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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.surfcoat.2007.04.041>

Surface & Coatings Technology, 202, 1, pp. 23-33, 2007-04-21

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Effect of substrate oxidation on spreading of plasma-sprayed nickel on stainless steel

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Received 13 November 2006; accepted in revised form 16 April 2007

Available online 21 April 2007

Abstract

Plasma-sprayed, molten nickel particles ($\sim 60\ \mu\text{m}$ diameter) were photographed during impact on oxidized 304L stainless steel surfaces that were maintained at either room temperature or at $350\ ^\circ\text{C}$. Steel coupons were oxidized by heating them at different temperatures. A fast charge-coupled device (CCD) camera captured time-integrated images of the spreading splat. A two-color pyrometer collected thermal radiation from particles and recorded the evolution of their temperature after impact. Molten nickel particles impacting on oxidized steel at room temperature fragmented significantly, while heating the surfaces produced splats with disk-like morphologies. Impact on steel that was highly oxidized induced the formation of finger-like splash projections at the splat periphery. Thermal contact resistance between splats and non-heated oxidized steel was calculated from splat cooling rates and found to decrease as the degree of oxidation increased. On heated, oxidized steel thermal contact resistance was much lower and did not change significantly with the degree of oxidation. It was concluded that thermal contact resistance was largely influenced by adsorbates on the steel surface that evaporated when the surface was heated or oxidized.

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Keywords: Plasma spraying; Particle impact; Adsorbates; Surface oxidation; Splashing

1. Introduction

Experimental studies have shown that many factors influence the spreading, fragmentation, and splashing of plasma-sprayed particles impacting a surface [1–6]. Fantassi et al. [2] varied the impact velocity of plasma-sprayed zirconia particles landing on smooth stainless steel substrates and found that the diameter of flattened splats increased as impact velocity increased. Similar results were obtained by Mehdizadeh et al. [7] during impact of water droplets on stainless steel. It was found that in addition to increasing maximum splat diameter, increasing impact velocity promoted splat fragmentation and material loss [7].

Surface conditions such as roughness also influence splat spreading and splashing. Moreau et al. [4] studied the spreading of plasma-sprayed molybdenum on grit-blasted molybdenum substrates. Two-color pyrometry was used to show that in-

creased surface roughness decreased the flattening degree and the flattening time of the spreading particles. Shakeri and Chandra [3] photographed the impact and spreading of millimetre-sized molten tin droplets on rough stainless steel. It was shown that increasing surface roughness enhanced the tendency of droplets to splash. However, increasing roughness beyond a critical value suppressed splashing [3].

Heating the substrate will change splat morphology, as shown by experiments in which nickel, copper, or molybdenum particles were plasma-sprayed on heated glass or stainless steel substrates [5,8,9]. Splats on heated surfaces had disk-like morphologies with negligible splashing. Impact on substrates at room temperature produced splats with irregular morphologies that appeared to have disintegrated during impact.

Heating a surface can influence the dynamics of an impacting plasma-sprayed particle in several ways. One expects higher substrate temperature to reduce splat cooling rate; however, experiments have shown the reverse to be true. Raising substrate temperature increases heat transfer from the molten particle and increases its solidification rate [9]. Heating the

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Fig. 1. Schematic of the experimental assembly.

surface cleans it by vaporizing adsorbed contaminants. Heating a metal surface in air oxidizes it, and the oxide film changes the surface thermal properties, topography and wettability, all of which affect heat conduction.

It has been suggested that splat fragmentation and splashing on non-heated surfaces is due to a gas barrier between the splat

and surface [5,10,11]. This gas barrier, formed due to vaporization of surface adsorbates beneath the molten particle, reduces physical contact between the splat and substrate. The splat spreads on the gas barrier into a thin fluid sheet, which eventually disintegrates and flies off the surface [9,12]. Heating the surfaces vaporizes the adsorbates before impact, permitting

Fig. 2. Images of nickel splats after solidification on non-heated stainless steel preoxidized at A) 150 °C, B) 250 °C, C) 350 °C, and D) 650 °C.

increased splat–substrate contact during spreading and the formation of disk-like splats [5,9–11]. The density and viscosity of the gas surrounding the impinging droplets may also play a role in their flattening and fragmentation of upon impact as reported by Xu et al. [13].

