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Microstructures and Characterization of Zirconia-Yttria Coatings Formed in Laser and Hybrid Spray Process

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Hybrid plasma spraying combined with yttrium-aluminum-garnet laser irradiation was studied to obtain optimum zirconia coatings for thermal barrier use. Zirconia coatings of approximately 150 μm thickness were formed on NiCrAlY bond coated steel substrates both by means of conventional plasma spraying and hybrid plasma spraying under a variety of conditions. Post-laser irradiation was also conducted on the plasma as-sprayed coating. The microstructure of each coating was studied and, for some representative coatings, thermal barrier properties were evaluated by hot erosion and hot oxidation tests. With hybrid spraying, performed under optimum conditions, it was found that a microstructure with appropriate partial densification and without connected porosity was formed and that cracks, which are generally produced in the post-laser irradiation treatment, were completely inhibited. In addition, hybrid spraying formed a smooth coating surface. These microstructural changes resulted in improved coating properties with regard to hardness, high temperature erosion resistance, and oxidation resistance.

Keywords densification, hot erosion resistance, hybrid spraying, NiCrAlY, oxidation resistance, plasma-spraying, roughness, thermal barrier coating, yttrium-aluminum-garnet, zirconia

1. Introduction

A plasma-sprayed coating of zirconia has been widely applied to gas turbines as a thermal barrier coating (Ref 1, 2). However, all plasma-sprayed ceramic coatings contain connected porosity and properties such as high temperature corrosion resistance, mechanical strength, and erosion resistance, which are, thereby, greatly reduced. To improve these properties, various methods have been proposed (Ref 3-5) such as post-laser irradiation and seal sintering with liquid alloys. Laser irradiation is a rapid and accessible method for densifying the microstructure of the ceramic coatings. However, in post-laser irradiation treatment, it is difficult to suppress the formation of microcracks during the process of rapid cooling due to the excessive thermal contraction of the densified microstructure (Ref 6-10).

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Conversely, hybrid spraying consisting of laser irradiation and plasma spraying has been studied in the spraying of ceramics, cermets, and metals (Ref 11-13). It is thought that the process enables control of the coating microstructure in a single process; melted powders are sprayed from a plasma gun, and heat control of the powders impinged on the substrate is performed by laser irradiation. According to a recent study, hybrid spraying seems to be effective in preventing the formation of cracks and in maintaining an appropriately densified microstructure. However, no studies have been conducted with reference to applications to thermal barrier coatings.

In this study, zirconia coatings were prepared by yttrium-aluminum-garnet (YAG) laser combined plasma hybrid spraying, and thermal barrier properties were evaluated in relation to changes in the coating microstructure. The properties of such coatings were compared with those of plasma as-sprayed coatings and coatings posttreated by laser irradiation following plasma spraying.

2. Experimental Procedures

2.1 Laser Combined Plasma Spraying System

The hybrid spraying system used in this study consisted of plasma-spraying and YAG laser irradiation. Both the plasma gun (SG-100 model, Miller Thermal, Inc., Appleton, WI) and the laser gun (focal length, f = 200 mm; NEC, Ltd., Sagamihara, Kanagawa, Japan) were supported by a six-axes articulated robot installed inside a chamber equipped with an exhaust system. The laser source used was an Nd:YAG laser (wave length, 1.064 μm; output power, 0.1 to 2.2 kW) with a continuous wave form. The laser beam was delivered by an optical fiber from the laser oscillator to a laser nozzle. Hybrid spraying was completed mainly in a horizontal direction at pressures ranging from 13.30

to 101.08 kPa. Table 1 shows the relationship between the defocus distance and the spot diameter of the laser beam measured by a beam analyzer. The beam diameter varied from 2.0 to 16.9 mm at defocus conditions corresponding to 0 to 90 mm, respectively.

2. Materials and Spraying Conditions

Two kinds of commercially available spraying powders, $ZrO_2(8wt\%Y_2O_3)$ and NiCrAlY (Showa Denko, Ltd., Shijiri, Nagano, Japan), were used. Table 2 gives the chemical composition and the particle size of these powders. The coatings were sprayed onto specimens of sandblasted JIS SUS403 steel 50 x 60 x 3 mm in size. Table 3 summarizes the plasma spraying parameters for the yttria-stabilized zirconia (YSZ) coatings and the conditions of applied laser irradiation. Before hybrid spraying, a heat-resistant NiCrAlY coating of approximately 40 μm thickness was prepared on the steel substrate as a bond coating at a pressure of 13.30 kPa argon gas atmosphere. During the spraying of zirconia coatings at 101.08 kPa atmosphere, the top layer was plasma sprayed onto the NiCrAlY coated substrate, and then hybrid spraying was completed. During the hybrid spraying, the laser beam was configured to overlap with the plasma spray jet, as shown in Fig. 1. The energy density of hybrid spraying was changed by adjusting the defocus distance of the laser beam under the constant plasma spraying conditions. For comparison with hybrid spraying, post-laser irradiation of the zirconia coating was also carried out under the conditions shown in Table 3.

