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Study of Substrate Preheating on Flattening Behavior of Thermal-Sprayed Copper Particles

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In this study, the effect of substrate preheating on flattening behavior of thermal-sprayed particles was systematically investigated. A part of mirror-polished AISI304 substrates were preheated to 573 and 773 K for 10 min, and then exposed to an air atmosphere for different durations of up to 48 h, respectively. Contact angle of water droplet was measured on the substrate under designated conditions. It was found that the contact angle increased gradually with the increase of substrate duration after preheating. Moreover, smaller contact angle was maintained on the substrate with higher preheating temperature. Commercially available Cu powders were thermally sprayed onto the substrates with the same thermal treatment history as contact angle measurement using atmospheric plasma-spray technique. The splat shape had a transitional changing tendency from a splash splat to a disk one on the substrate with a short duration after preheating, while reappearance of splash splat with the increase of duration was confirmed. In general, wetting of substrate surface by molten particles may dominate the flattening behavior of thermal-sprayed particles. The occurrence of desorption of adsorbed gas/condensation caused by substrate preheating likely provides good wetting. On the other hand, the poor wetting may be attributed to the re-adsorption of gas/condensation on the substrate surface with the increase of duration. In addition, the shear adhesion strength of coating fabricated on blasted AISI304 substrate was enhanced on the once-heated substrate, but weakened with the increase of duration. The changing tendency of the coating adhesion strength and the wetting of substrate by droplet corresponded quite well with each other.

Keywords thermal spraying, flattening, disk-shaped splat, splash splat, preheating, duration, wetting, adsorbed gas/condensation, adsorption/desorption

1. Introduction

Thermal spraying is a process in which melted materials with high velocity are sprayed onto a surface to form a dense coating (Ref 1). The feedstock material is heated by electrical (plasma or arc) or chemical means (combustion flame). Up to now, this technology is widely used in many industrial applications, typically used as thermal barrier coating, TBC, in power plants, owing to its advantages over other surface treatment methods. It is, however, pointed out that the controllability or reliability of the process has not been established yet until today. Hence, the question of how to improve the thermal-spray technology is quite worthwhile for paying more attention to. As a flattening of an individual thermal-sprayed particle on the substrate is a fundamental process for the coating formation; in other words, splat is unit cell for the entire coating build-up, coating microstructure and corresponding properties, such as porosity and adhesion strength, which depend strongly on the flattening nature of each splat (Ref 2). In order to establish the process controllability, it is necessary to study in detail the basic process of flattening behavior of the sprayed particles, not only from the point of view of scientific interest, but also from that of technical consequences.

As reported up to now, much attention has been increasingly paid to the study on the splat formation through experimental observation, theoretical, and numerical simulation in the past few decades. A transition phenomenon in a flattening behavior of the thermal-sprayed particle on the flat substrate surface was introduced in 1995 by Fukumoto et al. (Ref 3), which reported that when the substrate temperature was increased, the splat shapes of most materials sprayed onto flat substrates underwent a transition from a distorted shape with splash to a disk shape. The transition temperature, T_t, as a critical substrate temperature over which more than 50% of splats are disk shaped, can be considered as a useful tool for the process control. Existence of a similar transition was indicated recently; that is, the splat shape on the flat substrate had a transitional changing tendency from

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a splash splat to a disk one with a decrease of the ambient pressure in deposition chamber (Ref 4, 5). Moreover, spray conditions (Ref 6, 7), spray materials etc. have been investigated aggressively by many researchers (Ref 8, 9).

The Sommerfeld number K based on the study of water and ethanol droplet, has been often mentioned recently (Ref 10, 11), which was described as

$$K = We^{1/2}Re^{1/4} \quad \text{(Eq 1)}$$

where We and Re are the Weber and Reynolds numbers, respectively. If $K < 3$, splat rebounds; while $3 < K < 57.7$, it results in deposition; and, if $K > 57.7$, it induces splashing. However, for thermal-spraying conditions involved in particle solidification, these critical values do not seem applicable. Significant splashing occurred even if the K is lower than the critical value of 57.7 when alumina particles were thermally sprayed onto the stainless steel substrate (Ref 12). While in Li's study, nearly all the plasma-sprayed particles yield a K ranging from several hundreds to thousands, which is quite higher than the critical value, the splats deposited by those particles on preheated substrate always displayed a disk shape without any splashing (Ref 13). These results indicated that the model is not enough to clarify the splat formation process of the thermal-sprayed particles, because only the fluid dynamic of the droplet was considered in this model. Actually, the surface conditions, for example, substrate surface oxidation state (Ref 6, 8), surface roughness (Ref 14), and substrate temperature (Ref 15-18) also have effects on the splat formation.

Moreover, it has been proposed by the authors that the wetting of droplet to substrate surface may have an effect on the droplet flattening (Ref 5, 19-22). In general, wetting of the substrate surface by molten droplet plays an important role in the droplet flattening because it affects not only the surface effects, but also the contact thermal resistance at the splat-substrate interface, which is an important parameter for the development of the coating structure. The degree of wetting is described by the contact angle (θ) (Ref 23), the angle at which the liquid-vapor interface meets the solid-liquid interface. If the wetting is very favorable, the contact angle will be low, and the fluid will spread to cover a larger area of the surface. If the wetting is unfavorable, the fluid will form a compact droplet on the surface.

However, the splat formation process of the thermal-sprayed particles is not fully understood; yet, we still cannot answer why or how does disk-shaped splat appears, and what is the essential of the flattening problem. Given the limited understanding on the influence of substrate preheating, especially the substrate exposure to certain atmosphere (referred to as "duration" in this article), after preheating on the splat formation process, it was felt that there was a need for a detailed study of this aspect. In this study, the effect of substrate preheating on the wetting of the flat substrate to the droplet, and the flattening behavior of the thermal-sprayed Cu particles was investigated systematically. This article focuses, in particular, on the influence of substrate duration after preheating. In addition, the coating fabricated on the substrate with the same thermal-treatment history as the splat collection was evaluated as well.