Prolonged heating of metal substrates at high temperatures promotes the growth of a surface oxide layer [14,15]. Pershin et al. [16] showed images of nickel splats after solidification on heated stainless steel surfaces. Particles impacting on steel heated to 640 °C produced disk-like splats with finger-like splash projections around the periphery; impact on steel at 340 °C produced disk-like splats without splash projections. It was suggested that the presence of a nano-scale thick oxide layer improved contact between the splat and substrate at 640 °C, increasing splat cooling and solidification, and promoting splashing. Measuring the splat cooling rates on substrates oxidized to different degrees would confirm this hypothesis.

Atomic force microscopy (AFM) has been used to characterize the surface topology of metal surfaces exposed to prolonged heating [17–20]. It was shown that the nano-scale roughness of oxidized substrate surfaces influences splat morphology and cooling [18,19]. Skewness and kurtosis – two roughness parameters that describe the shape of the asperities on the rough surfaces – were used to show that on non-heated oxidized metals, the splat morphology was disk-like and the cooling rates were higher [18,20]. However, Fukumoto et al. [19] have suggested that even though changes in the surface topology of the oxidized metals influence splat morphology and cooling, adsorbates on the surfaces have greater influence on these parameters. Further experimental studies are needed to confirm this hypothesis.

The objectives of this study were to: (i) photograph splats formed by impact of plasma-sprayed nickel particles on oxidized stainless steel substrates; (ii) use two-color pyrometry to measure the temperature evolution and cooling rates of splats on these surfaces; and (iii) determine the effect of varying the degree of substrate oxidation on splat morphology and cooling rate.

2. Experimental method

Fig. 1 shows a schematic diagram of the experimental setup. A SG100 plasma torch (Praxair Surface Technologies, Indianapolis, IN, USA) was used to melt and accelerate nickel powder particles (56C-NS, Sulzer Metco, Westbury, NY, USA), sieved to $-63+38\ \mu\text{m}$. The powder feed rate was less than 1 g/min. The substrates were oxidized, rectangular 304L stainless steel samples, cut 2.5 cm wide by 8 cm long. The steel samples were heated in a high temperature furnace (Heatech Furnace, Lab-line Instruments, Inc., Melrose Park, IL, USA) for 30 min at 150 °C, 250 °C, 350 °C, or 650 °C to promote the growth of surface oxide layers. All samples were allowed to cool in air to room temperature. Some samples were reheated to 350 °C during spraying by placing them in a copper substrate holder that included cartridge heaters (Omega, Laval, QC, Canada).

The plasma torch was operated with a voltage of 35 V and a current of 700 A. The plasma gas mixture was argon at a flow rate of 50 liters per minute (LPM) and helium at 20 LPM. The

torch was passed rapidly across the substrates. In order to protect the substrate from an excess of particles and heat, a V-shaped shield was placed in front of the torch. This V-shaped shield had a 3.5 mm hole through which particles could pass. To reduce the number of particles landing on the substrate, two additional barriers were placed in front of the substrate, the first of which had a 1 mm hole and the second, a 0.6 mm hole. All the holes were aligned to permit passage of the particles with a horizontal trajectory (Fig. 1).

After exiting the third barrier and just before impacting the substrate, the thermal radiation of the particles was measured with a fast two-color pyrometric system. Mehdizadeh et al. [12] have described this system in detail. The system included an optical sensor head that consisted of a custom-made lens, which focused the collected radiation, with 0.21 magnification, onto an optical fiber with an 800 μm core [12]. This optical fiber was covered with an optical mask that was opaque to near infrared radiation, except for three slits. Two of the slits, with dimensions of 30 μm by 150 μm and 30 μm by 300 μm , were used to detect the thermal radiation of the in-flight particles. The

Fig. 3. Images of nickel splats after solidification on stainless steel heated to 350 °C: A) non-preoxidized, B) preoxidized at 250 °C, and C) preoxidized at 650 °C.

radiation was used to calculate the temperature and velocity of the in-flight particles [12,21]. The largest slit, measuring 150 μm by 300 μm , was used to collect thermal radiation of the particle as it impacted and spread on the substrate. With the thermal radiation from this slit, the splat temperature, diameter, and cooling rate were calculated at 100 ns intervals after the impact. The droplet average in-flight velocity was calculated by dividing the known distance between the centers of the two smaller slits by the measured time of flight. The distance between the centers of the two small slits was 60 μm .