Table 1 Relationship between defocus distance and diameter of laser beam

Defocus distance of beam (df), mm	Beam diameter, mm
+0	2.0
+15	3.0
+30	5.8
+40	8.1
+50	10.2
+60	12.2
+70	14.6
+90	16.9

Plus sign designates the defocus distance from the focus at the opposite side of the laser gun

2.3 Evaluation of Coating Microstructures and Thermal Barrier Properties

The microstructures of cross sections of the coatings were observed by scanning electron microscopy (SEM) (JSM-6300 model, JEOL, Ltd., Tokyo, Japan), and the chemical composition of the coating was analyzed with an electron probe microanalyzer (EPMA) (EPMA-C1 model, Shimadzu, Ltd., Kyoto, Japan). The hardness of the coatings was measured by a micro-Vickers hardness tester at a load of 300 g. The roughness (IS standard) of the coating surface was also investigated by a surface texture measuring instrument (Surfcom 470 model, Tokyo Seimitsu, Ltd., Tokyo, Japan). High temperature erosion resistance was evaluated by impacting the heated zirconia powder jet, where a relatively low powered plasma jet with a low atmos-

Table 2 Composition and size of powder used

Material	Composition, wt%						Size, μm
NiCrAlY	Cr, 21.70	Al, 9.98	Y, 1.13	O, 0.04	N, 0.01	Ni, bal	10-45
ZrO_2-8%Y_2O_3	Y_2O_3, 7.88	Al_2O_3, 0.02	SiO_2, 0.07	Fe_2O_3, 0.08	ZrO_2, bal		10-45

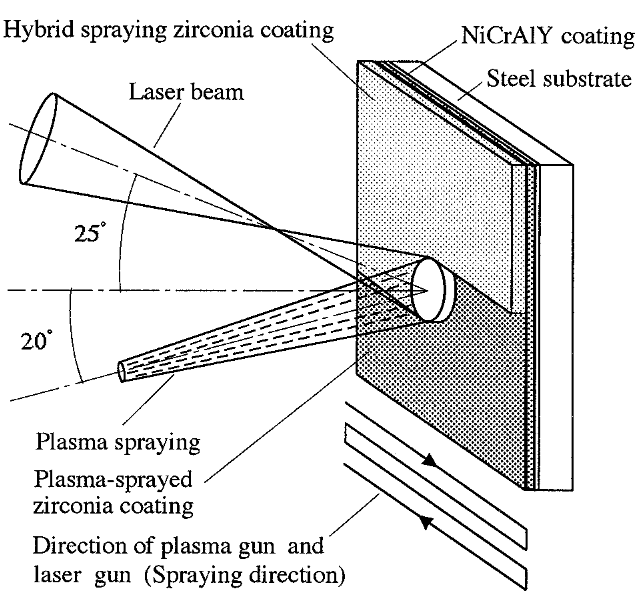

Fig. 1 Scheme of hybrid spraying process

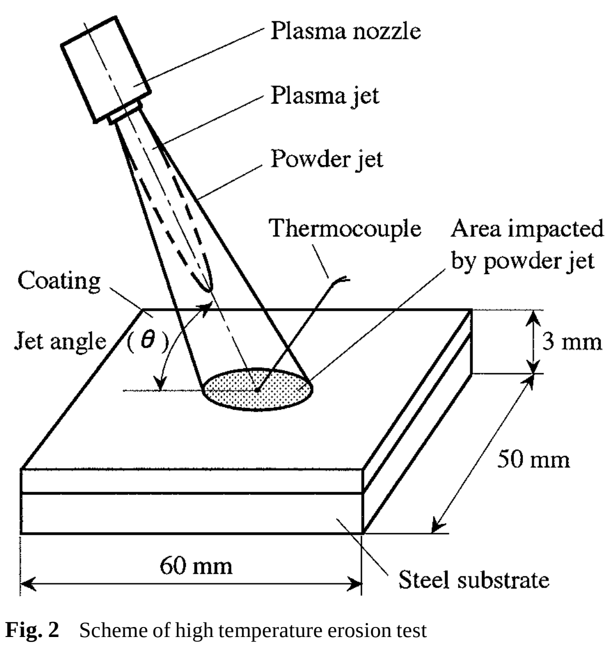

Fig. 2 Scheme of high temperature erosion test

pheric pressure was used to increase the number of solid particles to be impacted on the coating surface. A schematic diagram of the high temperature erosion and the parameters of the test are shown in Fig. 2 and Table 4, respectively. A hot oxidation resistance test was performed with an atmospheric furnace kept at 1473 K for 72 ks.

3. Results

3.1 Surface Morphology and Microstructures of the Coatings

Surface Roughness of Coatings. Figure 3 shows typical surface profiles of zirconia coatings: (a) plasma as-sprayed, (b) hybrid sprayed at a defocus distance of +40 mm, and (c) post-laser irradiated at a defocus distance of +15 mm. A smooth surface is observed in the hybrid sprayed coating. However, in the post-laser irradiated coating, unevenness is exhibited in the cross direction of the irradiation. This probably resulted from the formation of a wave on the surface of the coating melted by the laser irradiation. Table 5 shows the surface roughnesses (R_a) of various coatings. Smooth surfaces are obtained for the hybrid spray coatings except in the case of a small defocus distance of +30 mm.

