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Effect of Substrate Temperature on Adhesion Strength of Plasma-Sprayed Nickel Coatings

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We plasma-sprayed nickel coatings on stainless steel and cobalt alloy coupons heated to temperatures ranging from room temperature to 650 °C. Temperatures, velocities, and sizes of spray particles were recorded while in-flight and held constant during experiments. We measured coating adhesion strength and porosity, photographed coating microstructure, and determined thickness and composition of surface oxide layers on heated substrates. Coating adhesion strength on stainless steel coupons increased from 10-74 MPa when substrate temperatures were raised from 25-650 °C. Coating porosity was lower on high-temperature surfaces. Surface oxide layers grew thicker when substrates were heated, but oxidation alone could not account for the increase in coating adhesion strength. When a coupon was heated to 650 °C and allowed to cool before plasma-spraying, its coating adhesion strength was much less than that of a coating deposited on a surface maintained at 650 °C. Cobalt alloy coupons, which oxidize much less than stainless steel when heated, also showed improved coating adhesion when heated. Heating the substrate removes surface moisture and other volatile contaminants, delays solidification of droplets so that they can better penetrate surface cavities, and promotes diffusion between the coating and substrate. All of these mechanisms enhance coating adhesion.

Keywords coating adhesion, plasma spraying, substrate temperature

1. Introduction

To ensure strong adhesion of a thermal spray coating it is necessary to carefully prepare the substrate on which the coating is to be applied. Typically the substrate is grit-blasted, creating a rough surface pitted with tiny craters into which impinging droplets flow before they freeze. Mechanical interlocking between solidified droplets and the substrate produces durable bonds.

Coating strength is enhanced if droplets penetrate deep into surface cavities before they freeze. Coating properties are therefore highly dependent on fluid flow and heat transfer during droplet impact and are affected by both surface roughness and temperature. However, while the importance of controlling surface roughness is well understood in the thermal spray industry, the effect of varying substrate temperature is not as clear. Besides cooling the substrate sufficiently to prevent thermal distortion while spraying, coating applicators rarely make much effort to monitor or control substrate temperature.

Most studies into the effect of varying substrate temperature have examined splats formed by impact and flattening of individual droplets. Bianchi et al. demonstrated that the shape of splats formed by spraying alumina or zirconia droplets from a plasma torch onto a stainless steel plate varied as substrate temperature was increased.[1] Droplets landing on a cold substrate (below 100 °C) splashed extensively after impact and had very irregular contours, while those deposited on a hot surface (above 150 °C) were disk-like, almost perfectly circular. Other researchers[2-8] also observed this change of splat shape and showed that the "transition temperature," above which disk splats were obtained, was a complex function of particle and substrate material properties, [3] surface contamination,[4] and surface oxidation.[5] Fukomoto et al.[6] proposed that freezing along the bottom of an impinging droplet causes splashing: liquid flowing on top of the solid layer jets off and splashes. Delaying solidification, either by raising surface temperature or increasing thermal contact resistance at the droplet-substrate interface, is expected to suppress splashing.

In earlier studies we have observed the shape of individual splats formed by plasma-spraying nickel particles onto stainless steel coupons.[7-9] Figure 1 shows micrographs of splats produced by spraying nickel powder,[7] sieved to give a size distribution of +53-63 μm, onto stainless steel surfaces maintained at either 290 °C (Fig. 1a) or 400 °C (Fig. 1b). Particle temperature upon impact was measured to be 1600 ± 220 °C, and impact velocity was 73 ± 9 m/s. On the colder surface there was evidence of splashing and droplet break-up, while splats on the hotter surface were circular. Computer simulations[8,9] offered an explanation for this transition: freezing around the edges of spreading droplets caused splashing. Solidified metal acted as an obstruction to flow, triggering splashing. Reducing heat transfer from the droplet slowed solidification and allowed the droplet to spread into a disk before freezing. We found earlier that the rate of solidification was much more sensitive to values of thermal contact resistance than to substrate temperature.[9] Raising substrate temperature from 290- 400 °C had little effect on impact dynamics, but increasing thermal contact resistance from 10^{-7} m^2K/W to 10^{-6} m^2K/W diminished heat transfer sufficiently to prevent splashing (Fig. 2).

