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Three-dimensional transition map of flattening behavior in the thermal spray process*

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Abstract: Many kinds of both metallic and ceramic powder particles were plasma-sprayed onto the mirror-polished metallic substrate surface, and the effect of both substrate temperature and ambient pressure on the flattening behavior of the particle was systematically investigated. In the flattening behavior of the sprayed particle onto the substrate surface, critical conditions were recognized both in the substrate temperature and ambient pressure. That is, the flattening behavior changed transitionally on that critical temperature and pressure range, respectively. We defined and introduced a transition temperature, T_t, and transition pressure, P_t, respectively, for those critical conditions. The role of the related factors (such as solidification of the bottom surface of the splat, desorption of adsorbates on the substrate surface and wetting at interface) on the transition behavior in the flattening was clarified from several points of views. The fact that the dependence both of transition temperature and transition pressure on the sprayed particle material had a similar tendency indicated that the wetting of the substrate by the molten particles seemed to be a domination in the flattening. A three-dimensional transition map by combining both transition temperature and transition pressure dependence was proposed as a controlling principle of the thermal spray process.

Keywords: thermal spray; sprayed particle; flattening; transition temperature; splash splat; disk splat; splashing parameter; adsorbate/condensate; ambient pressure; surface oxidation; surface roughness; 3D map; wetting.

INTRODUCTION

As the flattening behavior of the thermally sprayed particle impinged onto the flat substrate surface can be recognized as a fundamental phenomenon of the coating formation of the thermal spray process, a clarification of the flattening behavior of an individual particle is essential. Theoretical analysis represented by Madejski's model [1] indicates that both in-flight temperature and velocity of the particle are the dominating factors in the flattening of the sprayed particles, and thus for controlling the thermal spray process. However, based on our experimental data, we have pointed out that the particle/substrate interface-oriented factors, such as a substrate temperature and desorption of adsorbates on the substrate surface, affect more significantly the flattening behavior of the sprayed particles [2–6]. Our experimental results have especially revealed that a splat shape of most metallic and ceramic material onto the flat substrate surface has a transitional changing tendency from a distorted shape with splash to a lenticular shape without splash at a narrow temperature range with an increase of the substrate temperature,

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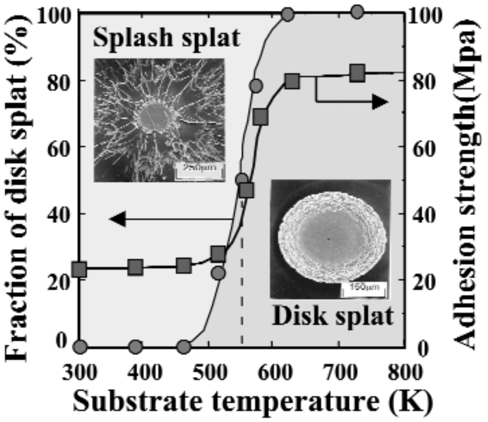

Fig. 1 Dependence of fraction of disk splat and adhesion strength on substrate temperature.

as shown in Fig. 1 [2–3]. The transition temperature, T_t, at which the particle's splat pattern changes to the form without splashing from the one with splashing, was defined and introduced by the authors [2]. Since then, the drastic change in the splat pattern nearby the transition temperature has become of great concern in recent years. Moreover, it was verified experimentally that the adhesion strength of the coating changed transitionally with the substrate temperature increasing, and its dependence on the substrate temperature corresponded quite well to that of the splat pattern [3]. Thus, the investigation of the flattening mechanism of the sprayed particle on the substrate surface is significant for the practical usage of the thermal spray process.

Based on the experimental, analytical, or numerical data, a unified explanation has been tried on the transition behavior. As the most possible domination, the role of solidification in the flattening particle [7], wetting at particle/substrate interface [2–3], and desorption of adsorbates on the substrate surface [8] on the flattening have been mainly investigated. The feasibility of each domination for the transition behavior in the flattening is discussed in this paper.

EXPERIMENTAL

Powder materials used are Ni, Ni–5Al, Ni–20Cr, NiCrAlY, Cu, Fe, Al, Cr, and Ti for metallic material and Al_2O_3, ZrO_2, and TiO_2 for ceramic material, respectively. Mirror-polished AISI 304 stainless steel, mild steel, Al-alloy, and brass plates with 25 × 25 × 5 mm were used for the substrate material. Both atmospheric plasma-spraying and low-pressure plasma-spraying were used, and the spraying conditions are shown in Table 1. To investigate the in-flight condition of the particles, powder materials were sprayed and collected into the water bath installed at the distance equivalent to the regular spraying for the coating formation. The cross-section microstructure both of the in-flight particle and the splat on the substrate surface were observed by scanning electron microscopy (SEM) and analyzed with electron probe microanalysis (EPMA). Both in-flight temperature and velocity of the sprayed particles were measured using the DPV-2000 system. Transition temperature, T_t, and transition pressure, P_t, for each powder material were also measured. The measuring methods can be referenced in our previous report [2]. In the measuring, around 50 or more splats were collected and observed on the substrate for every experimental trial. To investigate the chemical change of the AISI 304 substrate by heating, both Auger analysis in the depth direction and X-ray photoelectron spectroscopy (XPS) analysis on the surface were conducted. The surface roughness in nanometer order was also measured by using atomic force microscopy (AFM).

