlN phase in plasma spray process in our previous studies^{3, 4}. Regarding the γ -Al₂O₃ phase in the fabricated coating, the transformation of α -Al₂O₃ to transient γ -Al₂O₃ occurred easily at such high temperature and rapid solidification rates of atmospheric plasma spray process, as reported before⁸. It was possible to fabricate *c*-AlN/Al₂O₃ composite coating by plasma nitriding of Al₂O₃ powder in APS process and the coating contains Al₅O₆N and γ -Al₂O₃ phases. However, it was difficult to clarify the nitriding process of the Al₂O₃ particles from the fabricated coatings because the particles lose its shape and characteristics after colliding and flattening on the substrate surface.

Fig.1. (a) XRD spectrum of the feedstock Al₂O₃ powder, (b) XRD spectrum of the fabricated coating and (c) SEM cross section of the coating.

In order to understand and clarify the nitriding process of the Al_2O_3 particles, the powders were directly sprayed and collected in water (under the same spray conditions) without using substrate then dried. Spraying of the powders in water will provide enough high cooling rates for the sprayed particles. For more confirmation about the reactive plasma nitriding of Al_2O_3 powder, the Al-N bond in the collected powder was examined by FTIR measurement. Figure 2 shows the FTIR spectroscopy for the commercial Al_2O_3 (a), AlN (b), as well as the powder after spray (c). The spectrum for the sprayed powder showed a broad absorption band at around 750 and another band at 1330 cm^{-1} these two peaks are related to Al-N bond. These results agree with the reported data about Al-N bond^{7, 9}. The Al-O spectrum was observed at around 486, 356, 630 and 763 cm^{-1} . The background (BG) spectrum which is related to the KBr was observed at around 667, 2341 and 2360 cm^{-1} . Therefore, the FTIR results confirmed the plasma nitriding of Al_2O_3 powder in APS process. To clarify the nitriding process of the Al_2O_3 particles during spray, the microstructure of the collected particles after spraying in water and drying was observed.

Fig.2. FTIR spectra of the (a) commercial Al_2O_3 , (b) commercial AlN and (c) the sprayed powders.

Figure 3 shows the feedstock and the collected particles microstructure and cross section. It is clear that, the polygonal feedstock powders (a) changed to spherical shape after spraying (b-d). This result agrees with the reports about powder spheroidization by plasma spraying¹⁰. As the powders injected in the plasma stream, they are heated and eventually melted. Then the molten particles are spheroidized by rapid cooling from the liquid phase as a result of surface tension during flight. Furthermore, some of the spherical particles have different surface morphology (c, d). It seems that some crystals started to grow on the surface of some particles and it looks like crystal islands. This crystal islands grow only on the surface of the particle to cover some particle surface (d). To confirm this crystal growth and to observe its shape, the surface morphology of the collected particles were observed by the field-emission scanning electron microscope (FE-SEM) using 2nd electron and back scatterings images Fig.3 (e-h). The crystal islands were confirmed on the surface of the sprayed particles (e). The crystals had cubic or rectangular shapes as it is clear in (f). The shapes of these crystals are corresponding to *c*-AlN which agrees with the previous report by S. Mohri et al¹¹ and/or AlON as reported by K. F. Cai et al¹². These particles are consistently corresponding to the XRD peaks of *c*-AlN and/or AlON phases. However, it was difficult to differentiate between AlN or AlON crystals. The crystal islands grow gradually on the particle surface and cover the whole surface of some particles (g). The crystals had a clear cubic or rectangular shape as it is shown in the higher magnification in (h). It indicates that the nitriding reaction start from the surface of the Al₂O₃ particles. And to confirm that, the cross section microstructure of the sprayed and feedstock particles was observed Fig. 3 (i-l). It is clear that, some particles (j) have spherical shape but still have the same cross section morphology of the feedstock Al₂O₃ powder (i). However, some particles show different cross section morphology containing a clear shell on the surface of the particle (k, l).

Fig.3. The microstructure of: (a) feedstock powder, (b-d) sprayed particles, (e-h) FE-SEM of the sprayed particles, and the cross sections of: (i) feedstock powder, (j-l) sprayed powder.

These images agree with the surface observation of some sprayed Al_2O_3 particles in (c-g). Hereby, the nitriding process of Al_2O_3 can be explained as follow: during the plasma spray nitriding of Al_2O_3 powders, the AlN nuclei formed firstly on the surface of the Al_2O_3 particle and produced the oxygen-stabilized cubic structure. Thus, during the nitriding of Al_2O_3 powders the aluminum oxynitride phase ($\text{Al}_5\text{O}_6\text{N}$) was formed and it is easy nitrated to form *c*-AlN phase as J.C. Kuang et al reported¹³. Both of $\text{Al}_5\text{O}_6\text{N}$ and *c*-AlN phase have the same cubic symmetry. The crystal structure of *c*-AlN and the non-metal arrangement in $\text{Al}_5\text{O}_6\text{N}$ is cubic and closely packed. Generally with the AlN nuclei growth in a N_2 atmosphere, the cubic phase is gradually crystallizes to form hexagonal AlN structure. However, the high quenching and rapid solidification rates of the APS plasma flame prevented AlN growth to form the hexagonal phase. This led to formation of cubic phase in plasma spray process.

4. Conclusions

It was possible to fabricate *c*-AlN/ Al_2O_3 coating through reactive plasma nitriding of Al_2O_3 powder in APS process. The reactive plasma nitriding of the Al_2O_3 particles in APS process can be explained as follow: The Al_2O_3 particles accelerated, heated, melted and spheroidized in the surrounding N_2/H_2 plasma. The nitriding reaction started firstly on the surface of the molten spherical particles and aluminum oxynitride was formed. Then the particles Collide, flatten, and rapidly solidify on the substrate. The aluminum oxynitride phase easily forms the *c*-AlN phase by continuous reactions (the same cubic symmetry). The high quenching rate of the deposited particles on the substrate prevents the crystal growth and formation of the hexagonal AlN phase.

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