2. Experimental Procedures

2.1 Contact Angle and Substrate Surface Topography Measurement

As the contact angle provides an inverse measure of wettability, the contact angle of water droplet was measured experimentally in this study, based on the standard sessile drop test. Mirror-polished AISI304 plates with the same thermal-treatment history as the splat collection which will be mentioned later were used as the substrate. Commercially available interface measurement and analysis system (FAMAS), Drop Master 300, was used in this study. The droplet volume was 10^{-3} mL. Drops were released by a micro-pipette onto the substrate surface, and the profile photographs were taken using a camera attached to an optical microscope. The tests were conducted in air at room temperature. Dedicated software was used to calculate the wetting angles.

As nanometer scale surface topography of the substrate may affect friction coefficient between sprayed particle and substrate surface, flattening speed, and thermal conduction, surface topography and surface roughness of the mirror-polished AISI304 substrate under the designated conditions were measured using atomic force microscopy (AFM, SPM-9500J3, Shimadzu Co., Ltd. Tokyo, Japan) covering an area of 1 μm^2.

2.2 Materials Used and Thermal-Spraying Apparatus

Commercially available Cu powders with 75 μm or less in diameter as shown in Fig. 1 (Kojundo Chemical Lab. Co., Ltd., Japan.) were used as the feedstock for the

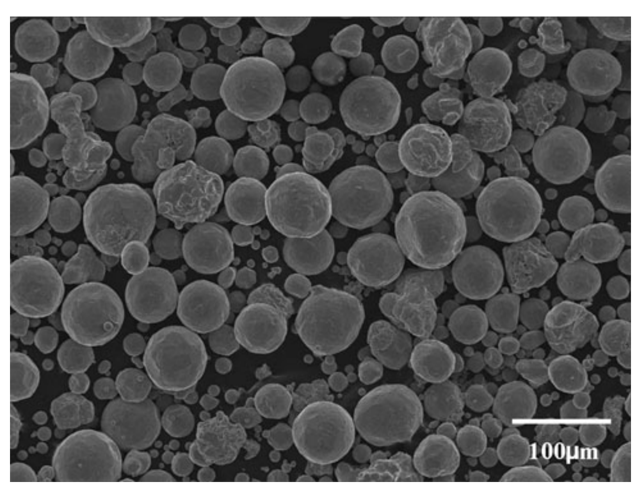

Fig. 1 SEM image of Cu powder used

Table 1 Plasma-spraying conditions

Substrate preheating temperature, K	573, 773
Spray distance, mm	100
Arc current, A	500
Arc voltage, V	51
Operating gas flow rate, L/min	
1st: Ar	105
2nd: H_2	12
Powder carrier gas: Ar, L/min	3

spraying. Mirror-polished AISI304 plates with 20 × 20 × 6 mm were used as the substrates. The plates were finally polished with 0.3 μm Al_2O_3 buff prior to spraying. A part of plates were preheated to 573 and 773 K for 10 min, and then they were exposed to an air atmosphere for different durations of up to a maximum of 48 h. The heating was conducted using a Corning PC-600D Laboratory Hot Plate.

Plasma spraying was carried out by atmospheric plasma spray (APS), Metco (NY, USA) 9 MB torch in atmospheric condition. Table 1 summarizes the spraying conditions. During deposition, the substrate surface was held vertically, and the spray gun was held horizontally so that the direction of droplet stream was perpendicular to the substrate surface. Splats were collected on the substrate by moving the plasma torch rapidly in one direction. Almost no increase in the substrate temperature was recognized by this collection.

2.3 Evaluation Methods

The splat shape was evaluated using the Nikon Eclipse LV100 optical microscope (OM, Nikon Co., Ltd., Japan). Splats were classified as either disk-shaped splat or splash splat. Around one hundred or more splats were collected, and the number of disk-shaped splats and splash splats were counted on every trial in the experiments. The fraction of disk-shaped splat was defined as the ratio of the number of disk-shaped splats to the total splats.

The splat morphologies in detail were observed using scanning electron microscope (SEM, JSM-6390TY JEOL, Co., Ltd., Tokyo, Japan). First, the top surface morphologies of the splat collected under the designated conditions were observed. Following this, carbon tape was pressed onto the sprayed region, then pulled off, and some splats were removed. The bottom surface of the splat collected on carbon tape was observed by SEM (Ref 4, 24). Image analysis software (UTHSCSA Image Tool, National Institutes of Health) was employed to quantify the pore size and distribution on the bottom surface of the splats.

In addition, Cu coating was fabricated on the blasted AISI304 substrate which has the same thermal-treatment history as the wetting behavior measurement and splats collection. The shear adhesion strength of the fabricated coatings was evaluated by Autography AGS-L. The measuring method can be referred to a previous article (Ref 25). Moreover, the coating's cross section microstructure and elements distribution was performed using

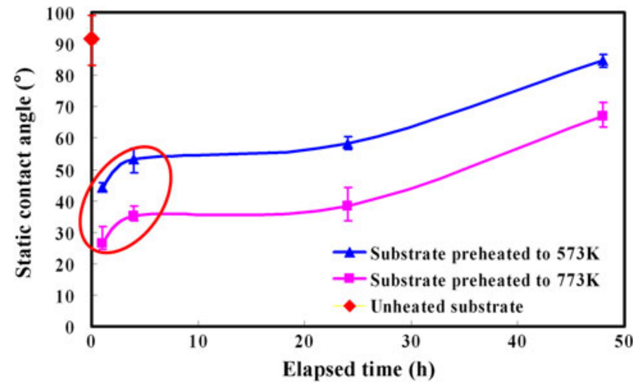

Fig. 2 Dependence of contact angle on substrate preheating temperature and elapsed time

Energy Dispersive X-Ray, Fluoresence Spectrometer (EDX), JSM-6300 as well.