The collected thermal radiation was transmitted through the optical fiber to a detection unit that contained optical filters and two photodetectors. The radiation beam was divided into two equal parts by a beam splitter. Each signal was transmitted through a band pass filter with a wavelength of either 785 nm or 995 nm and then detected using a silicon avalanche photo detector (model C30817, RCA, Durant, OK, USA). The photo detector had a response time smaller than 0.1 μs [22]. The ratio of the radiation intensity at these wavelengths (referred to as D_1 and D_2 , respectively) was used to calculate the particle temperatures with an accuracy of ± 100 $^{\circ}\text{C}$ [21]. The signals were recorded and stored by a digital oscilloscope.

A 12-bit CCD camera (QImaging, Burnaby, BC, Canada) was used to capture images of the spreading particles. The electronic shutter of the camera was triggered to open by a signal from the D_4 sensor (Fig. 1). The camera was attached to a 30 cm long optical extension tube that was connected to a diaphragm (Tominon, Waltham, MA, USA). The diaphragm included a lens with a 135 mm focal length and an f -stop from 4.5 to 32. The diaphragm was set to an f -stop of 16, so that the diameter of the opening was 8.4 mm. In order to photograph the

Table 1

Average maximum spread factors ($\xi_{\text{max}} = D_{\text{max}}/D_0$) and maximum spread diameters (D_{max}) of nickel splats on preoxidized stainless steel (not heated during spraying)

Preoxidizing temperature $^{\circ}\text{C}$	150	250	350	650
ξ_{max}	9.7 ± 0.2	10.4 ± 0.3	10.8 ± 0.3	9.5 ± 0.2
D_{max}	μm 525 ± 10	640 ± 20	655 ± 20	520 ± 15
D_0	μm 54.7 ± 1.5	62.2 ± 2.2	60.8 ± 1.5	55.0 ± 1.5

in-flight particles and the splats, the shutter of the camera was opened for about 500 μs , with no added illumination. This produced single, time-integrated images of the splats. The images captured by the camera were then digitized by a frame grabber and recorded on a personal computer.

3. Results and discussion

Nickel was plasma-sprayed on oxidized stainless steel samples that were either held at room temperature or heated to 350 $^{\circ}\text{C}$ during spraying. The average in-flight particle velocity was 70 m/s and the average in-flight temperature was 2130 $^{\circ}\text{C}$, while the standard deviations were 6 m/s and 100 $^{\circ}\text{C}$, respectively.

Fig. 2 shows scanning electron microscope (SEM) images of splats after spreading and solidification on preoxidized steel coupons kept at room temperature during spraying. On a surface preoxidized at 150 $^{\circ}\text{C}$ (Fig. 2A) the splat had almost completely broken up, with a small central portion intact surrounded by annular rings of debris. The final splat diameter, indicated beneath each image, was that of the central portion of the splat that remained mostly intact, excluding the surrounding

Fig. 4. Images of nickel splats on non-heated stainless steel preoxidized at A) 150 $^{\circ}\text{C}$, B) 250 $^{\circ}\text{C}$, C) 350 $^{\circ}\text{C}$, and D) 650 $^{\circ}\text{C}$.

fragments or fingers formed due to splashing. As the preoxidizing temperature increased, the central core became larger (Fig. 2B and C), and the splat on steel preoxidized at 650 °C (Fig. 2D) was significantly larger than the others.