Table 3 Conditions of plasma spraying and laser irradiation

Plasma spraying	
Arc current, A	600
Arc voltage, V	53
Arc power, kW	32
Plasma gas (Ar), L/s	1
Auxiliary gas (N_2), L/s	0.0667
Powder carrier gas (Ar), L/s	0.0833
Spraying distance, mm	100
Powder feed rate, (g/s)	0.0833
Traverse speed, mm/s	250
YAG laser irradiation in hybrid spraying	
Wave form	Continuous wave
Laser power, kW	2.0
Defocus distance, +, mm	30-90
Shield and purge gas (Ar), L/s	1.1667
Traverse speed, mm/s	25
Interval distance of spray pass, mm	4

Traverse speed of 15 mm/s and defocus distance of +15 mm were used in the post-laser irradiation

Table 4 Conditions of high temperature erosion test

Jet erosion apparatus	Miller thermal, SG-100
Nozzle diameter, mm	8
Arc current, A	300
Arc voltage, V	30
Arc power, kW	9
Plasma gas (Ar), L/s	1
Distance from nozzle to sample, +, mm	120
Jet powder type	$ZrO_2(8\%Y_2O_3)$
Jet powder size, µm	44-10
Powder feed rate, g/s	0.333
Jet angle, degree	30-75
Atmosphere, Pa	1.33×10^4
Temperature of coating surface, K	1003

Coating Microstructures. Figure 4 shows cross sectional microstructures of zirconia coatings: (a) plasma as-sprayed (as-coat), (b) post-laser irradiated at a defocus distance of +15 mm, and (c) hybrid sprayed at a defocus distance of +40 mm. Densification of the microstructure is observed with the post-laser irradiated coating. However, there are a few microcracks in the coating. In the hybrid sprayed coating, cracks produced in the post-laser irradiation are not seen. It was also found that the porosities in the hybrid sprayed coatings decreased in comparison with the plasma as-sprayed coating, and that a good interface was obtained between the coating and the substrate.

Figure 5 shows changes in the microstructure of the upper part of the zirconia layer with the defocus distance of laser irradiation in hybrid spraying. In the plasma as-sprayed coatings, the existence of connected porosity, the nonbonded areas between flattened particles and the vertical micropores, can be observed, while the nonbonded areas decreased in the hybrid sprayed coatings with defocus distances of the laser beam less than +70 mm. The vertical micropores also decreased and disappeared at defocus distances of +50 and +40 mm. Densification

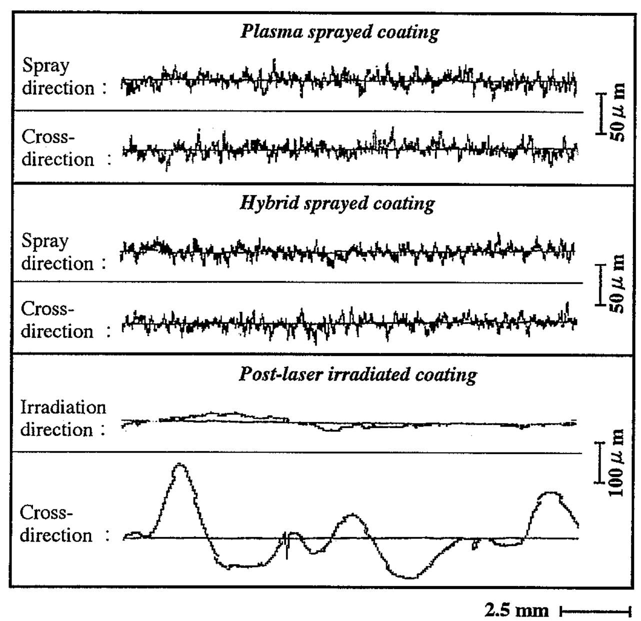

Fig. 3 Surface roughness of various zirconia coatings

Table 5 Surface roughness of various coatings (Ra), µm

	As-sprayed	Post-laser irradiated	Hybrid sprayed, laser defocus distance, +, mm				
			90	70	50	40	30
Spray direction	5.4	1.4	5.0	5.2	4.9	4.8	2.2
Cross direction	5.4	7.5	5.0	5.1	5.2	5.0	6.4

of the microstructure was greatly improved at a distance of +30 mm. It is clear that densification in the coatings was caused by the heating effect of laser irradiation in the hybrid spraying.

3.2 Mechanical Properties of the Coatings

Hardness of Coatings. Figure 6 shows the hardness (the mean value of 15 points) of the cross section of plasma sprayed zirconia coatings. The hybrid sprayed coatings show higher hardness than the plasma as-sprayed coating. The hardness increases in the range of 8,400 to 12,980 N/mm^2 with a decrease in the defocus distance. The increase in hardness is considered due to strengthening of the bonding among the particles and a decrease in the porosity.