3. Results and Discussion

3.1 Study of Wetting

It is believed that wetting of substrate surface by molten droplet can strongly affect the splat-formation process of thermal-sprayed particles. However, it is difficult to detect the wetting behavior directly with the prevailing technology. Instead, the fundamental static wetting behavior of water droplet onto flat surface was investigated. Static contact angle of water droplet was measured on the substrate under the designated conditions. Figure 2 is a summary of the contact angle measurements in this study. In order to clarify the effect of substrate preheating on the substrate topography change, the surfaces of the substrates with the same thermal-treatment history as wetting study were also observed using atomic force microscope (AFM) covering an area of 1 μm^2 as shown in Fig. 3.

In general, two aspects will be discussed in this article:

(1) Substrate with different durations after preheating; and
(2) Substrate with different preheating temperatures.

3.1.1 Effect of Substrate Durations After Preheating. A part of substrate was preheated to 573 K for 10 min, and then exposed to an air atmosphere for different durations up to 48 h. Figure 2 shows the typical contact angle measurement results. According to the results, the contact angle of water droplets was 91.6° on the unheated AISI304 substrate, which means that wetting of the substrate surface is unfavorable so that the fluid will minimize contact with the surface and form a compact liquid droplet. Meanwhile, a contact angle of 44.2° was maintained on the substrate with duration of 1 h after preheating, which indicates that wetting of the substrate surface is favorable, and the fluid will spread over a large

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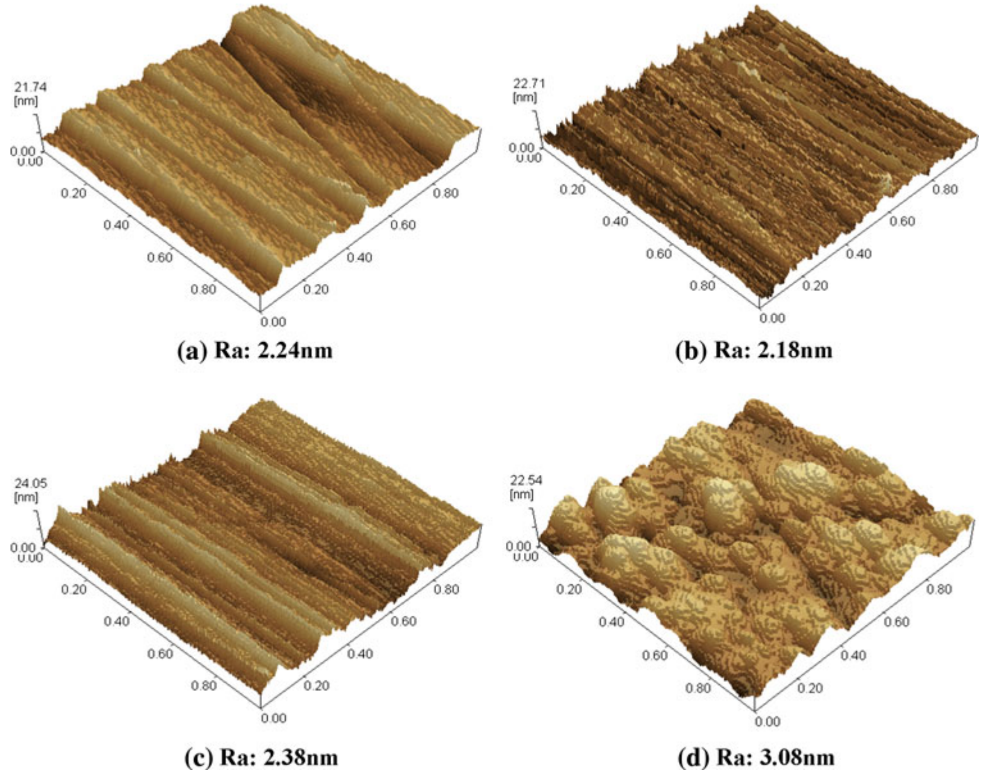

Fig. 3 AFM profiles of AISI304 substrate under designated conditions: (a) unheated; (b) preheated to 573 K, with duration of 1 h; (c) preheated to 573 K, with duration of 48 h; and (d) preheated to 773 K, with duration of 1 h

area of the substrate surface. However, with the increase of duration, the contact angle began to increase gradually. Finally, a contact angle of 84.6°, a value slightly below 90°, was maintained on the substrate for a duration of 48 h, which indicates that the wetting of substrate surface by molten droplet becomes poor with the increase of duration, however, still better than the initial unheated condition.

In order to clarify the reasons of this transition, the substrate surface topography was evaluated by AFM. As the substrate material used in this study was stainless steel, and the substrates were stored for appropriate periods in an atmosphere at room temperature in a dry condition, it is observed that no significant oxidation occurred during the process under this situation. As a result, it was found that no significant topography and surface roughness change took place by increasing substrate duration after heating once to 573 K for 10 min (Fig. 3a-c). Measurement results of R_a of once-heated substrate kept in an air atmosphere at room temperature for a long time revealed that the value was almost the same as the substrate just after cool down from heating, regardless of the elapsed time (Ref 26). Thus, neither the surface topography nor surface roughness change, but some other factors, may have an effect.

Actually, most metal surfaces exposed to air atmosphere will be oxidized to cover a thin oxide film with a thickness over several nanometers. The adsorption to a metal surface will occur usually through the oxide film of the metal at atmospheric pressure. A careful study of adsorbates and condensates at the substrate surface has been conducted by Li and coworkers (Ref 27, 28). It is known that water and other substances can be adsorbed on clean solid surface, but the most common condensate adsorbs water from moisture. Its adsorption on an oxide surface is usually the result of one of the three possible mechanisms, or combinations of them, depending on the temperature of the measurement, intrinsic reactivity of the surface, and the number of defect sites at the surface, as follows:

1. Physisorption of molecular water;
2. Chemisorption of molecular water; and
3. Chemisorption of molecular followed by dissociation.