Table 1 Plasma spray conditions.

Atmospheric plasma spray			Low-pressure plasma spray		
			Chamber pressure (torr)		30–760
Spray distance (mm)		200	Spray distance (mm)		200–300
Arc current (A)		600	Arc current (A)		900
Operating gas flow (*l*/min)	1st: N_2	70.8	Operating gas flow (*l*/min)	1st: Ar	50
	2nd: H_2	4.72		2nd: He	12
Arc voltage (V)		70	Arc voltage (V)		40
Powder carrier gas; Ar (*l*/min)		5.0	Powder carrier gas; Ar (*l*/min)		5.0
Powder feed rate (g/min)		6.0	Powder feed rate (g/min)		6.0

RESULTS AND DISCUSSIONS

Role of solidification and desorption of adsorbates on the flattening behavior of the particle

First of all, the transition temperature, T_t, for each powder material onto stainless steel substrate was measured. To conduct this, the fraction change of the disk splat on the substrate surface with substrate temperature increasing was measured. The measured T_t values are summarized in Table 2. Standard deviation of T_t is 5–10 K. From the table, it is recognized that the T_t varies widely with particle material and oxide ceramic materials have relatively low T_t. As T_t is defined as a critical substrate temperature for an appearance of disk splat instead of the splash splat with the substrate temperature increasing, the problem is to determine what dominates the transition phenomenon.

Table 2 Transition temperature for each powder material on AISI 304 stainless steel substrate.

Powder material	Spraying device	Transition temperature (K)
Ni	APS	610
Mo	APS	474
Cu	APS	394
Cr	APS	387
Cu–30Zn	APS	505
Al_2O_3	APS	318
TiO_2	APS	350
YSZ	APS	345

Substrate: AISI 304 stainless steel

The bottom surface microstructures for both the splash splat and the disk splat were observed. The results are shown in Figs. 2 and 3, respectively. From Fig. 2, quite porous microstructure can be recognized on the bottom surface of the splash splat obtained on the cold substrate surface. The radial flow pattern with porous structure from collision center to the periphery indicates that rapid solidification occurred simultaneously with the flattening. On the other hand, a dense and homogeneous solidification microstructure can be recognized entirely as a whole part of the bottom surface of the disk splat obtained on the hot substrate surface, as shown in Fig. 3. The dense microstructure indicates that the intimate contact between splat and substrate surface was attained; in other words, good wetting of the substrate by the splat was given in this case.

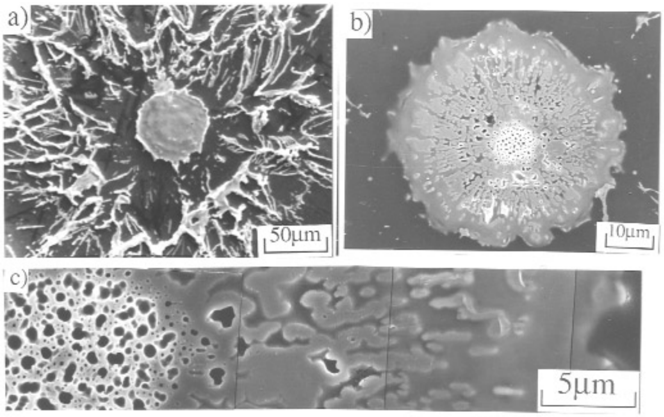

Fig. 2 Bottom surface microstructure of splash splat of Ni on cold stainless steel substrate surface. (a) top surface, (b) magnified bottom surface of center part of (a), (c) magnified of (b).

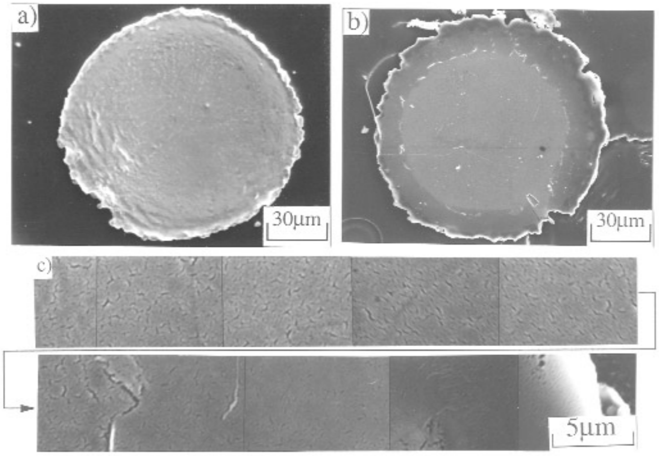

Fig. 3 Bottom surface microstructure of disk splat of Ni on hot stainless steel substrate surface. (a) top surface, (b) bottom surface of (a), (c) magnified of (b).