Thermal contact resistance can be created by gases or solid impurities trapped at the droplet-substrate interface. In our experiments the stainless steel coupon was heated in air so that an

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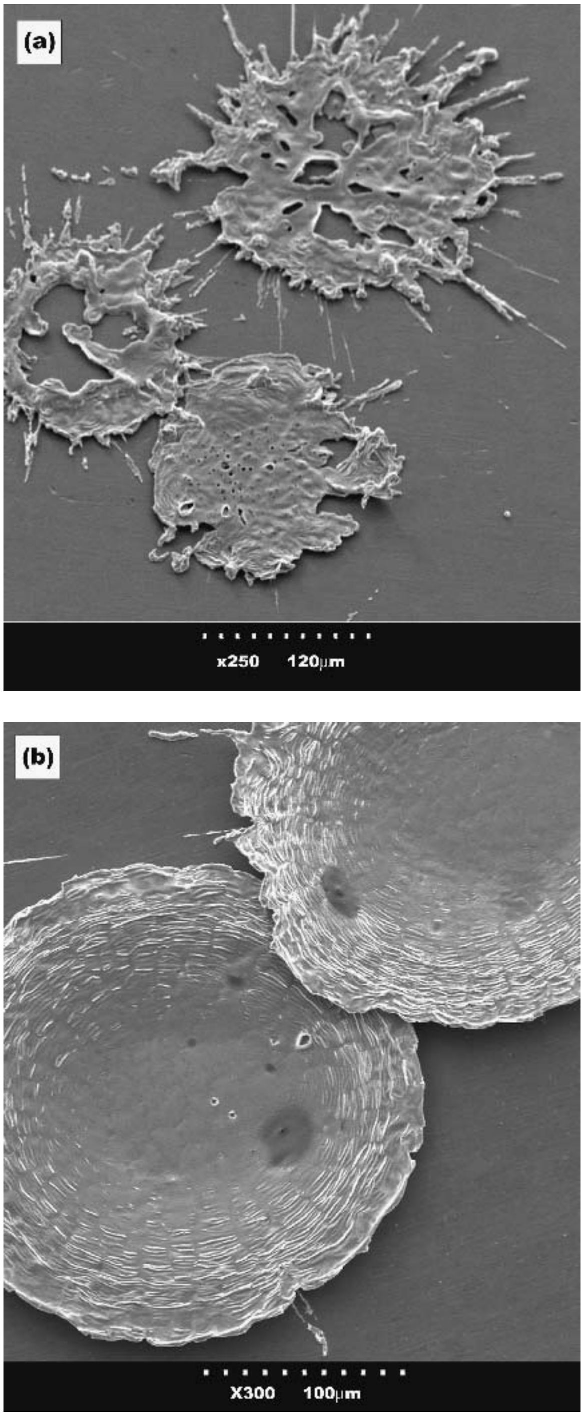

Fig. 1 Splats formed by spraying molten nickel particles on a stainless steel surface initially at **(a)** 290 °C and **(b)** 400 °C. The particle size distribution was −53 to +63 μm, particle temperature before impact 1600 ± 220 °C, velocity 73 ± 9 m/s.

oxide layer grew on its surface.[9] The amount of oxidation increased with both surface temperature and the duration of heating. Measurements showed that oxide layer thickness increased by an order of magnitude when substrate temperature was raised from 290-400 °C: thermal contact resistance would rise by the same amount.

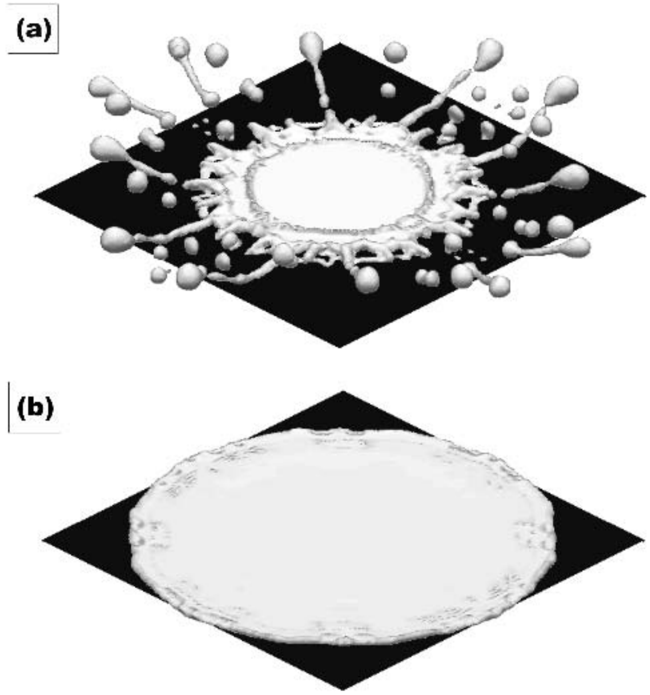

Fig. 2 Computer-generated images of splats formed by impact of 60 μm diameter nickel droplets at 1600 °C landing with a velocity of 73 m/s on a stainless steel substrate at 400 °C; thermal contact resistance between the droplet and substrate **(a)** 10^{-7} m^2K/W and **(b)** 10^{-6} m^2K/W