Physisorption corresponds to very weak interaction between the substrate and adsorbates, it is characterized by the lack of a true chemical bond between adsorbate and substrate. Adsorbed water species will be desorbed when the surface is heated up to a critical temperature. For example, physisorbed water molecules can be completely removed by preheating up to 423 K on TiO_2 substrate (Ref 29). However, chemisorption is a classification of adsorption characterized by a strong interaction between an adsorbate and a substrate surface. The types of strong interactions include chemical bonds of the ionic or covalent variety, depending on the species involved (Ref 30). Hence, the thermal desorption temperature depends on adsorbed features and the subsequent product. Furthermore, this type of adsorption takes place only in a monolayer; it may not be enough to affect the splat deposition and pore-formation process.

In this study, physisorption was considered to be completely removed by the substrate preheating, and a clean surface having nearly no adsorbed gas/condensation can be obtained just after preheating the substrate up to 573 K, so that good wetting can be achieved on the cleaned substrate surface due to the more intimate contact between substrate and liquid droplet. Hence, the static contact angle significantly decreased on the substrate just after preheating, which indicates that the wetting was enhanced through this process. When the substrate was exposed to atmospheric pressure, with the increase of duration, no chemical modifications and surface topography change occurred on the substrate, the re-adsorption of gas/condensation would likely occur and recover the substrate surface gradually, that is the only possible physical change that took place on the substrate surface. Moreover, the slope of the curve as shown in Fig. 2 is sharper at the initial step just after preheating than the later steps, which indicates that there is a typical favorable wetting to normal wetting transition, and that favorable wetting may exist on the substrate without adsorbed gas/condensation at the initial step just after preheating. The velocity of the favorable wetting to normal wetting transition decreased gradually with the re-adsorption of gas/condensation on the substrate surface. In other words, good wetting can be expected when desorption of adsorbed gas/condensation occurred on the substrate surface.

3.1.2 Effect of Preheating Temperature. In this study, two preheating temperatures were used. According to Fig. 2, similar transition tendency of the contact angle was confirmed with the increase of duration on the substrate heated once to 773 K, but lower contact angle was maintained on the substrate with higher preheating temperature after same duration of treatment. McDonald et al. (Ref 17) proposed that heating the substrate cleans the surface and reduces thermal contact resistance. Surface oxidation decreases the ability of a surface to adsorb ambient vapors, and, therefore, less adsorbed gas/condensation on the substrate with higher preheating temperature, which enhanced the wetting. Hyland and coworkers reported that the heat treatment prior to the thermal spraying may have an effect on the content of the various oxides and hydroxides on the surface. However, it is difficult to identify with precision the exact concentration of the elements with the current available technology (Ref 31, 32).

Meanwhile, the surface roughness and topography of the substrate with different preheating temperature evaluated by AFM is shown in Fig. 3(a), (b), and (d). From the figure, it is found that no significant topography and surface roughness change took place on the substrate just heated to 573 K, while the surface roughness increases remarkably after being heated to 773 K, as more valleys and peaks can be observed. Cedelle et al. pointed out that the thickness of the oxide layer may increase, but without changing its composition (Ref 33). It seems that there are two opposite aspects for the influence of surface roughness (Ref 13). First, the roughness would increase the friction of flowing liquid (Ref 34). On the other hand, Wenzel's law proposed that if the original contact angle is less than 90°, then a small increase of surface roughness would lead to a reduction of the contact angle (Ref 35). Our experimental results verified the latter factor. Meanwhile, similar result has been reported by Uelzen and Muller (Ref 36). To summarize, surface roughness increase in nano-scale may promote the wetting.

In summary, the wetting of substrate by liquid droplet can be strongly affected by substrate preheating and different duration. Good wetting may be generated by removing the adsorbed gas/condensation through substrate preheating and surface roughness increase in nano-scale. However, the effect of wetting changes due to substrate preheating and controlling the duration on the flattening behavior of thermal-sprayed particles is still not clear. As a confirmation of the above, splats were collected on substrate with the same thermal-treatment history as contact angle measurement in this experimental study.

3.2 Splat Characterization

As the surface temperature prior to splat deposition is one of the key factors for the splat formation, the substrate surface temperature was measured after preheating. Its temperature decreased with duration. However, it took less than half an hour cooling to room temperature even though the substrate had been preheated to 773 K. Thermal-sprayed Cu particles were collected on the AISI304 substrate through atmospheric plasma spray technique, while keeping all other conditions constant. First of all, collected splats were examined using OM as shown in Fig. 4, it can be observed that the fraction of disk-shaped splat increased significantly just after preheating, but decreased gradually with the increase of duration. Most splats deposited on the unheated substrate performed a typical splash-like shape with a center splat surrounded by a ring of fragments (Fig. 4a), which we named as ring-shaped splash splat. While the splat deposited on the substrate with duration of 1 h after having been preheated to 573 K changed from its original form with splashing to the one without splashing (Fig. 4b) which was defined as disk-shaped splat. However, with the increase of substrate duration, splash splat formed again gradually (Fig. 4c), but the splash fingers always connected with the central solidification area, we named it as radiation-shaped splash splat. In other words, the disk-shaped splat appeared only on the substrate once heated in air, and within a short period after the heating at atmospheric pressure. Moreover, similar transition tendency was confirmed on the substrate once having been heated to 773 K, but the fraction of disk-shaped splat is higher on the substrate with higher preheating temperature with same duration.