Why and how does the splashing occur on the cold substrate surface? The possible reasons can be the rapid solidification on the bottom surface of the splat, adsorbates on the substrate surface, poor wettability, and so on. Computer simulations of the flattening behavior of the sprayed particle have been conducted by several researchers [9]. Fard et al. indicated that the unstable situation in liquid flow occurs at the spreading periphery of the particle at the time sequence of around 1.4 μs after the collision. Their simulation revealed that the rapid solidification on the bottom surface of the splat occurred correspondingly at the time sequence of around 1.1 μs after the collision. The preferential solidification at the bottom surface of the splat may affect the flowing of the melted part located on the solidified layer. Thus, the computer simulation has indicated that the rapid solidification on the bottom surface can be a trigger for the splashing.

We have pointed out that the initial solidified layer affects the splashing of the particle in the case of metal particles [2,4]. However, the Al_2O_3 splat on the Au-coated stainless steel substrate scatters without any central solidified part [6]. That is, it is indicated that the initial solidified layer is not always the necessary condition for the splashing. The splashing of ceramic splat might have taken place maybe because of the poor wetting. To clarify this, the splat was collected on the substrate whose surface was partially Au-coated. T_t is 420 and 370 K for Au-coated and naked stainless steel substrate, respectively.

The splat morphology was observed, which impinged onto the boundary between the Au-coated and naked substrate surface. The substrate temperature was 400 K, at which the splash splat was observed on Au-coated substrate and the disk splat was observed on naked substrate.

The typical splat morphology is shown in Fig. 4. It was clarified that the splat was composed of both characters, that is, the splash splat appeared on the Au-coated surface and the disk splat on the naked surface. Furthermore, it is notable that on the Au-coated surface, the splash splat was formed without any initial solidification part of the splat. This fact indicates that the initial solidification is not always a necessary condition for the splashing. Thus, while the role of solidification on the flattening is not always clearly understood yet, we estimate that the wetting affects more strongly this phenomenon.

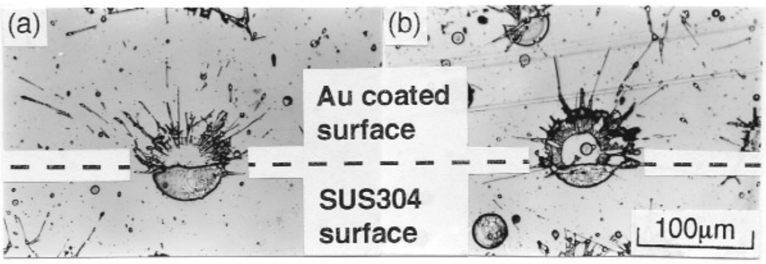

Fig. 4 Al_2O_3 splat morphologies onto AISI 304 substrate at 400 K.

Another possible explanation for the transition phenomenon can be given by the desorption of the adsorbates on the substrate surface owing to the heating. The effect of adsorbates/condensates on the substrate surface on the flattening behavior of the thermally sprayed particles has been precisely investigated by Jiang et al. [8]. The transition phenomenon from splash splat to the disk splat with substrate temperature increasing can be explained reasonably by this hypothesis. Namely, on the hot substrate surface, better contact between droplet and substrate can be attained by the desorption of adsorbates. On the cold substrate surface, on the other hand, adsorbates become a source of interface porous microstructure and also assist the radial flow from center to the periphery on the bottom surface of the splash splat. Moreover, in a certain case, adsorbates can induce the extremely rapid expanding or flowing of the splat owing to its explosion by the rapid heating.

In general, however, it is well known that the break-up phenomenon of the liquid film generated by the collision of the particle to the solid surface can be evaluated by the splashing parameter, K, in the fluid dynamics field [10]. K is defined as $We^{0.5}Re^{0.25}$, and it is based on the in-flight kinetic information of the liquid particle. Here, $We = \rho dv^2/\gamma$, and $Re = \rho dv/\eta$; where ρ is density, d is diameter, v is velocity, γ is viscosity, and η is surface tension, respectively. K has a critical value, $K_c = 57.7$, and if the K value of the particle exceeds K_c, the liquid film shows the break-up after the collision onto the solid surface.

To investigate the K value, measurement of the in-flight information of the regular thermally sprayed particles was conducted using the DPV-2000 system. Typical examples of the measured values are shown in Fig. 5 as a function of the spray distance. By introducing the measured temperature into each physical constant (i.e., density, surface tension, and viscosity), the K value was obtained as shown in Fig. 6 for a few kinds of sprayed metallic materials. The K_c value was indicated in the figure for the comparison. As obviously recognized in the figure, K values were remarkably larger compared to K_c regardless of the sprayed material. More details on the K value of the sprayed particles were investigated recently [11], and an almost similar tendency has been confirmed. Namely, the regular-sprayed particle has enough driving force for the splashing.