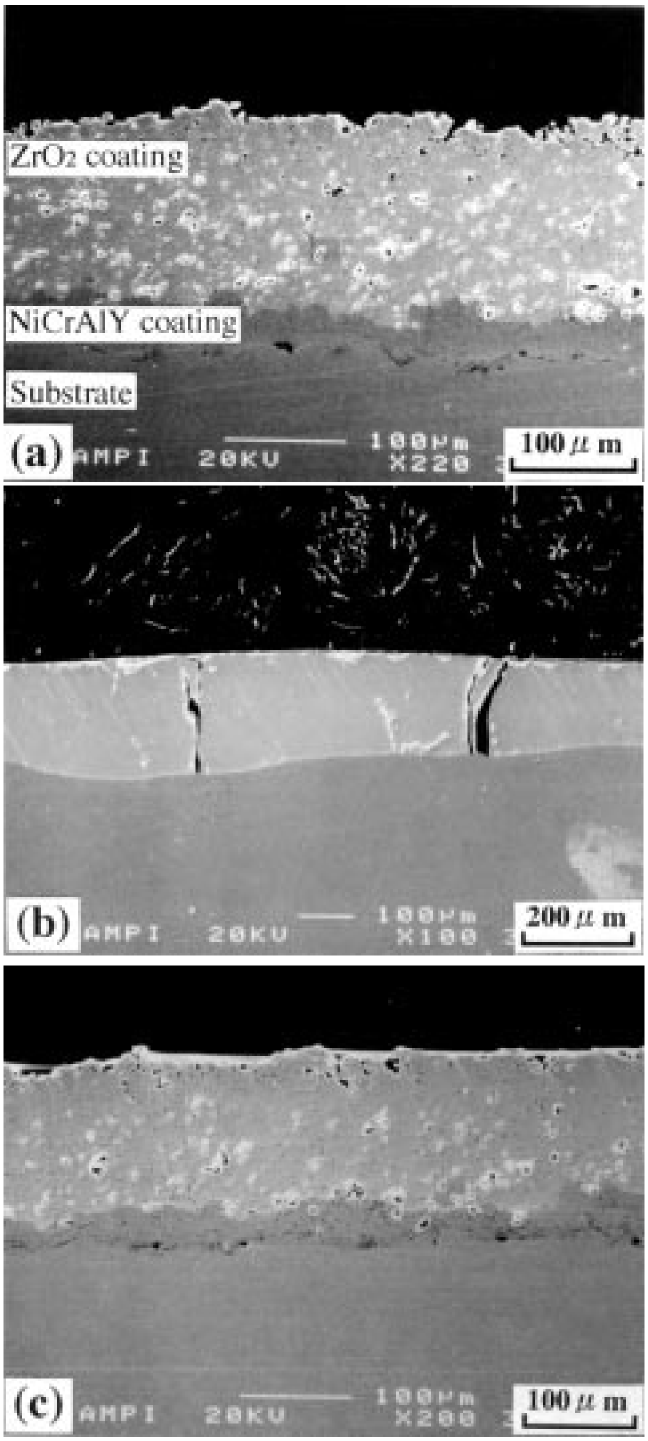

Fig. 4 Cross sections of various zirconia coatings. (a) Plasma as-sprayed. (b) Post-laser irradiation. (c) Hybrid sprayed

High Temperature Erosion Resistance. Figure 7 shows the relationship between the defocus distance of the laser beam and the weight loss rate of the zirconia coating in a high temperature erosion test carried out at 1004 K and 13.3 kPa environmental pressure. The weight loss rates of the plasma as-sprayed coating and the post-laser irradiated coating show 45.12 and 27.37 mg/min, respectively. The rate of the hybrid sprayed coatings decreases considerably with a decrease in the defocus distance of laser irradiation. Figure 8 shows typical surface morphologies of plasma as-sprayed coatings, (a) and (b), and hybrid sprayed coatings, (c) and (d), before and after the erosion test. It is clear that the surface of the hybrid sprayed coating (c), which has melted is smoother than that of the plasma as-sprayed coating (a). For the plasma-sprayed coating after the high temperature erosion test as shown in Fig. 8(b), the fracture surface consists of a relatively rugged area of the cross sections of multilayers and a plane area showing pan cake splat surfaces. This is probably caused by insufficient bonding among individual sprayed particles. While for the hybrid sprayed coating after the same erosion test shown in Fig. 8(d), a fine fracture surface was observed, which might be produced by shearing of well bonded sprayed particles. From these results, it is thought that a greater rate of erosion loss was caused by particle detachment in the plasma-sprayed coating, while an increase in bonding areas and strengthening of the bonding force among the particles in the hybrid sprayed coatings resulted in an improvement in the high temperature erosion resistance.

3.3 Hot Oxidation Resistant Property of the Coatings

Hot Oxidation Resistant Property. Figure 9 shows cross sections of ZrO_2-NiCrAlY-steel substrates of plasma as-sprayed and hybrid sprayed coatings heated at 1473 K in an atmosphere for 72 ks. Dark layers produced at the interfaces of the ZrO_2-NiCrAlY and NiCrAlY-steel substrate were observed in both the plasma as-sprayed and hybrid sprayed coatings. With regard to the width of the layers between the ZrO_2-NiCrAlY, the plasma as-sprayed coating is about twice the width of the hybrid sprayed coating. The chemical composition of point A in the dark layer was determined by EPMA analysis to be oxides consisting mainly of aluminum oxides, and a typical composition is shown in Table 6. A large number of researchers have reported this typical oxidation layer existing at the interface between the

Table 6 Chemical composition of point A, wt%

Element	Composition, wt%
Al	54.44
O	32.98
Ni	3.17
Cr	2.12
Y	2.61
Fe	bal

ZrO_2 top coat and NiCrAlY bond coat (Ref 14). This research demonstrates that the existence of the oxidation layer generally results in detachment of the zirconia top coating from the interface with the NiCrAlY coating during high temperature operating environments. The oxidation layer is thought to form by a hot oxidation reaction of the NiCrAlY bond coating, in which O_2 comes from the atmosphere through the connected porosity in the top coating. Accordingly, the decrease in the width of the