The splat morphologies in detail were evaluated using SEM. The top surface morphologies of Cu particles

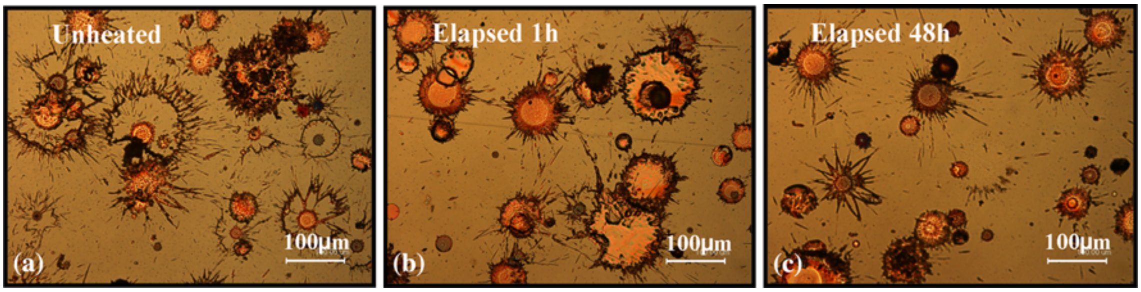

Fig. 4 OM images of splat deposited on AISI304 substrate without preheating and with different durations after preheated to 573 K for 10 min

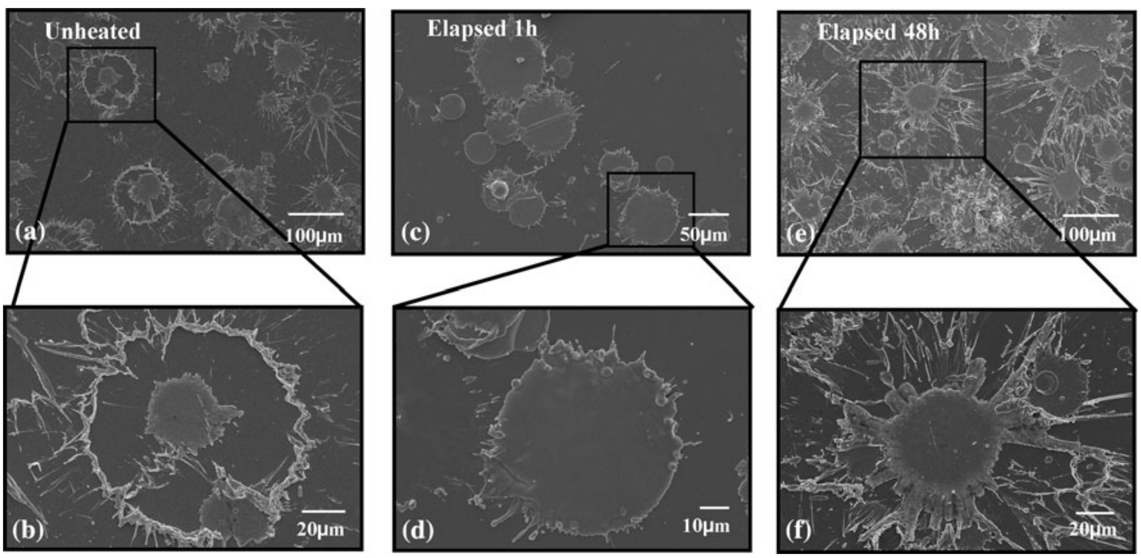

Fig. 5 Top surface morphologies of Cu particles sprayed onto AISI304 substrate without preheating and with different durations after preheated to 573 K for 10 min

sprayed onto AISI304 substrate with different durations after preheating to 573 K are shown in Fig. 5. The shapes of splat deposited on the unheated substrate were splash splat (Fig. 5a). With substrate preheating, typical disk-shaped splat appeared, the central solidification area of the splat was enlarged, and almost no splash fingers can be observed (Fig. 5c). While the splat was deposited on the substrate with duration of 48 h, typical splash splat with longer and sharper splash fingers can be obtained (Fig. 5e). The magnified views of the individual splats are shown in Fig. 5(b), (d), and (f). Splats deposited on the unheated substrate have highly fragmented shapes which generated a large quantity of debris; the splash fingers always do not connect with the center solidification area in this case. Splats prepared 1 h after substrate preheating showed a contiguous disk-like shape. Most splats prepared 48 h after substrate preheating showed a uniform morphology with clear flow pattern and long projections along the periphery of the splat. However, the splash fingers remain always connected with the center solidification area.

The precise observations for the microstructure of the bottom surface of Cu splats deposited under various conditions were conducted as shown in Fig. 6. The splat with splashing obtained on the unheated substrate is shown in Fig. 6(a) and (b), numerous pores were observed at the bottom surface of the splat. When a molten droplet impacts on a polished substrate surface, the lateral flattening of the liquid fluid along the substrate surface takes place. The dynamic impact pressure toward the substrate surface will be generated to keep the fluid flowing along the substrate surface (Ref 27). The impact pressure also forces the adsorbed gas/condensation trapped between the droplet and substrate to rapidly dissolve into the molten metal. The rapid decompression to ambient pressure supersaturates the gas dissolved in the molten metal and causes high nucleation rates of bubbles. Solidification occurs within several microseconds; the bubbles grow somewhat and are pulled by liquid motion before being ''frozen'' into the structure. Finally, the pores are formed (Ref 37). Therefore, the contact at the splat-substrate interface was usually poor with the increase of nano-pores,