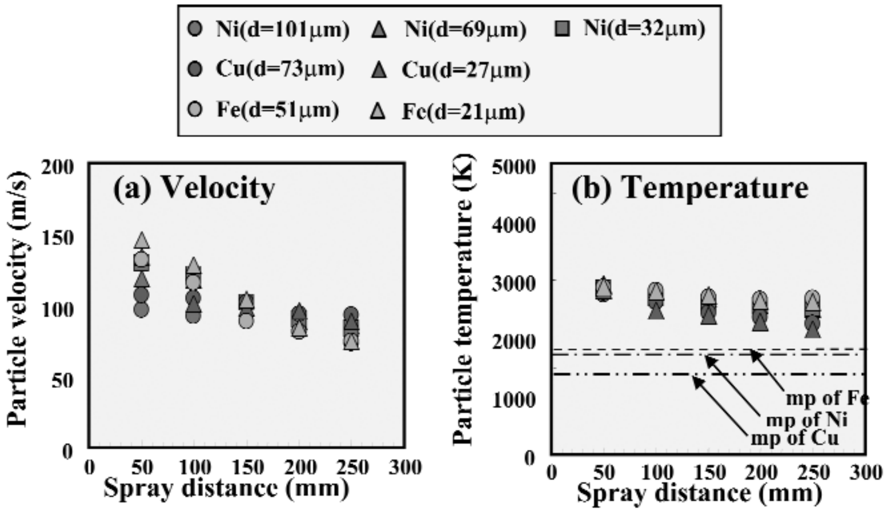

Fig. 5 Measurement results of particle's in-flight characters at various spray distances. (a) particle velocity, (b) particle temperature.

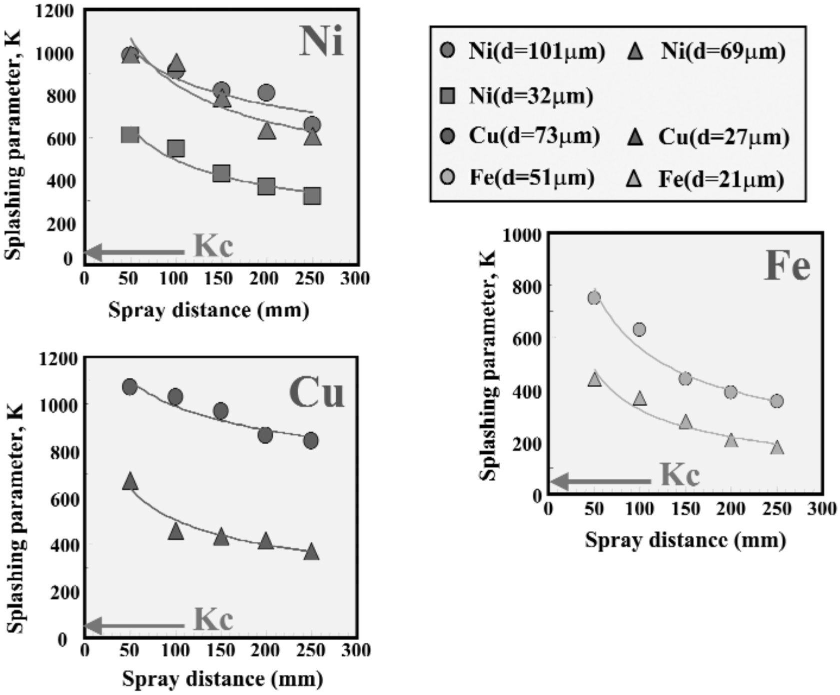

Fig. 6 Measured splashing parameter, *K* of regular sprayed particles.

The results mentioned above indicate that the essential point of the transition problem lies in not why and how the splashing occurs on the cold substrate surface, but why and how the disk splat appears on the hot substrate surface instead of the splash splat.

The effect of desorption of adsorbates on the flattening behavior was systematically investigated in the low-pressure plasma spraying by reducing the ambient pressure. The substrate temperature was kept at room temperature. The typical splat morphologies of metallic particles onto stainless steel substrate surface were shown in Fig. 7. From the results, it is found that the disk splat appears easily by reducing the ambient pressure while the substrate temperature is kept constant at room temperature. Experiments also revealed that the transition behavior from the splash splat to the disk one was recognized in most of the metallic materials by reducing the ambient pressure, as shown in Fig. 8. The transition pressure, P_t, at which the particle's splat pattern change to the disk splat from the splash splat was defined and introduced by the authors. The effects of spraying distance on the fraction of disk splat appearance under three kinds of chamber pressures were investigated. From the results, it was found that the fraction of disk splat did not change so much regardless of the spraying distance and in any chamber pressures. This indicates that the in-flight conditions of regularly sprayed particles does not change so much even in low-pressure spraying, and thus in-flight conditions do not affect so much the flattening. Hence, the fact mentioned above indicates that the desorption of adsorbates can affect independently the flattening behavior as a transition from splash to the disk. Transition pressure distribution for each sprayed material was summarized in Fig. 9. In the figure, dependence of the transition temperature on the sprayed material was also shown for the comparison purpose. From the figure, it is recognized that the dependence of T_t and P_t on the particle material has quite a similar tendency. This fact indicates that both substrate temperature and ambient pressure may have an equivalent effect on the transition.

