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Synthesis of Ceramic Protective Coatings for Chemical Plant Parts Operated in Hi-temperature and Corrosive/Erosive Environment

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Some feasibility studies are conducted to produce an advanced ceramic coating, which reveals superior chemical and mechanical strength, on metal base structure used in chemical plant. This advanced coating on metallic frame can replace ceramic delivery pipe and reaction chamber used in chemical plant, which are operated in hi-temperature and corrosive/erosive environment.

An dual spraying is adopted to reduce the residual stress in order to increase the coating thickness and the residual stress is estimated by in-situ manner. Then new methodology is tried to form special coating of yttrium aluminum garnet(YAG), which reveals hi-strength and low-creep rates at hi-temperature, superior anti-corrosion property, hi-stability against Alkali-Vapor corrosion, and so on, on iron base structure. To verify the formation of YAG during thermal spraying, XRD(X ray diffraction) technique was used.

***Keywords** : superior chemical and mechanical strength, corrosion-erosion environment, in-line dual spraying, yttrium aluminum garnet(YAG)*

1. Introduction

Thermal spray coating is widely used to produce various protective coatings which requires wear resistance,[1)] thermal isolation, corrosion resistance,[2)-4)] and so on, because of its hi-working speed, relatively low cost, ease of repair. When ceramic materials are successfully coated on metallic materials, that can replace lot of ceramic parts used in chemical plants because of its mentioned advantages. However, ceramic coating on metallic structure, produced via thermal spraying, causes many problems resulted from big difference in coefficient of thermal expansion(CTE) between both coupled materials, drastic temperature changes of the coating materials from liquid to warm solid during process resulting in enormous residual stress and eventually deterioration of mechanical strength of the ceramic coat. Therefore, many researcher have devoted themselves to find solutions how to reduce residual stress. Well known methodology to reduce residual stress is to introduce intermediate metallic layer(medium CTC) between metallic substrate(high CTE) and ceramic coating (low CTE). More advanced trial has been executed by in-line dual spraying called gradient thermal coating,[5)] where the feed rate of coating materials is gradually changed from metallic powder to ceramic powder during spraying. In this study, the residual stress[5)] is measured by in-situ manner and spraying conditions is optimized to reduce residual stress by using in-line dual spraying.

In additions, it is tried to form an advanced ceramic coating materials, which reveals corrosion resistance as well as erosion resistance, during thermal spraying. Yttrium aluminum garnet(YAG, $3Y_2O_3 \cdot 5Al_2O_3$)[6)-8)] is considered as the advanced spraying materials which is known to have higher hardness than Al_2O_3 and 10 times corrosion resistance against alkali-vapor corrosion than Al_2O_3. Various methods to produce YAG have been reported; for example, precipitation of hydroxides,[9)] sol-gel processes,[10)] urea method,[11)] spray pyrolysis,[12)] and combustion synthesis.[13)] However, most methods mentioned above still require high working temperature and prolonged fabrication time. In this study, the possibility to form YAG coat on metallic structure by co-spraying of commercialized Al_2O_3 powder and Y_2O_3 powder simultaneously and surface heat treatment of thermal sprayed coat of Al_2O_3+Y_2O_3 mixture coat is investigated. And alternative rout to form in-situ YAG coating via thermal spraying is investigated by preparing specially designed thermal spray feed stock(granule) consisting of nano-sized Y_2O_3 and Al_2O_3 powders.

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2. Experiments

2.1 Thermal spraying

Ceramics protective coating was formed on iron substrate using PT800 plasma technique equipment with spraying conditions of Ar gas flow rate; 50l/min, H2 gas flow rate; 14l/min, current; 600A, powder feed rate; 16 g/min. Ni-20%Cr and Al_2O_3 feedstock were used to measure the residual stress and Ni-20%Cr and 35%Y_2O_3+ 65%Al_2O_3 mixed powder was used to form YAG coating. Gun scanning speed was 250 mm/s.