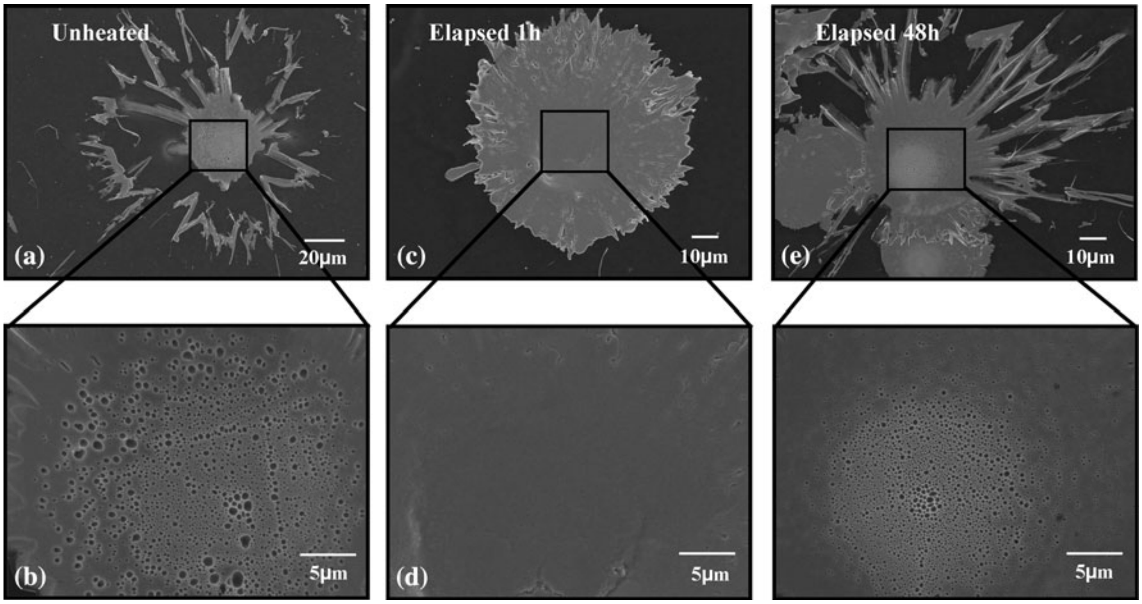

Fig. 6 Bottom surface morphologies of Cu particles sprayed onto AISI304 substrate without preheating and with different duration after preheated to 573 K for 10 min

which may affect the heat transfer from molten droplet to substrate, and finally affect the splat formation. Disk-shaped splat was achieved on the substrate exposed to an air atmosphere for 1 h after preheating as shown in Fig. 6(c) and (d), and almost no pore can be observed from the bottom surface view, due to lack of adsorbed gas/condensation on the substrate surface, and the solidification structure looks quite homogeneous. The pore number, pore area, average size, and area fraction decreased significantly through substrate preheating, which indicated that more intimate contact between the molten droplet and substrate surface during the flattening and solidification process can be expected on the preheated substrate. In other words, the heat transfer efficiency from the molten droplet to the substrate surface was improved. Figure 6(e) and (f) shows the bottom surface view of splat deposited on the substrate with a duration of 48 h after preheating. A large amount of pores were observed again, with most of the pores having gathered in the center solidification area. Re-appearance of these pores may be attributed to the re-adsorption of the gas/condensation on the substrate surface. Similar transition tendency was found on the substrate once heated to 773 K.

In order to get more information of the individual splat, the bottom surface analysis was conducted by software Image-Tool based on the SEM image with a magnification of 4000. Figure 7 shows the area fraction of nano-pores existing at the central area of the splats deposited on the substrate under designated conditions. It can be observed that the fraction decreased significantly just after preheating, and increased along with the increase of duration. In addition, lower fraction existed on the substrate with higher preheating temperature, which should be due to the less adsorbed gas/condensation adsorbed at the substrate surface with higher preheating temperature.

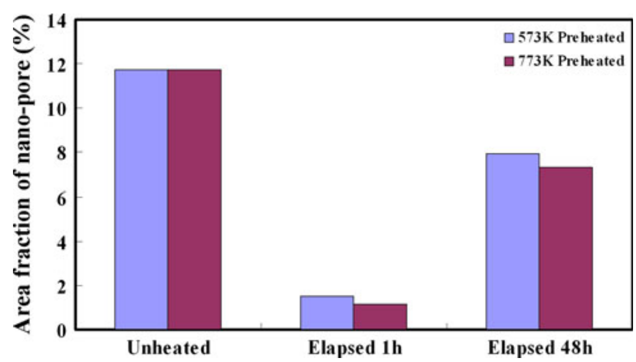

Fig. 7 Dependence of area fraction of nano-pore on substrate preheating temperature and duration

3.3 General Discussions

Based on the study above, it is verified that most of the adsorbed gas/condensation was removed by preheating the substrate (Ref 4, 17, 19, 20, 29), and that more intimate contact and higher cooling rate can be obtained, which resulted in a good wetting. Fukumoto and coworkers already noted (Ref 5, 21, 22) that the contact property of the splat with substrate surface strongly depends on the wetting of the solid substrate by molten droplet, but not the surface oxidation itself. McDonald et al. (Ref 17) reported that by substrate preheating, the oxide film thickness is too low for the effect of thermal contact resistance to be significant. Hyland and coworker also proposed that the splat morphology was not influenced by the thickness of the oxide layer of the substrate surface by simulation method (Ref 31). Moreover, the previous studies (Ref 38-40), both in numerical simulation and experimental observation proposed that, in collision of thermal-sprayed particles onto flat substrate, initial rapid cooling usually occurs and a rapidly solidified layer affects the flattening of the particles. Hence, when the molten droplet impacts on a heated or oxidized surface, contact is improved, and the spread of particles is arrested before fragmentation; the heat transfer at splat/substrate interface is high, so the splat solidifies rapidly. As the temperature inside of the splat decreases rapidly and the viscosity increases, the flattening is restrained because a driving energy for the flattening transfers to viscous energy effectively and finally disk-shaped splat formed (Ref 40). With the increase of duration, re-adsorption of adsorbed gas/condensation takes place on the substrate, which results in the poor wetting. Then, the spread time must be extended, and splash splat re-formed. On the other hand, surface roughness increases in nano-scale promote the wetting. Owing to the better wetting, the boundary of the molten droplet can move on the substrate surface more easily, hence the fluid will spread to cover a larger area of the surface, more intimate contact can be obtained, the increased contact between the splat and substrate increased the viscous dissipation losses (Ref 41). Therefore, solidification behavior of the individual splat should be strongly affected. Actually, the boundary of the molten droplet is in motion during the flattening process, but many aspects of the dynamic wetting are still not clear at present. A more intensive research is necessary in future.

Moreover, a solidification parameter (Θ) which was defined as the ratio of the solid layer thickness (s) to splat thickness (h) was proposed by Dhiman and coworkers (Ref 1, 42) to predict the splat morphology in a thermal-spray process. Hence, by improving the wetting between substrate surface and molten droplet, the solidification behavior of the sprayed particles can be strongly affected. If the solid layer grows by a significant amount during spreading ($s \sim 0.1$-0.3 h, or $H \sim 0.1$-0.3), then it will restrain the splat from spreading too far and becoming thin enough to rupture. In this case, a disk-shaped splat will be produced. This can be treated as the effect of wetting on the flattening behavior of individual thermal-sprayed particle. In brief, although there are not enough direct evidences to prove the sole domination at present, wetting likely has an important role in the thermal-spray process.