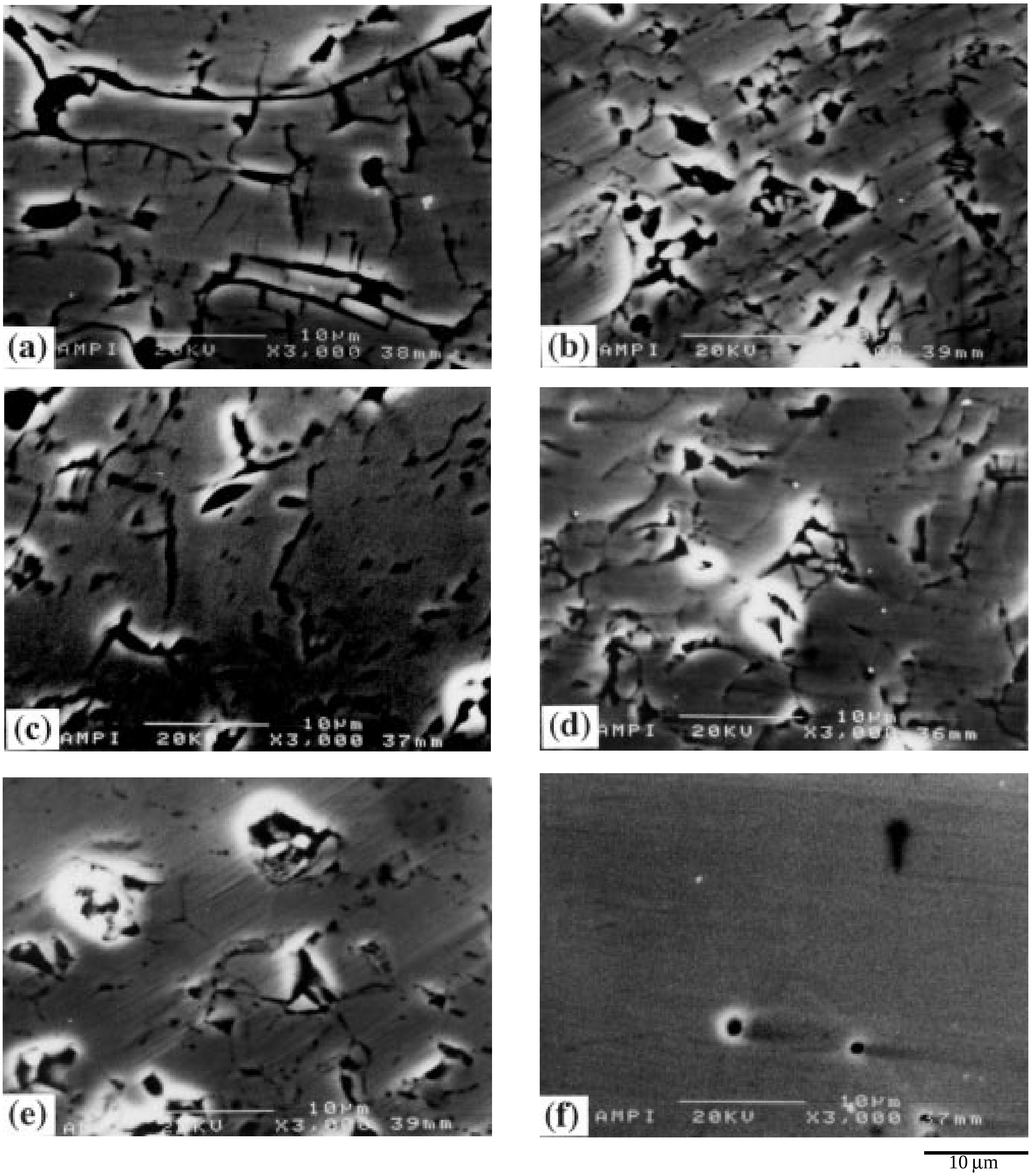

Fig. 5 Typical microstructures of (a) plasma as-sprayed and hybrid sprayed (b to f) coatings, (b) laser defocus distance of +90 mm, (c) laser defocus distance of +70 mm, (d) laser defocus distance of +50 mm, (e) laser defocus distance of +40 mm, and (f) laser defocus distance of +30 mm

oxidation layer in the hybrid sprayed coating may be considered as the result of the densification effect of the zirconia coating because the top coating without connected porosity reduces the pathways for O_2 transport. This result implies that the hybrid sprayed coating improves the hot oxidation resistance of the zirconia coating.

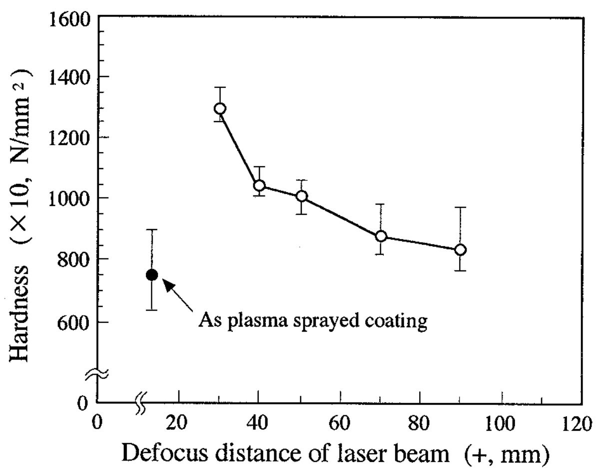

Fig. 6 Hardness of cross sections of plasma as-sprayed and hybrid-sprayed coatings