2.2 In-situ measurement of residual stress and temperature

Metallic and ceramic powder was spray coated on a prismatic band with length x width x thickness of 200 mm x 9 mm x 2 mm, respectively. Both ends of the substrate band were fixed not to move forward and backward but not to restrict itself to be bent as shown in Fig. 1. The displacement of the center point was then measured in order to calculate the band curvature by using linear variable differential transformer(LVDT). Temperature was also recorded from the back of the band during spraying.

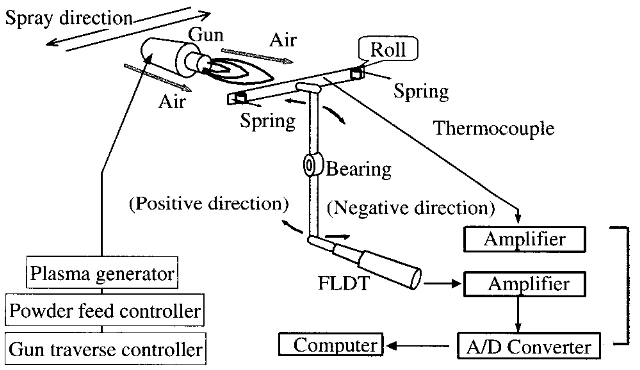


Fig. 1. The schematic of the equipment to record substrate curvature and surface temperature variation during spraying.

2.3 Formation of yttrium aluminum garnet(YAG, $3Y_2O_3 \cdot 5Al_2O_3$)

Al_2O_3 and Y_2O_3 powder was mixed, fed into the plasma flame and deposited on metallic substrate. Then electron beam was radiated on the coat for surface remelting in order to form a YAG. And specially designed intermediate was produced by heterocoagulation method, where 1-5 ㎛ Y_2O_3 powder was successfully surrounded by 10-20 nm Al_2O_3 powder which will be agglomerated in 30-60 ㎛ diameter for plasma spraying.

2.4 XRD investigation

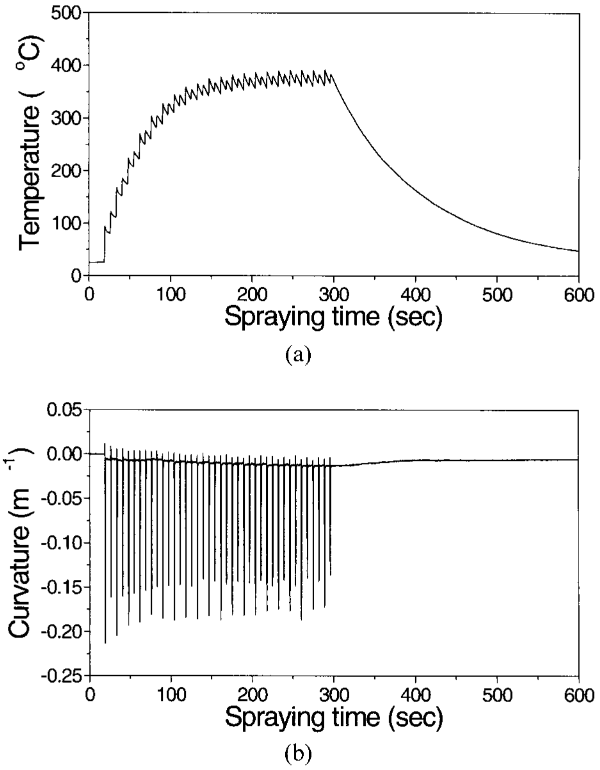
The phase transformation of ceramic feed stocks during plasma spraying and following heat treatment was investigated using XRD apparatus(MO3XHF22, MAC Science Co. Ltd) using Cu-Ka target with scanning speed of 0.4°/min.

3. Results and discussion

3.1 Improvement of bonding strength between the ceramic coating and metal substrate.

Fig. 2 shows the measured temperature and curvature during plasma spraying without powder feeding. In Fig. 2(a) the substrate temperature changes periodically in accordance with plasma gun movement and gradually increases up to 380 ℃ with spraying time because of heat flux into the substrate via plasma flame. In Fig. 2(b) the curvature of the substrate varies with equivalent periodic time to the temperature variation period, that is mainly resulted from temperature gradient through the substrate exposed to plasma flame.