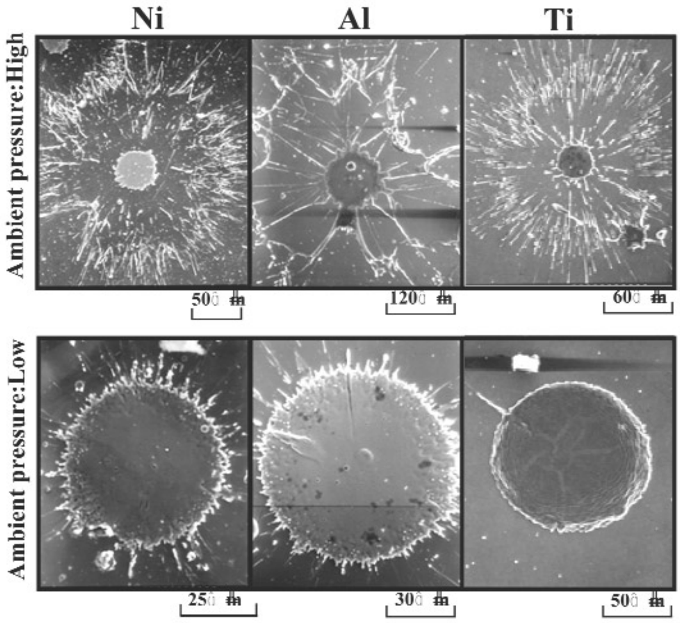

Fig. 7 Splat morphologies of metallic particles on AISI 304 stainless steel substrate.

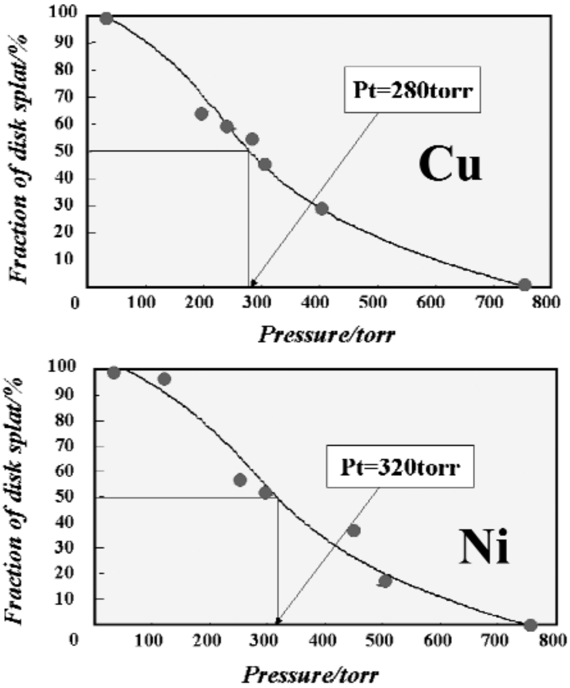

Fig. 8 Fraction change of disk splat with ambient pressure reduction.

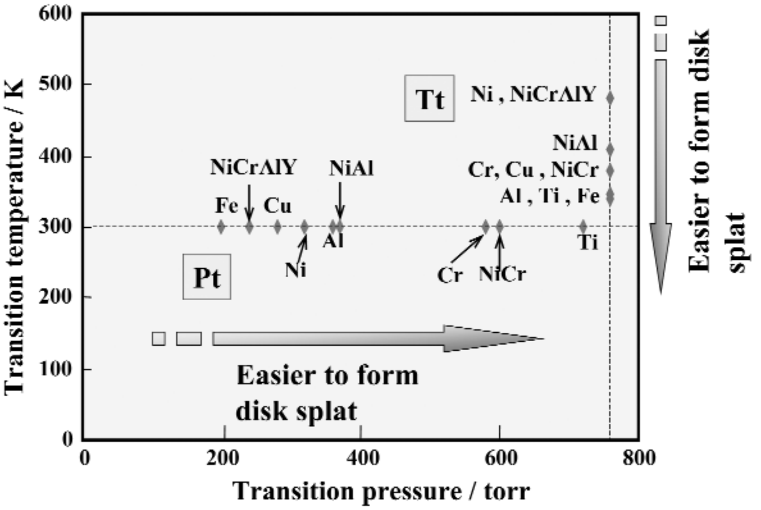

Fig. 9 Transition in thermally sprayed particle with substrate temperature and ambient pressure.

Major phenomena in flattening of the sprayed particle

Here, we can show interesting results to clarify the domination in flattening of sprayed particle. The microstructure of the Ni–Cr particles/substrate interface was observed. Prior to that, the in-flight condition of the sprayed Ni–Cr particles was observed by investigating the powders sprayed and collected into the water. The water bath was installed on the same distance from the plasma torch as in the case of the coating formation. The cross-section microstructure of the Ni–20Cr original powder before the spraying revealed that both Ni and Cr elements distribute homogeneously entirely whole inside of the powder. To compare with the original powder, the cross-section microstructure of the Ni–20Cr powder sprayed and collected in the water was observed. From the results, it was found that the sprayed particles were fully melted, sphere in a shape and oxidized on their surfaces during spraying in an air atmosphere. The surface oxide layer was detected as a Cr-rich layer by EPMA analysis. The Cr-rich layer was formed at the surface region of the powder after the spraying while the Ni element distributed homogeneously in the particle. Accumulation of the Cr element to the powder surface can be estimated as a result of the diffusion of the element toward the surface. Moreover, it is indicated that the diffusion may be induced due to the preferential formation of oxide in this element at the surface of the particle in an air atmosphere. Hence, it is found from the results that in the plasma spraying of Ni–Cr powder, melted, sphere-shaped, and covered by oxide layer particles collide with the flat substrate surface.