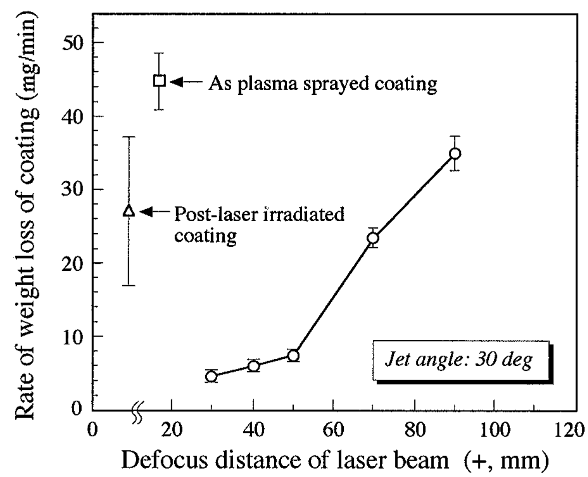

Fig. 7 Relationship between defocus distance of laser beam in hybrid spraying and weight loss rate of the coating

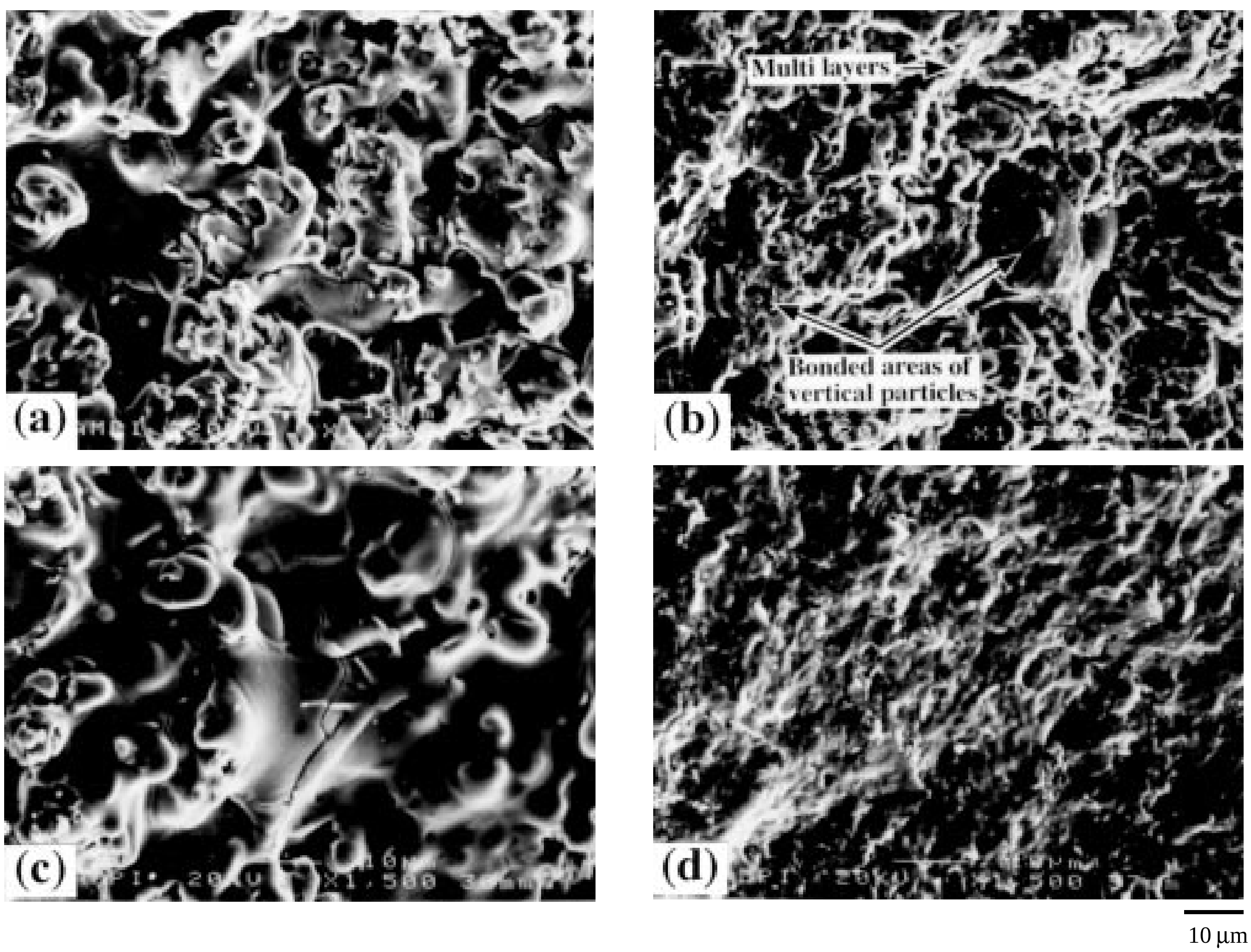

Fig. 8 Surface morphologies of zirconia coatings. (a) Plasma as-sprayed. (b) After hot-erosion test of (a). (c) As hybrid-sprayed. (d) After hot-erosion test of (c)