When Ni-20Cr powder is fed into the plasma flame, the amount of deformation increases and results in curvature of 0.47(m^{-1}) at the spraying time 287 seconds and considerable induced tensile stress does not release

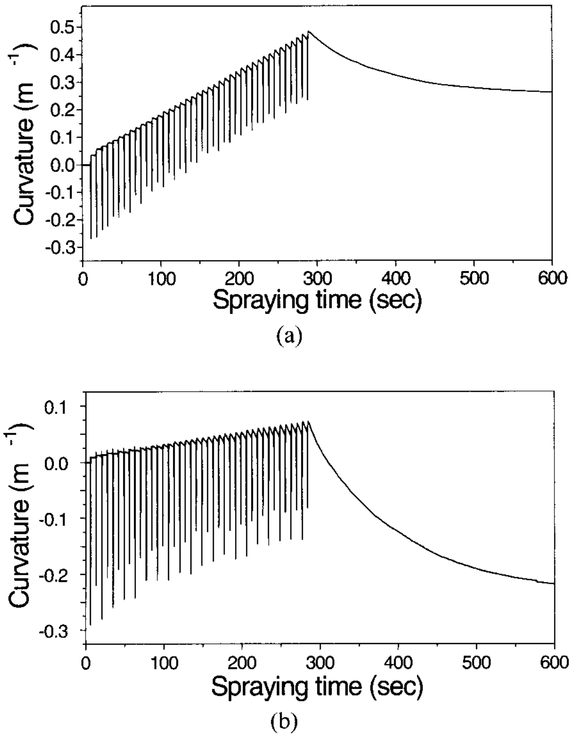


(a)

(b)

Fig. 2. (a) measured temperature and (b) curvature variation during spraying without powder feeding.

out remaining curvature of 0.26(m^{-1}) after cooling as shown in Fig. 3(a). This is because impinging NiCr powder introduces tensile stress into the coating when it dwindles in its volume during solidification and cooling after deposition on substrate. On the contrary, Al_2O_3 powder makes relatively low tensile stress during spraying and leaves compressive stress after cooling as shown in Fig. 3(b). This is because tensile stress, which is induced by shrinking Al_2O_3 impinged on coating surface, released out by microcrack formation through the Al_2O_3 grain boundaries.[5] During cooling stage a compressive stress (negative curvature) is introduced to Al_2O_3 coating by metal substrate diminishing which has relatively high coefficient of thermal expansion.



(a)

(b)

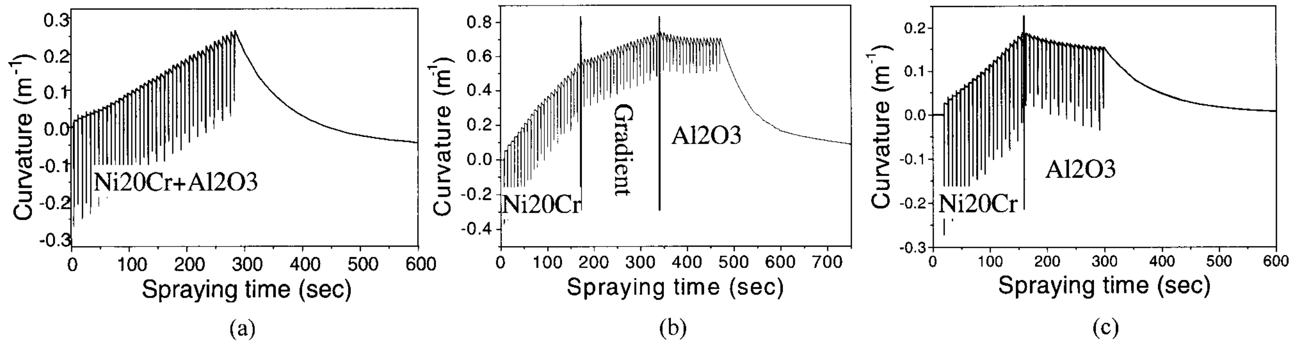
Fig. 3. Measured curvature variation during spraying with (a) Ni-20Cr powder (b) Al_2O_3 powder.