Photographs of plasma-sprayed particles impacting on non-heated substrates have shown that they produce splats with very large maximum spread diameters and significant loss of material [9,12]. This was attributed to the presence of a gas barrier, formed by evaporation of adsorbed surface contaminants, between the splat and substrate that restricted contact between the two surfaces [9]. The splat spread into a thin liquid sheet, disintegrated, and splashed off the surface, leaving a solidified core that was significantly smaller than the splat at the maximum extent. On heated substrates, where contact was improved, the splat spread to a smaller extent and material loss was greatly reduced [9].

On heated preoxidized steel, material loss and splat fragmentation were greatly reduced. Fig. 3 shows SEM images of

Fig. 5. Images of nickel splats on stainless steel heated to 350 °C: A) non-preoxidized, B) preoxidized at 250 °C, and C) preoxidized at 650 °C.

Table 2

Average maximum spread factors ($\xi_{\max} = D_{\max}/D_o$) and maximum spread diameters ($D_{\max}$) of nickel splats on preoxidized stainless steel (heated to 350 °C during spraying)

Preoxidizing temperature	°C	None	250	650
$\xi_{\max}$		5.7±0.3	5.5±0.3	5.1±0.2
$D_{\max}$	μm	355±10	355±15	270±5
D_o	μm	63.1±3.6	65.9±4.0	54.1±3.2

splats formed on stainless steel surfaces heated to 350 °C during spraying. There were little differences between splats on a substrate that had not been preoxidized (Fig. 3A) and that which had been preoxidized by heating it to 250 °C (Fig. 3B). On steel oxidized at 650 °C (Fig. 3C), finger-like projections radiated out from the splat, similar to those previously seen by Pershin et al. [15] for plasma-sprayed nickel particles on highly oxidized stainless steel. A possible explanation for the fingers is that they were due to solidification of the splat periphery before spreading was complete. The solidified portion acted as an impediment to flow during spreading of the rest of the fluid, promoting splashing. Such radial fingers are indicative of high splat cooling rates and low thermal contact resistances between the impacting droplet and substrate.

Impacting particles were photographed to measure the maximum extent to which they spread. Fig. 4 shows time-integrated images of different particles on preoxidized stainless steel held at room temperature during spraying. The steel samples were preoxidized at 150 °C. The in-flight diameter was estimated by measuring the width of the streak-like comet. Table 1 shows average values of initial particle diameters (D_o), maximum spread diameters ($D_{\max}$), and maximum spread factors ($\xi_{\max} = D_{\max}/D_o$) of splats, which ranged from 9.5 to 10.8. Due to the low intensity of the splat images in some cases, it was difficult to measure the splat diameter. The best possible measurements were made in cases where the splat was visible.

Preoxidizing stainless steel substrates at different temperatures changed the morphology of the splats significantly. In Fig. 4A the splat appeared circular at its maximum extent on steel preoxidized at 150 °C. The circular morphology of this splat is similar to those reported for molybdenum on non-heated mirror-polished inconel and glass [9,18]. As the preoxidizing temperature and degree of surface oxidation were increased, the morphology of the splats at the maximum extent became significantly distorted (Fig. 4B and C), as a result of changes in splat morphology. On the surface preoxidized at 650 °C (Fig. 4D), the intensity of the splat image was much lower, indicating that the radiation emitted had diminished more rapidly due to the faster cooling rate as compared to previous images.

Fig. 5 shows time-integrated images of splats on heated stainless steel substrates. Fig. 5A shows an image on a heated stainless steel sample that was not preoxidized; Fig. 5B and C shows images of splats on oxidized stainless steel, preheated at 250 °C and 650 °C, respectively, cooled, and then heated to 350 °C during spraying. The images of Fig. 5 show that the morphology of the splats on the heated surfaces is similar: the splats are circular and disk-like with little or no fragmentation

Fig. 6. Typical cooling curves of nickel splats on non-heated stainless steel preoxidized at A) 150 °C, B) 250 °C, C) 350 °C, and D) 650 °C.

and splashing. When the preoxidized substrates are heated during spraying, the degree of oxidation does not appear to influence the splat morphology significantly. Table 2 shows average splat maximum spread factors and maximum diameters on each heated surface. The results reported in the table show that the maximum spread factors on the heated steel surfaces are only slightly affected by the degree of oxidation. The maximum spread factors reported in Table 1 for splats on non-heated steel are almost two times larger than those on heated steel (see Table 2). Previous studies show similar results for a variety of plasma-sprayed materials [9,18].