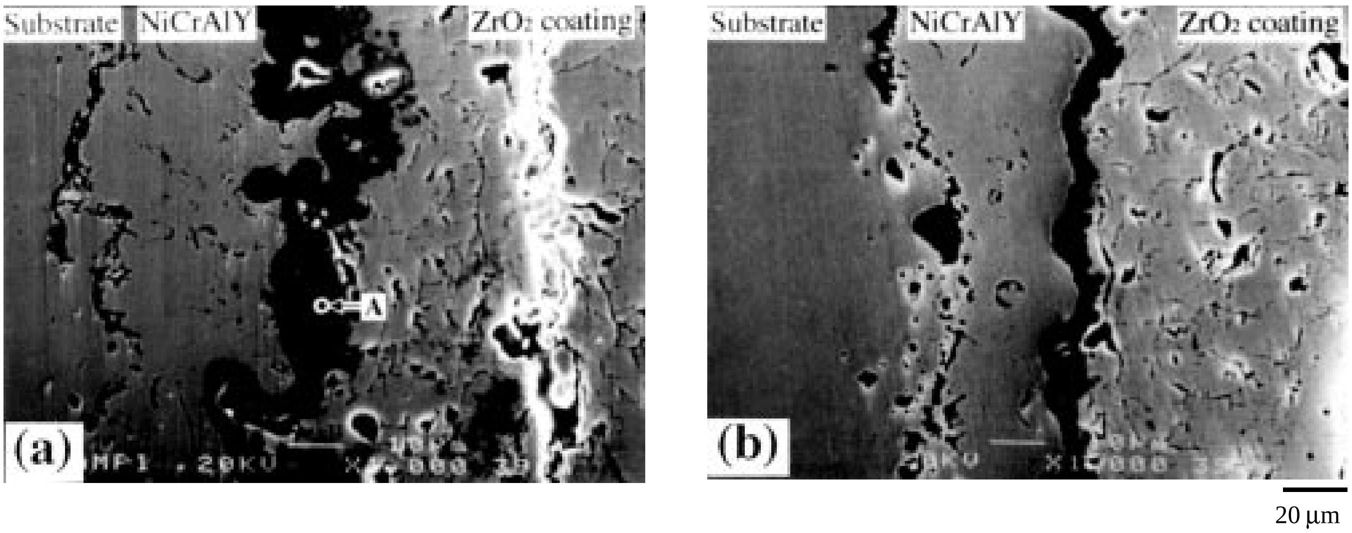

Fig. 9 Interface of zirconia coatings heated at 1473 K for 72 ks. (a) Plasma sprayed. (b) Hybrid sprayed

4. Discussion

4.1 Effect of Laser Irradiation on the Formation of Microstructures in the Hybrid Spraying Process

The previously mentioned results reveal that bonding among zirconia particles in the coating can be increased by both post-laser treatment and hybrid spraying. Hybrid spraying can form a coating with closed porosity without the connected cracks that are generally produced in the post-laser treatment. It is thought that this difference is caused by the different behavior of heating and cooling in the two processes. In the case of post-laser treatment, as illustrated in Fig. 10 (a), a laser beam with high energy density is directed onto the coating to melt the plasma as-sprayed coating with a certain thickness, where the melting and fusion of the coating particles occur at the area of laser irradiation and cracks form by the internal tensile stresses. A large contraction of the dense part is inclined to occur in the extremely short time process of rapid cooling after the laser beam irradiation. Conversely, in the case of hybrid spraying shown in Fig. 10(b), laser irradiation with a relatively low energy density over a relatively large irradiated area is used. When plasma-sprayed particles in a state of melting or partial melting enter the area of laser irradiation and pile up on the surface of the coating layer, the surface temperature of the particles is maintained or raised, and this results in an increase in bond areas among the particles. The microcracks in the coating, produced in the process of plasma-spraying, are suppressed by the heating effect of laser irradiation and the thermal barrier effect of layers of sprayed particles, which causes the particles to be cooled at a relatively slow speed. This effect is called the heat retention effect. In this process, a relatively small energy input of the laser irradiation works to mitigate the contraction of the dense part in addition to limiting the heated regions and temperature. Figure 11 shows the influence of the heat retention effect as speculated based on the laboratory studies, compared with the thermal behaviors in the post-laser treatment and a normal plasma spraying. In contrast with the relatively rapid cooling seen in the processes for post-laser treatment and normal plasma spraying, there is a slower cooling curve in the process for hybrid spraying. In hybrid spraying, sprayed particles, which are in the process of cooling after melting in the plasma jet, are held or heated when the particles enter the area of laser irradiation, and then the particles tend to cool slowly, even after the laser beam is removed from the area. Therefore, it is thought that the internal stress remaining in the coating is decreased.

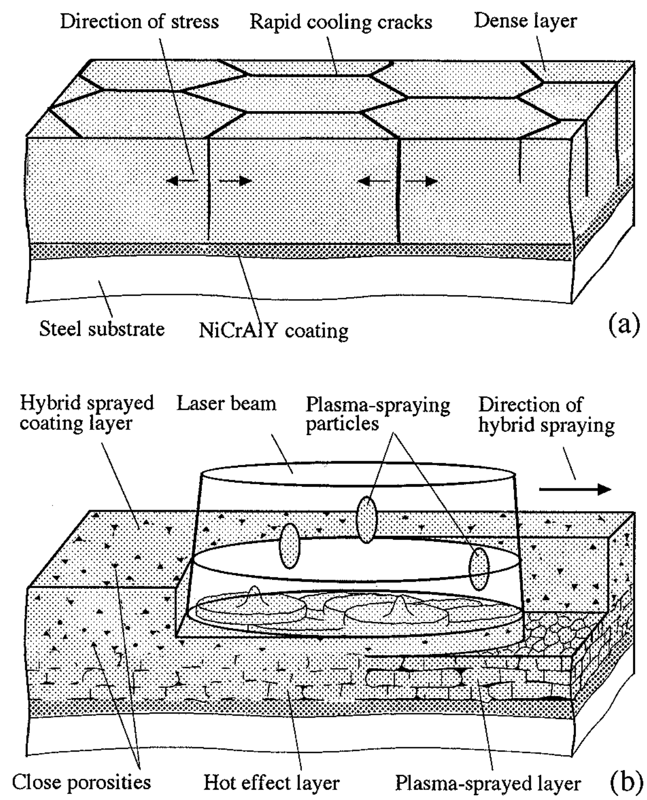

Fig. 10 Schemes of forming processes of zirconia coatings for (a) post-laser irradiation treatment and (b) hybrid spraying