The cross-section microstructures of the splat/substrate interfaces onto the substrate surface kept at room temperature and 600 K were observed. The results are shown in Fig. 10. It is found from Fig. 10 that Ni concentration at the particle/substrate interface is almost similar for both cases. Cr concentration at the particle/substrate interface, however, is quite lower on the substrate kept at room temperature, while it is higher on the substrate kept at a higher temperature range. It is found from the results that the Cr oxide exists at the splat/substrate interface region preferentially on the hot substrate surface, while Cr oxide exists not at the interface region, but at the surface region of the splat on the room temperature substrate. It is indicated that there are some reasons for the existence of oxide at the interface on the heated substrate. This difference of the elemental distribution at the splat/substrate interface with the substrate temperature difference is not always explained by the gas desorption hypothesis. The more possible reason for this can be given as the wetting effect of the substrate surface by the melted droplet.

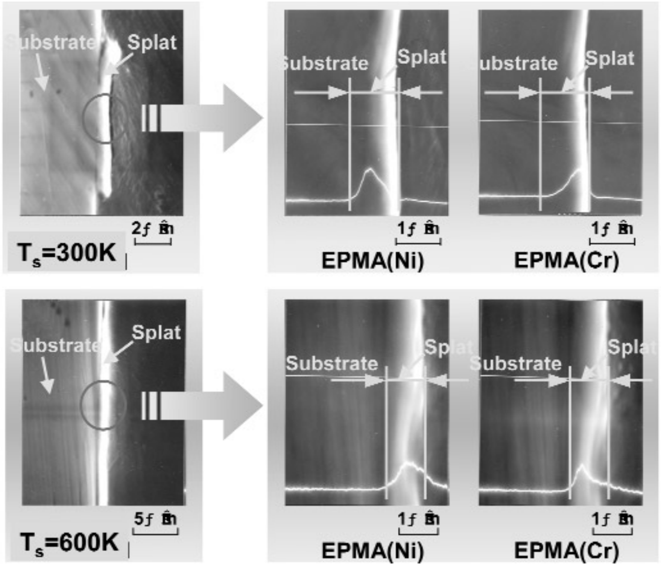

Fig. 10 Cross-section microstructures of Ni–20Cr splats onto substrate with different temperatures.

It is estimated that the contact property of the splat with substrate surface strongly depends on the wetting of the liquid metal to the solid substrate. In the case of substrate heating up to some elevated temperatures, the wetting seems to be affected mainly by the oxide formation on the surface. Here, the effect of oxide formation can be divided into two kinds of changes, that is, one is the chemical change in the material of the substrate surface and another is the change in the surface roughness of the substrate. The effects of each factor on the wetting and/or the flattening behavior of the droplet were investigated.

The chemical change of the substrate surface owing to the heating in air was examined. By heating the stainless steel substrate, iron and chromium oxide are formed on the top surface of the material and the chemical composition of the oxide may change with the substrate temperature. The results of Auger analyses in the depth direction on the stainless steel substrate indicated that iron and chromium oxide already existed on the surface even in a polished condition. After the heating, however, the chemical composition on the surface does not change so much, while the thickness of the oxide layer increases by the heating. XPS spectrum for the substrate as shown in Fig. 11 also revealed the same tendency. Both results indicate that the chemical change of the substrate surface by the heating does not affect so much the wetting condition.

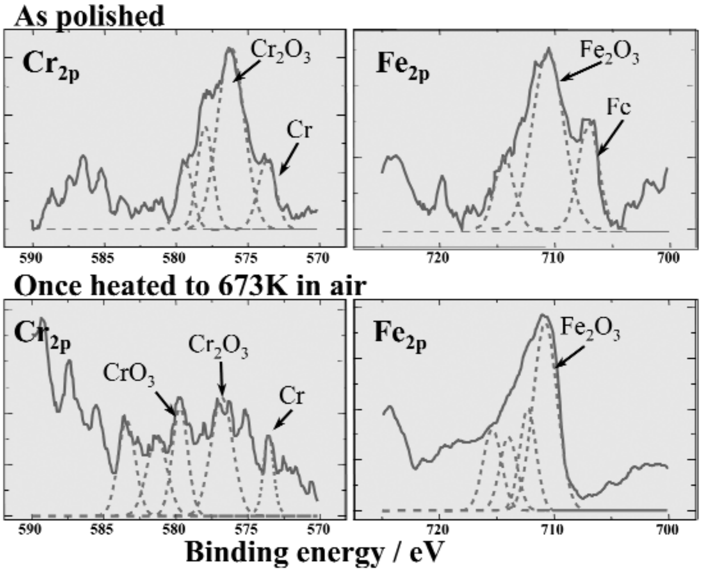

Fig. 11 XPS spectrum for AISI 304 stainless steel substrate.