On non-heated oxidized steel, the maximum spread diameters (520–655 μm) shown in Table 1 were significantly larger than the final spread diameters (40–155 μm) shown in Fig. 2. The difference was due to splat fragmentation and material loss. At the maximum spread extent, the average splat diameters on the heated steel samples ranged from 270 μm to 355 μm (Fig. 5 and Table 2). Fig. 3 shows that the final spread diameters were larger (170–195 μm) and closer to the maximum spread diameters, indicating reduced material loss.

Fig. 6 shows typical cooling curves of nickel splats on non-heated, oxidized stainless steel coupons. Straight lines of best fit are drawn through each curve, starting at the time the splats reached their maximum extent. Splat temperatures at that point are indicated, confirming that they were well above the melting point of nickel (1455 °C). The slopes of these lines were defined to be the cooling rate (dT/dt) of the splat, indicated in Fig. 6. Cooling rates increased with preoxidizing temperature, increas-

ing from 3.0×10^7 K/s on a surface preoxidized at 150 °C (Fig. 6A) to 9.4×10^7 K/s on a surface preoxidized at 650 °C (Fig. 6D). A similar trend has been previously observed for impact of molybdenum particles on preheated inconel [18].

Splat cooling rates increased significantly on steel surfaces that had been preheated. Fig. 7 shows cooling curves of nickel particles spreading on stainless steel surfaces heated to 350 °C during spraying that were either not preoxidized (Fig. 7A), or preoxidized at either 250 °C (Fig. 7B) or 650 °C (Fig. 7C). On these surfaces, the cooling rate was as high as 1.0×10^8 K/s, even on non-oxidized steel, and increased to 1.5×10^8 K/s on steel oxidized at 650 °C.

Measured cooling rates are shown in Fig. 8 as a function of preoxidizing temperature, for both heated and non-heated stainless steel. Each data point is the average of at least 4 samples and the error bars show the standard errors of the mean. Splat cooling rates on heated surfaces were significantly higher than those on non-heated surfaces, and cooling rates on both sets of substrates increased with preoxidizing temperature.

A mathematical model was developed [23] to estimate the thermal contact resistance between the splat and substrate, by assuming that the splat was a thin disk at temperature, T_s , and the substrate was a flat surface at temperature, T_w that was suddenly brought into contact. Heat flux (q) flowed from the splat to the substrate by one-dimensional heat conduction across a thermal contact resistance, $R_c = (T_s - T_x)/q$, created by imperfect contact. The model uses measured values of splat cooling to estimate thermal contact resistance values from a

Fig. 7. Typical cooling curves of nickel splats on stainless steel heated to 350 °C: A) non-preoxidized, B) preoxidized at 250 °C, and C) preoxidized at 650 °C.

solution of the one-dimensional, transient heat conduction equation [23]. The values of contact resistance calculated with this model are shown in Fig. 9. The thickness of the steel samples was 0.75 mm. Thermal properties of molten nickel and solid 304L stainless steel were taken from the literature [24–26]. Thermal contact resistance on non-heated surfaces decreased significantly as the surfaces became more oxidized. On heated surfaces thermal contact resistance was an order of magnitude lower and decreased by only a small amount when substrates were preoxidized.

An oxide film can affect heat transfer in three different ways: (i) the oxide layer itself may act as a thermal barrier; (ii) it may change the surface topology and consequently the contact area between the splat and substrate; and (iii) it may affect the adsorption of contaminants, such as water vapor, on the surface.

Fig. 8. Splat cooling rate (dT/dt) as a function of preoxidizing temperature.