3.4 Corresponding Coating Adhesion Strength

The fundamental purpose of investigation on flattening behavior of the individual splat aims to obtain the desired coating's property. Up to now, the thermal-spray process is usually controlled by controlling the spray conditions (Ref 6, 7), measuring the in-flight velocity and temperature of the particles (Ref 43) and by feeding these data back into the input power of the equipment. In this study, Cu coating was fabricated on the blasted AISI304 substrate with the same thermal-treatment history as the wetting behavior investigation and splat collection. Figure 8 shows the cross section microstructures of the fabricated coatings. From the figure, typical multilayer structures can be observed both on the unheated substrate and on the substrate once heated to 573 K but with different durations. Remarkable difference in the contact condition within these cannot be observed.

Figure 9 shows the shear adhesion strength of the fabricated coatings. The shear adhesion strength of the fabricated coating was greatly enhanced on the substrate with duration of 1 h after preheated to 573 K. It also has been pointed out that the adhesion/cohesion of coatings obtained on the rough substrate with high temperature is remarkably higher than that of coatings sprayed on the cold substrates (Ref 44). Pershin et al. (Ref 15) reported

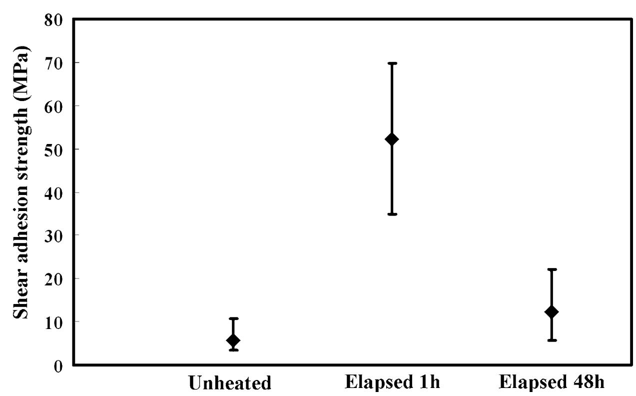

Fig. 9 Shear adhesion strength of Cu coating fabricated on AISI304 substrate without preheating and with different durations after preheated to 573 K for 10 min

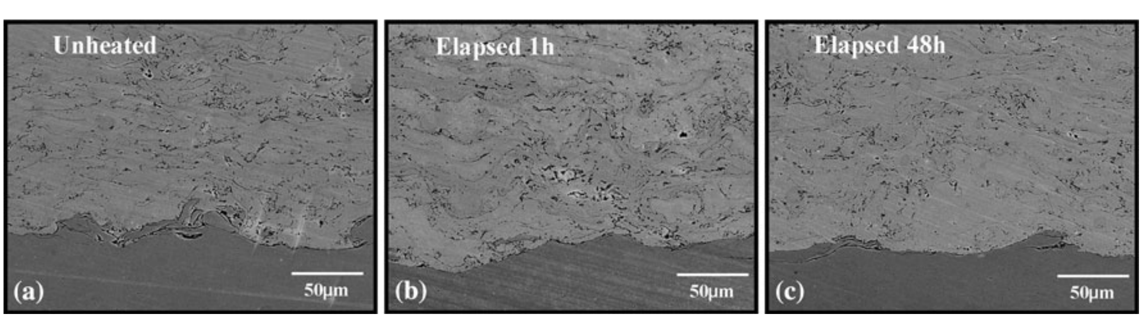

Fig. 8 Cross-sectional microstructures of Cu coating fabricated on AISI304 substrate without preheating and with different durations after preheated to 573 K for 10 min

that when a coupon was heated to 650 °C and allowed to cool before plasma coating, its coating adhesion strength was much less than that of a coating deposited on a surface maintained at 650 °C; hence, surface oxidation by preheating alone did not explain the increase in adhesion strength. However, in this study, the shear adhesion strength decreased significantly with the increase of duration, but still higher than the coating fabricated on the original unheated substrate.

If linking the adhesion strength result to the contact angle study, then it can be found that

(1) The contact angle on the unheated substrate is the largest, corresponding with the worst wetting, and the lowest shear adhesion strength of the coating on the unheated substrate.
(2) Once the substrate was heated, best wetting can be obtained for the smallest contact angle. As a confirmation, highest shear adhesion strength of the fabricated coatings was maintained.
(3) With the increase of substrate duration after preheating, wetting becomes worse, however, still better than that on the unheated substrate. Same tendency was confirmed for the shear adhesion strength.

The comparison above indicates that the shear adhesion strength corresponds well with the wetting study. In general, the adhesion of the initial layer of the coating to the substrate can strongly affect the shear strength of the fabricated coatings, while the initial adhesion is determined by the wetting between substrate surface and molten droplet, that is why the shear adhesion strength of the fabricated coating corresponded quite well to that of the contact angle results, which suggested that wetting is important in the bonding or adherence of two materials. Also, Fukumoto et al. (Ref 45) have noted that, when a surface was polished to a particular average roughness R_a, coating adhesion was not as strong as it was when the same roughness was produced by preheating. Heating the substrate removes moisture and other volatile contaminants on the surface. Hence, the wetting of substrate surface by molten droplet was enhanced, followed by affected solidification behavior (Ref 1, 42).