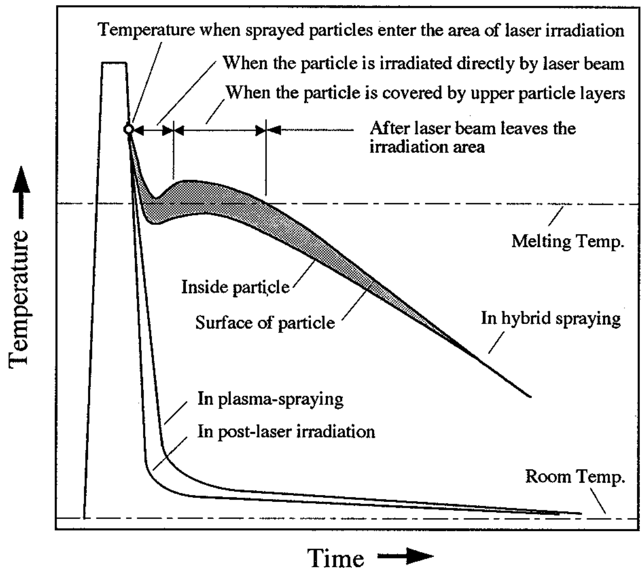

Fig. 11 Schematic illustration of thermal behaviors of a sprayed particle at certain distances from the coating surface during hybrid spraying, post-laser irradiation, and normal plasma spraying

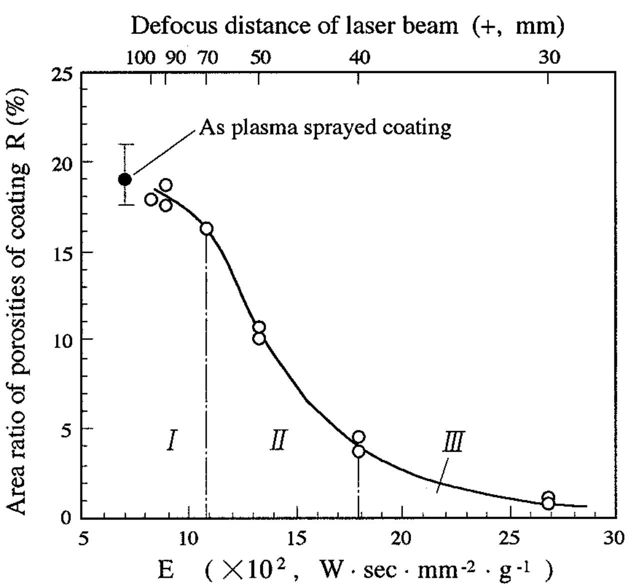

Fig. 12 Relationship between (with energy density of laser irradiation at a given rate of zirconia powder feeding and porosity ratio of) hybrid sprayed coatings

Figure 12 shows the effect of unit energy density, *E*, of the laser irradiation, at a certain rate of zirconia powder feeding, on the area ratio of porosity, *R*, in a cross section of the zirconia coating. Here, *E* and *R* are calculated from the following equations, respectively:

$$E = \rho/V = \rho \cdot t/P = \rho \cdot L/v \cdot t \cdot V \quad \text{(Eq 1)}$$

$$R = p/(p + s) \quad \text{(Eq 2)}$$

where ρ is the total energy density of the laser irradiation; *V* is the rate of zirconia powder feed; *P* is the amount of zirconia powder feed at time, *t*; *v* is the moving speed of the hybrid spraying, $v = L/t$; *L* is the moving distance at time, *t*, in Eq 1; *p* is the total area of porosity per cross section of coating area; and *s* is the total area of zirconia particles in the cross section of the coating in Eq 2.

This result shows that the ratio of the porosity in the zirconia coating decreases with an increase in the energy density of the laser irradiation. The effect of the energy density on the microstructure can be divided into three stages. The bonding areas among the particles increase when the *E* value increases from stage I to stage II, where the temperature at an area of laser irradiation attains or exceeds the melting point of the zirconia particles. The bond areas among the particles increase and a certain amount of porosity remains in the coating at stage II. At stage III, the density of the coating increases greatly (more than 98%), but cracks are produced (Fig. 12f).

5. Conclusions

Hybrid spraying using YAG laser irradiation combined with plasma spraying was applied to produce zirconia thermal barrier coatings. The following results were obtained:

- It was found that the bonding force among the particles in the hybrid sprayed coating increased greatly and the connected micropores and cracks that are generally produced in the post-laser irradiation were prevented. A good interface between the coating and the substrate and smooth coating surfaces were obtained.
- The microstructure was controlled by adjusting the energy density of the laser irradiation. The prevention of rapid cooling cracks in hybrid spraying can be attributed to the thermal barrier effect of the so-called heat retention effect.
- Properties of the coating such as hardness, high temperature erosion resistance, and hot oxidation resistance were greatly improved due to the formation of the dense coatings without connected porosity or cracks.

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