The thermal resistance of the oxide layer can be estimated, to within an order of magnitude, by assuming that it is of uniform thickness, t with thermal conductivity, k . The thermal resistance of this film is

$$R_{\text{oxide}} = \frac{t}{k}, \quad (1)$$

Pershin et al. [14] measured the oxide film thickness on 304L stainless steel coupons heated to 650 °C, held at constant temperature for 2 min, and air-cooled to room temperature for a total cycle of 50 min. The total oxide deposit thickness was 288 nm, consisting of layers of chromium oxide (204 nm thickness) and iron oxide (84 nm thickness). Using oxide thermal conductivities from the literature [27,28] and a thickness weighted average, it was found that $k=8.5$ W/m K and $R_{\text{oxide}}=3.4 \times 10^{-8}$ m² K/W. The oxide thermal resistance (R_{oxide}) is several orders of magnitude lesser than the R_c values measured in Fig. 9. So, the thermal resistance of the oxide layer is a negligible portion of the total thermal contact resistance.

Atomic force microscopy (AFM) was used to determine the roughness and topography of the substrate surface. Fig. 10 shows the surface topologies of stainless steel samples subjected to preheating to promote oxidation. Increasing the pre-oxidizing temperature of the steel greatly increases the number of asperities (Fig. 10D and E), as the oxide layer becomes thicker. Three parameters for characterizing the roughness were

Fig. 9. Thermal contact resistance (R_c) as a function of preoxidizing temperature.

Fig. 10. Surface topologies of stainless steel surfaces either A) non-oxidized or preoxidized at B) 150 °C, C) 250 °C, D) 350 °C, and E) 650 °C.

studied: average roughness (R_a), skewness (R_{sk}), and kurtosis (R_{ku}). The average roughness is the arithmetic average of the height of the surface asperities, above a hypothetical, smooth plane [29]. The skewness shows the degree of symmetry of the rough surface profile and can be used as a measure of the balance between the peaks and valleys of the asperities [30]. The kurtosis shows the degree of pointedness or bluntness of the asperities on the surface [30]. Smaller skewness values

indicate that the surface has asperities with large plateaus and single deep valleys, while larger skewness values are typical of surfaces with isolated, steep peaks [30,31]. Smoother surfaces will have smaller kurtosis values, while surfaces with steep asperities will exhibit larger kurtosis values [30,31]. Contact with a surface having smaller skewness and kurtosis values will be improved as the asperities become flatter and smoother [18].

Table 3
Average roughness (R_a), skewness (R_{sk}), and kurtosis (R_{ku}) of preoxidized stainless steel

Preoxidizing temperature	Preoxidized, but not reheated				Preoxidized and reheated to 350 °C		
	150 °C	250 °C	350 °C	650 °C	Non-preoxidized	250 °C	650 °C
R_a (nm)	1.2	0.60	2.9	40.3	3.6	4.3	32.0
R_{sk}	0.45	0.90	0.75	0.40	0.95	1.7	0.70
R_{ku}	5.3	8.1	3.5	3.2	6.5	10.5	5.2

Table 3 shows values of average roughness, skewness and kurtosis for two sets of steel substrates. The first were preoxidized at different temperatures (150 °C, 250 °C, 350 °C and 650 °C) and then cooled to room temperature. The others were preoxidized at either 250 °C or 650 °C, cooled, then heated to 350 °C while spraying, and then cooled again. Increasing the preoxidizing temperature to 650 °C increased the average roughness significantly, while decreasing R_{sk} and R_{ku} . Lower oxidizing temperatures did not produce significant changes in surface topography. The second heating cycle did not appear to change the surface noticeably; the surface oxidized at 650 °C was again the one with largest surface roughness.

Changes in surface roughness do not appear to be sufficient to explain the decrease in thermal contact resistance observed with surface oxidation. Thermal contact resistance decreases significantly on non-heated steel when the surface is oxidized at 250 °C (Fig. 9), even though surface roughness does not change markedly (Table 3). The order of magnitude difference between thermal contact resistance on the heated and cold surfaces

(Fig. 9) does not correspond to any major difference in surface roughness parameters (Table 3).