The effect of substrate surface roughness owing to the oxidation on the wetting and flattening was considered. Two kinds of substrate specimens were prepared, that is, one was as polished and the other was once heated up to 673 K air to form the oxide layer on the surface. The mean surface roughness, Ra, was measured for each substrate material by using AFM. The measured area is 20×20 µm. As the typical measurement results, surface morphologies and Ra value on stainless steel substrate are shown in Fig. 12. From the figure, it is recognized that nanometer-order roughness can be recognized on the surface and the surface roughness increases by the heating.

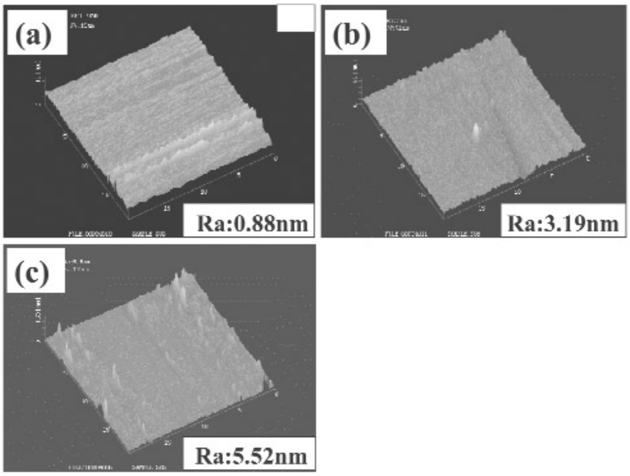

Fig. 12 Measurement results of surface morphologies on stainless steel substrates by AFM. (a) as polished, (b) heated up to 673 K in air, (c) heated up to 673 K in vacuum.

Figure 13 shows the average value of the surface roughness measurement results both for stainless steel and aluminum substrates as polished and after heating in air and vacuum. Each value is given as a mean value measured at three different places on an individual substrate specimen. In the figure, it is found that the surface roughness increases by the heating and shows increasing tendency in the same order for both substrate materials. Exactly the same tendency was found in the brass substrate. The result means that the effect of substrate surface roughness on the flattening of the splat cannot be denied absolutely. The effect of surface roughness on the wetting behavior of solid substrate by liquid droplet has been investigated. In general, the contact angle of Young's equation on the rough surface decreases more than that on the smooth surface in a good wetting condition [12,13]. That is, the surface roughness induces the wetting, and the better wetting brings about the change in the splat morphology to the disk type. From the facts described above, we may conclude that the substrate temperature increasing induces the nanometer-order surface roughness on the substrate owing to the oxidation, and better wetting by the roughness brings about the change in the flattening behavior of the sprayed particle.

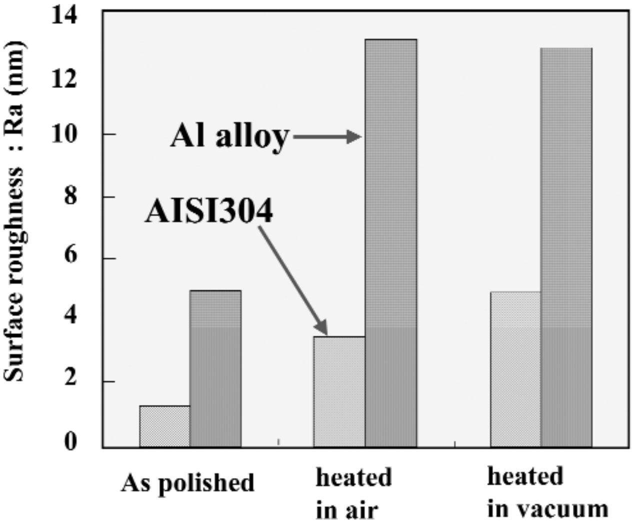

Fig. 13 Surface roughness change with heating.

As a confirmation to the above, interesting evidence was reported. Thermally sprayed Ni particles were collected on the stainless steel substrates kept at room temperature. Those substrates have a different thermal history for one another, namely, as polished, once heated to 673 K in air, and once heated to 673 K in vacuum, respectively. The results are shown in Fig. 14. From the figure, it is found that on as-polished substrate, the splash splat was major. On the other hand, on both once-heated substrates, the fraction of disk splat reached almost 80 %, contrary to the expected. The adsorbed condition on the substrate was common for all in this case because the substrates were kept at exactly the same situation, namely, in air at room temperature. The only difference between as-polished and once-heated substrates is heating history. Especially, nanometer surface roughness due to the heating seems to be the main reason for the difference. Thus, the result indicates that the roughness-induced wetting plays a significant role on the flattening behavior of the thermally sprayed particles.