From the experimental results as shown in Fig. 3, it can be expected that stress free coating can be produced by combination of proper coating materials using proper coating manner. At first, a mixed powder of Ni20Cr and Al_2O_3 was spray coated and the curvature of the substrate was recorded as shown in Fig. 4(a). By this manner, the amount of tensile stress during spraying can be reduced comparing to the results of Fig. 3(a) and the eventual residual stress can be removed. Gradient coating is also a good alterative to reduce residual stress as shown in Fig. 4(b). As the Al_2O_3 powder starts to substitute Ni20Cr powder in gradual manner, the increase rate of the curvature is reduced. When Al_2O_3 powder substitutes all Ni-20Cr powder, the curvature starts to decrease and no curvature remained after cooling. Also well known process introducing interlayer called bond coat between metallic substrate and ceramic coating also resulted in acceptable residual stress as shown in Fig. 4(c). Fig. 5 shows the microstructure of Ni20Cr-Al_2O_3 composite coating and gradient coating of Ni20Cr-Al_2O_3.

3.2 Synthesis of Improved materials for thermal spray

As mentioned in previous paragraph, YAG reveals excellent physical and chemical properties; i.e. equivalent or higher hardness than Al_2O_3, 10 times corrosion resistance of Al_2O_3 in alkali vapor as well as superior hi-temperature strength. Therefore, the phase transformation of Al_2O_3+Y_2O_3 mixture during plasma spraying was investigated to verify the possibility to form YAG by in-situ manner and the XRD data were compared to those of Al_2O_3, Y_2O_3 powders.

Fig. 6 shows the XRD data recorded from ceramic powders used in this plasma spraying and from ceramic coatings after plasma spraying. The original α-Al_2O_3 powder(Fig. 6(a)) significantly transformed to cubic struc



(a)
(b)
(c)

Fig. 4. (a) Ni20Cr-Al_2O_3 composites coatings (b) gradient coatings of Ni20Cr-Al_2O_3 (c) multi-layer coatings of Ni20Cr and Al_2O_3.

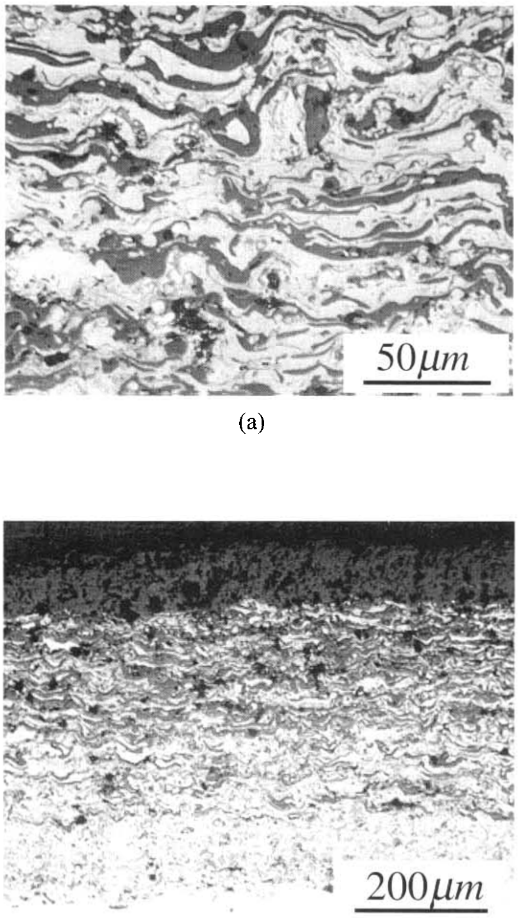


Fig. 5. Microstructure of (a) Ni20Cr-Al_2O_3 composites coatings (b) gradient coatings of Ni20Cr-Al_2O_3.

tured alumina but small amount of α-Al_2O_3 remained(Fig. 6(b)). On the contrary there was no phase transformation for Y_2O_3 ceramics as shown in Fig. 6(c) and (d)). For the mixture of 35%Y_2O_3+65%Al_2O_3 powders, strong Y_2O_3 peaks and some unidentified peaks around 2θ of 30° are observed but distinguishable YAG peaks are not seen. This result is reasonable because two different kind of powders, of which diameter are in the range of 20-70 ㎛, do not have chance to be mixed in liquid state during plasma spraying.