The mechanisms of adhesion between the fabricated coating and the substrate have a significant influence on the mechanical properties. In general, three different bonding mechanisms are involved in thermally sprayed coating: chemical bonding, physical bonding, and mechanical bonding (Ref 16, 42, 46). Chemical bonding is the one that presents when a chemical reaction takes place at the splat-substrate bonding interface. Physical bonding takes place due to van der Waals' forces which are the weak intermolecular attractions between molecules. Since the van der Waals' forces are relatively weak compared to normal chemical bonds, little energy is needed to overcome the physical bonds. Mechanical bonding takes place when the substrate is roughened by mechanical interlocking, and this bonding mechanism usually prevails for most coatings. In this study, the coating and substrate elements distribution evaluated by EDX is shown in Fig. 10. The figure clearly indicates that neither Cu can be found in the substrate, nor any of the substrate composition elements (for example, Fe, Ni, and Cr) can be observed from the coating view, both for the coatings

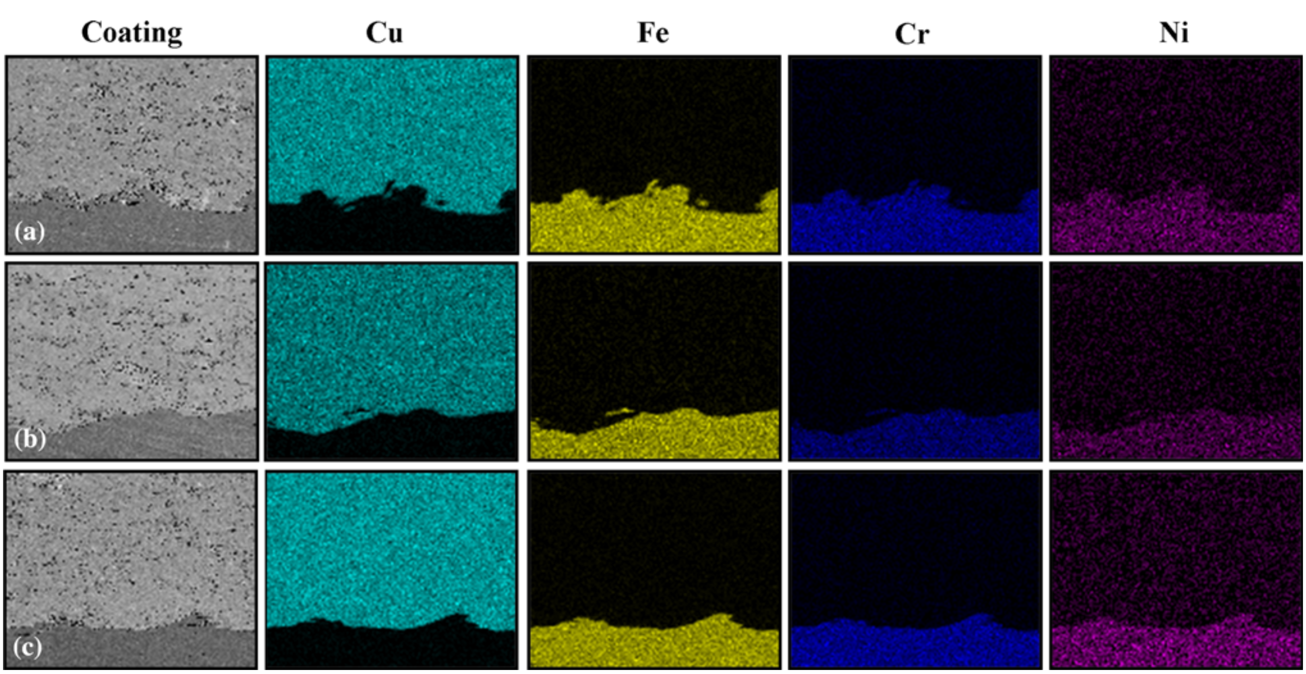

Fig. 10 Cross-sectional microstructure and elements distribution of coating fabricated on AISI304 substrate once heated to 573 K: (a) unheated, (b) elapsed 1 h, and (c) elapsed 48 h

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fabricated on the substrate unheated and substrate once heated to 573 K but with different durations. The result indicates that there has been no significant diffusion and chemical reaction occurring at the interface between the coating and substrate; mechanical bonding is the only bonding mechanism occurring during the thermal-spraying process. In other words, not only the bonding mechanism changed, but also the individual splat formation behavior under designated conditions affected the coating adhesion strength. The mechanical bonding was enhanced by the more intimate contact and improved wetting caused by removing the adsorbed gas/condensation through substrate preheating; hence, the adhesion strength of the coating fabricated on the substrate just after preheating was significantly improved. With the increase of substrate duration, for the re-adsorption of gas/condensation that occurred on the substrate surface, the intimate contact and wetting became poor, the mechanical adhesion was weakened, and, hence, this resulted in the poor adhesion strength between the coating and substrate.

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 (Ref 2, 15, 47-49). The increase of adhesion strength by increasing the preheating temperature may be attributed to the enhanced mechanical adhesion caused by the better wetting and the existence of more valleys and peaks above the critical preheating temperature.

Based on the study of the splat formation process and corresponding coating adhesion strength, all these results indicate that the investigation of the flattening behavior of individual sprayed particle on the substrate surface is significantly meaningful for the practical usage of the thermal-spray process.

4. Conclusions

In order to evaluate the effect of substrate preheating on flattening behavior of thermal-sprayed particles, wetting behavior of water droplet on AISI304 substrate was studied under the designated conditions. Individual Cu particle's flattening behavior and corresponding coating adhesion strength on AISI304 substrate with the same thermal-treatment history as wetting measurement were investigated systematically. The results obtained in this study are summarized as follows:

(1) Splats were collected on the mirror-polished AISI304 substrate. The splat shape had a transitional changing tendency from a splash splat to a disk-shaped one on the substrate with a short duration after preheating. Wetting of substrate surface by molten droplet may dominate the flattening behavior of thermal-sprayed particles. The good wetting may be generated by removing the adsorbed gas/condensation through substrate preheating. Moreover, surface roughness, increased in nanometers scale, also promoted the wetting. On the other hand, radiation-shaped splash splat re-appeared with the increase of duration after substrate preheating due to the poor wetting, the re-adsorption of adsorbed gas/condensation likely leads to the poor wetting.

(2) No remarkable differences of coating microstructure and contact condition between coating and substrate can be observed. While coating adhesion strength was enhanced just after preheating, but it weakened with the increase of substrate duration, which has the similar changing tendency to the wetting study and splat morphologies change. The results suggest that the coating adhesion change was attributed to the individual splat formation behavior than bonding mechanisms.

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