Neither oxide film thermal resistance nor surface roughness changes can fully explain the reduction in thermal contact resistance with surface heating or oxidation. The remaining explanation appears to be that adsorbates on the surface vaporize under an impinging particle and create an insulating vapor film. Jiang et al. [10] have previously demonstrated that condensates play an important role in splat fragmentation. Particles sprayed onto substrates that had previously been placed in a vacuum chamber, to eliminate adsorbates, formed disk splats, whereas those on contaminated surfaces fragmented. It has been shown that desorption of water molecules begins when stainless steel surfaces are heated to 230 °C [32]. Heating substrates to a temperature of 350 °C before spraying, as in our experiments, would vaporize adsorbed materials and clean their surface. This ensured good splat–substrate contact and greatly reduced thermal contact resistance on heated stainless steel.

Fig. 11. High magnification images of nickel splats after solidification on non-heated stainless steel preoxidized at A) 150 °C, B) 250 °C, C) 350 °C, and D) 650 °C.

It is more difficult to understand why preheating a surface and then cooling it should reduce thermal contact resistance. Adsorption of water molecules and other contaminants on the metal substrates typically occurs at defect sites on the surface [33,34]. Preheating the substrates forms an oxide layer that changes the defect sites [33,35] and reduces readsorption of contaminants during cooling. Kawasaki et al. [33] showed that when porous glass is heated above 350 °C, then cooled, less water was readsorbed than on a surface that had never been heated. Kittaka et al. [35] have shown that preheating chromium oxide reduces the ability of the surface to adsorb water, and that increasing the preheating temperature reduces the adsorption of water even further.

Close examination of SEM images of splats after spreading and solidification (Fig. 11) on preoxidized steel held at room temperature shows the existence of holes in the splats on surface preoxidized at 150 °C (Fig. 11A) or 250 °C (Fig. 11B). Holes in the solidified splats have been attributed to the presence of gases entrapped between the splats and non-heated substrates [36,37]. Preoxidizing the surfaces at temperatures above 350 °C, eliminated the appearance of these holes (Fig. 11C and D), as did heating the surface during spraying (Fig. 3). This supports the hypothesis that either heating or highly oxidizing the surface reduces the presence of gases at the splat–substrate interface that are created by evaporation of adsorbed substances.

Heating to oxidize a metal surface may change the surface chemistry, permitting other factors to play a role in generating the results observed in this study. Even though the desorption and readsorption of adsorbates appears to play a vital role, other mechanisms may be involved. It is possible that the surface chemistry changes induced by oxidation also changed the dynamic wetting behavior of the droplet or the rate of adsorption and desorption of contaminants. These would be difficult to measure for high-speed plasma-sprayed droplets with current technology, and remain the subject of future studies.

4. Conclusion

The influence of substrate surface oxidation on splat morphology, splat cooling rates, and thermal contact resistance between the splat and substrate was studied. Plasma-sprayed nickel particles that impacted on preoxidized stainless steel at room temperature fragmented, whereas those on heated oxidized stainless steel remained intact and formed disk-like splats. As the degree of oxidation was increased, splat break-up decreased on non-heated surfaces. Thermal contact resistance, calculated from measured splat cooling rates, was much lower on heated steel surfaces than on those held at room temperature during spraying. Thermal contact resistance also decreased with increased surface oxidation.

Three possible effects of surface oxidation on thermal contact resistance were examined. The oxide film may itself create an insulating layer, but the film thickness is too low for this to be significant. Oxidation produces changes in surface roughness, which may alter splat–substrate contact area. However, surface roughness changes do not correlate with changes in thermal contact resistance. The oxide film may also affect the dynamic

wetting behavior of the droplet or the rate of adsorption and desorption of contaminants. However, the most probable hypothesis appears to be that thermal contact resistance is caused largely by adsorbed contaminants on the substrate, that vaporize when a hot particle impacts and forms an insulating vapor film. 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 also lowers thermal contact resistance.

When an impacting particle has poor contact with the substrate, it remains liquid long enough to spread into a thin film until it disintegrates. On a heated or oxidized surface, contact is improved and the spread of particles is arrested before they fragment, producing disk splats. If contact is very good, the periphery of the molten particle may freeze during spreading, obstructing the flow of liquid and creating fingers along the edges.

Acknowledgements

This work was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC). The authors gratefully acknowledge the technical assistance of M. Lamontagne with the assembly of the experimental apparatus and the operation of the plasma-spraying equipment.

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