The sprayed coat was radiated by electron beam for a short time to re-melt down the 35%Y_2O_3+65%Al_2O_3 mixture coat to verify the phase transformation of the coat. Fig. 6(f) shows the XRD data recorded from e-beam radiated 35%Y_2O_3+65%Al_2O_3 mixture coat, which matches to that of YAG. However e-beam radiation on ceramic coat surface resulted in serious damages on metallic substrate.

In the mentioned process of e-beam radiation, 35%Y_2O_3+65%Al_2O_3 mixture coat melt down and solidify in an instant. From the experimental result, it is expected that YAG can be easily formed during plasma spraying when two phases of Y_2O_3 and Al_2O_3 are cohered with each other before they are fed into the plasma flame. To make such a complex powder, an intermediate was produced by hetero-coagulation method, where Al_2O_3 powders are forced to be in negative electric charge and Y_2O_3 in positive electric charge by controlling the Ph of the solutions containing each powders. A uniform coagulation was then successfully formed by this process as shown in Fig. 7.

The produced intermediates are agglomerated in diameter of 30-60 ㎛ for effective plasma spraying and the spraying ability of the developed powders will be discussed elsewhere.[14]

4. Conclusion and summary

Some feasibility studies were conducted to produce advanced ceramic coatings on metallic frame in order to replace ceramic delivery pipe, reaction chamber used in chemical plant. For these applications, both mechanical and chemical strength of the coating should be improved.

For this purpose, new technology was introduced to estimate residual stress in in-situ manner by measuring the substrate curvature. From the in-situ measurement results, informations for possible combination of materials in order to remove residual stress could be given. For example, Ni20Cr and Al_2O_3 composites coatings and gradient coatings of Ni20Cr-Al_2O_3 was helpful to remove residual stress.

Also, studies to synthesize advanced materials for thermal spray were executed. YAG, which is known to be very stable in corrosive and erosive environment, could not produced during plasma spraying when commercialized Y_2O_3 and Al_2O_3 powder are used. However, YAG coating was successfully synthesized on the surface of metallic structure by heat treatment after plasma spraying. But this secondary e-beam radiation processing resulted in serious damage on metallic structure.