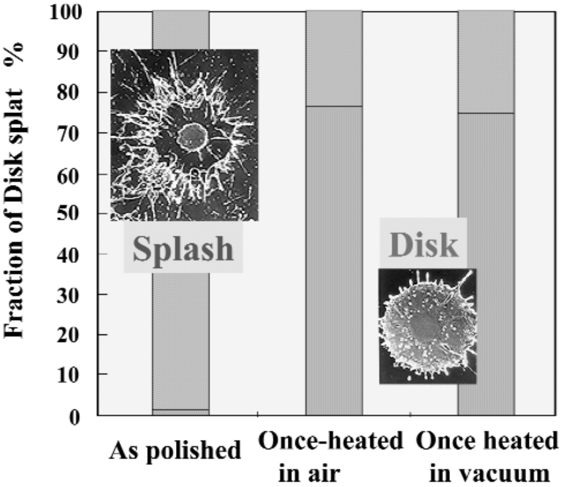

Fig. 14 Morphology change of thermally sprayed Ni particle on various substrate surface kept at room temperature.

Figure 15 shows the bottom surface microstructures change both by changing the ambient pressure and the substrate temperature, respectively. The similar tendency in microstructure change from the porous to the dense is observed in both cases. The dependence of fraction of disk splat both on the substrate temperature and ambient pressure was summarized schematically as shown in Fig. 16. By selecting the optimum operating conditions in both factors in the thermal spraying, we can control the coating microstructure and some other properties of the coating. Thus, control of the thermal spray process can be attained by introducing both T_t and P_t as critical factors.

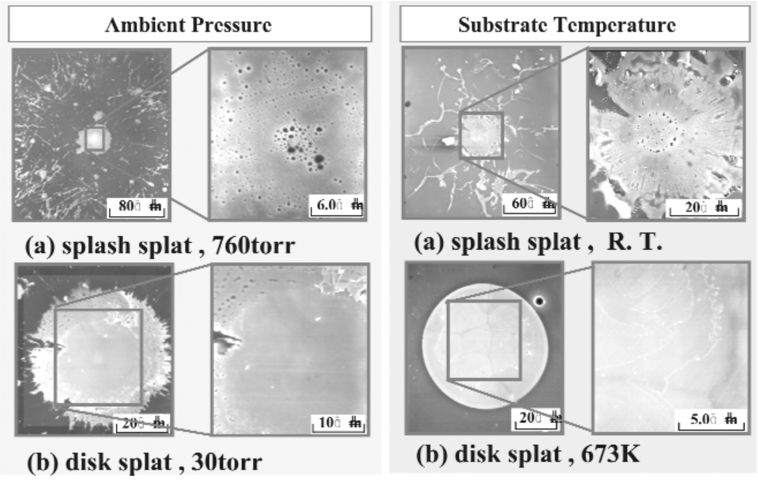

Fig. 15 Bottom surface microstructure change with ambient pressure and substrate temperature.

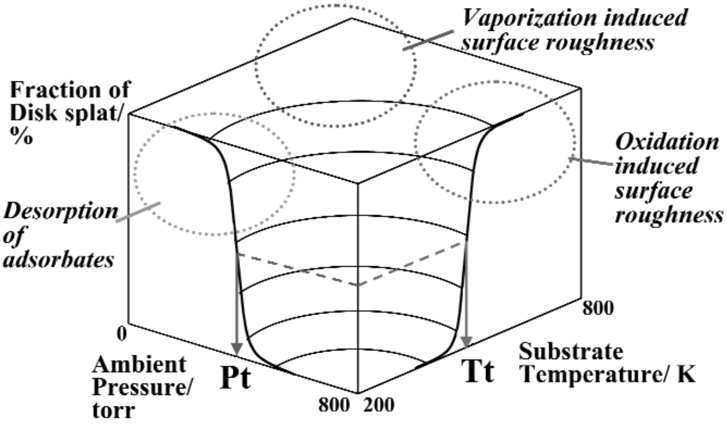

Fig. 16 3D transition map of flattening behavior in the thermal spray process.

SUMMARY

Based on the experimental and analytical results on the flattening behavior of the thermally sprayed particle, the feasibility of each domination for the transition phenomenon in the flattening was discussed. The essential points in this paper are summarized as follows:

- The initial solidification on the bottom surface of the splat is not always a necessary condition for the splashing. It is estimated that the wetting affects more strongly the transition phenomenon.
- From the measurement results in K value, it was found that the regular sprayed particle has enough driving force for the splashing. This indicates that the essential point of the transition problem lies in not why and how the splashing occurs on the cold substrate surface, but why and how the disk splat appears on the hot substrate surface instead of the splash splat.
- The transition behavior from the splash splat to the disk one was recognized in most of the metallic materials by reducing the ambient pressure. This fact indicates that the desorption of adsorbates can affect independently the flattening behavior as a transition from splash to the disk.
- It was recognized that the dependence of T_t and P_t on the particle material has quite a similar tendency. This fact indicates that both substrate temperature and ambient pressure may have an equivalent effect on the transition.

- The substrate heating in air induces the nanometer-order roughness on the surface due to the oxidation, and the better wetting by the roughness brings about the change in the flattening behavior of the thermally sprayed particles.
- By selecting the optimum operating conditions both in substrate temperature and ambient pressure in thermal spraying, we can control the coating microstructure and some other properties of the coating. Thus, the control of the thermal spray process can be attained by introducing both T_t and P_t as critical factors.

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