Acknowledgement

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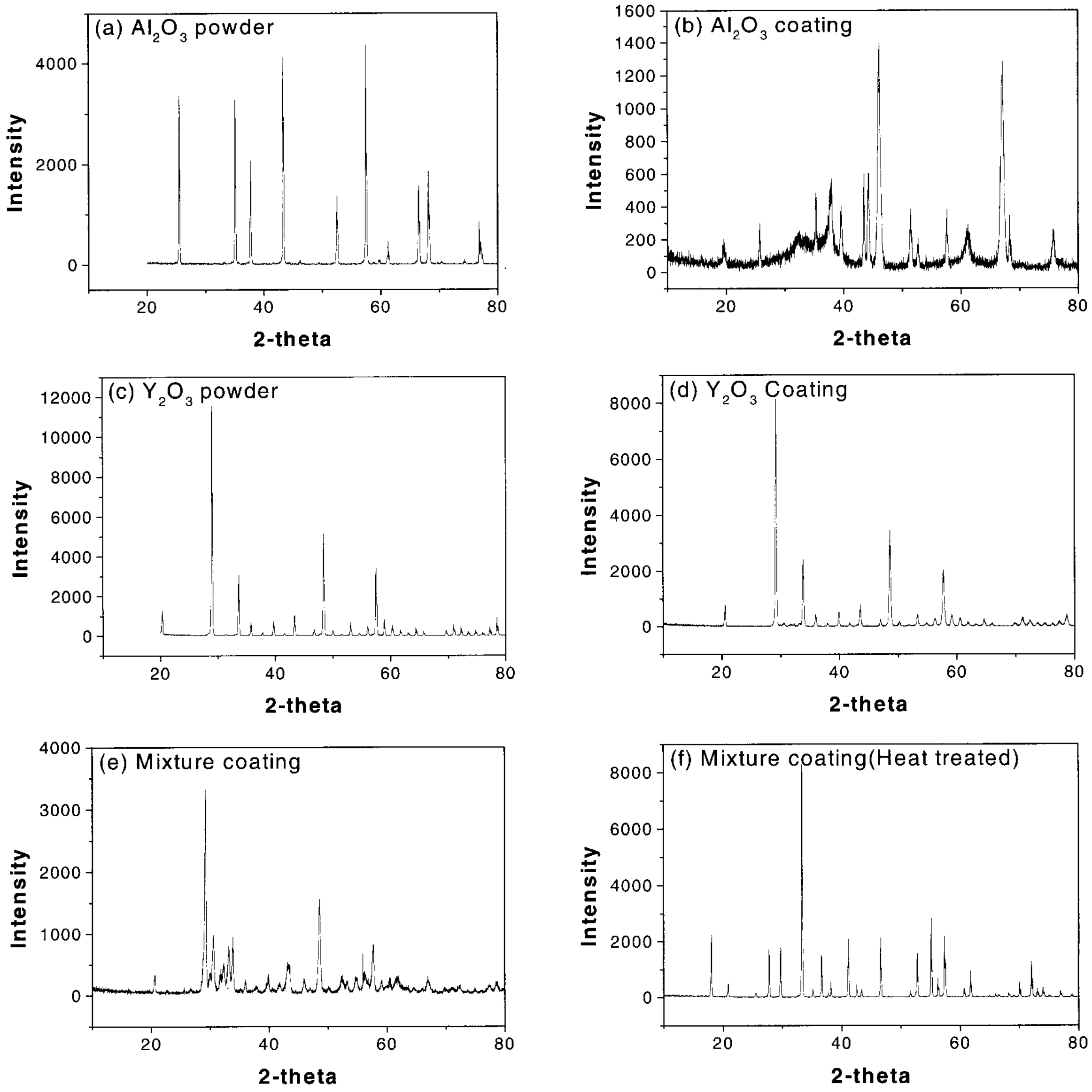
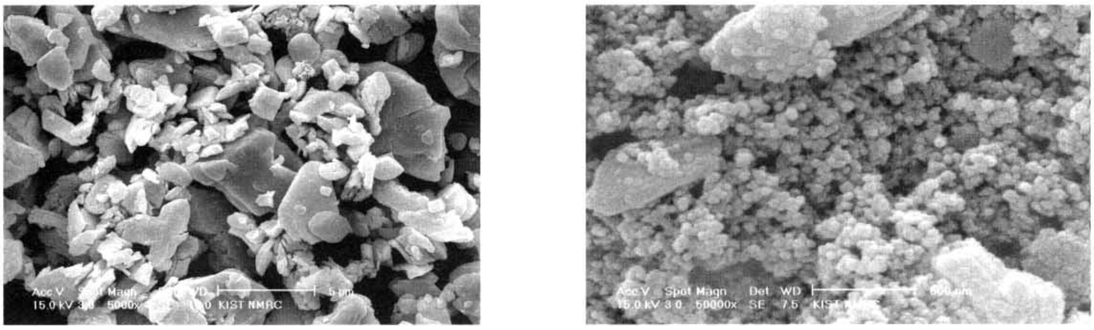


Fig. 6. XRD data of (a) Al_2O_3 powder (b) plasma sprayed Al_2O_3 coating (c) Y_2O_3 powder (d) plasma sprayed Y_2O_3 coating (e) plasma sprayed 35%Y_2O_3+65%Al_2O_3 mixture coating (f) plasma sprayed and heat treated 35%Y_2O_3+65%Al_2O_3 mixture coating.



(a) (b)

Fig. 7. (a) SEM image of micro size Y_2O_3 powder, (b) complex Y_2O_3 powders surrounded by nano size Al_2O_3 powders.

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