Splat morphology has been shown to have an important effect on coating quality. The transition temperature for yttria-stabilized zirconia particles plasma-sprayed on a polished stainless steel surface is approximately 150-200 °C; coatings deposited on surfaces heated above this temperature, so that they consisted mostly of disks splats, showed a significant increase in adhesion strength.[10] Voids created at the coating-substrate interface due to splashing and break-up of splats may reduce adhesion.[11] Also, heating the surface improves its wettability and slows solidification, promoting penetration into surface cavities.[10]

This study was undertaken to determine if the changes in splat shape with surface temperature that we observed earlier had a significant effect on coating properties.[7,9] Nickel powder was sprayed onto both stainless steel and cobalt alloy coupons that prior to coating were held at temperatures ranging from 25-650 °C. We measured coating adhesion strength and porosity and analyzed changes in coating structure and substrate composition when the substrate was heated.

2. Experimental Method

Nickel coatings were deposited with a SG-100 (Miller Thermal, Appleton, WI) plasma torch operating at a power of 20 kW and an argon flow rate of 60 g/min. Nickel powder (type 12313, Westaim Corp., Edmonton, Alberta, Canada) was sieved to obtain a narrow particle size distribution of −53 to +63 μm. The shape of powder particles is shown in Fig. 3. In-flight particle

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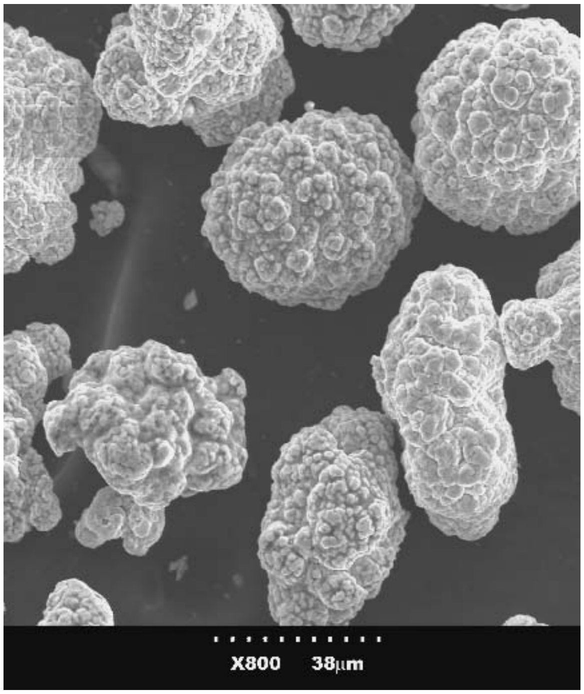

Fig. 3 Nickel powder particles before spraying

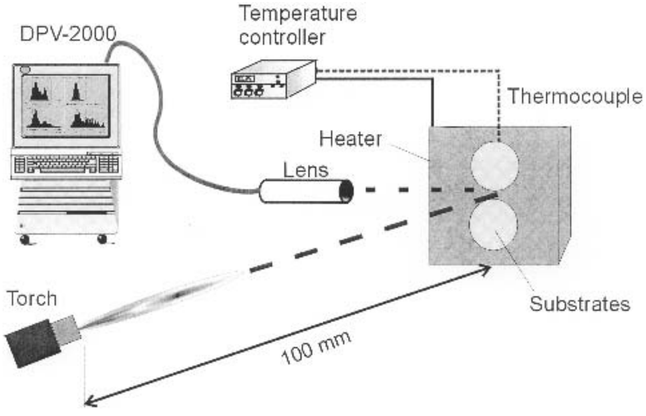

Fig. 4 Schematic of experimental apparatus

conditions such as velocity and temperature upon impact were measured with a DPV-2000 monitoring system (Tecnar Ltée, Montreal, Quebec, Canada) and kept constant during experiments. At a distance of 100 mm from the torch exit, where the test coupons were placed, particle temperatures were measured to be 1570 ± 220 °C, and their velocity was 62 ± 9 m/s.

The test surfaces on which coatings were applied were the flat ends of cylindrical specimens, 53.8 mm long and 24.7 mm in diameter, made from either 304L austenitic stainless steel (composition by weight: C-0.03%, Mn-2%, P-0.045%, S-0.03%, Si-1.0%, Cr-18-20%, Ni-8-12%, N-0.1%, balance Fe) or cobalt alloy L605 (composition by weight: Cr-20%, Ni-10.8%, W-15%, Fe-1.5%, balance Co). They were grit blasted with alumina grit (average size 700 μm) for 3 min to obtain a surface roughness (R_a) in the range of 3-5 μm, and then the surfaces were cleaned with a dry air jet.

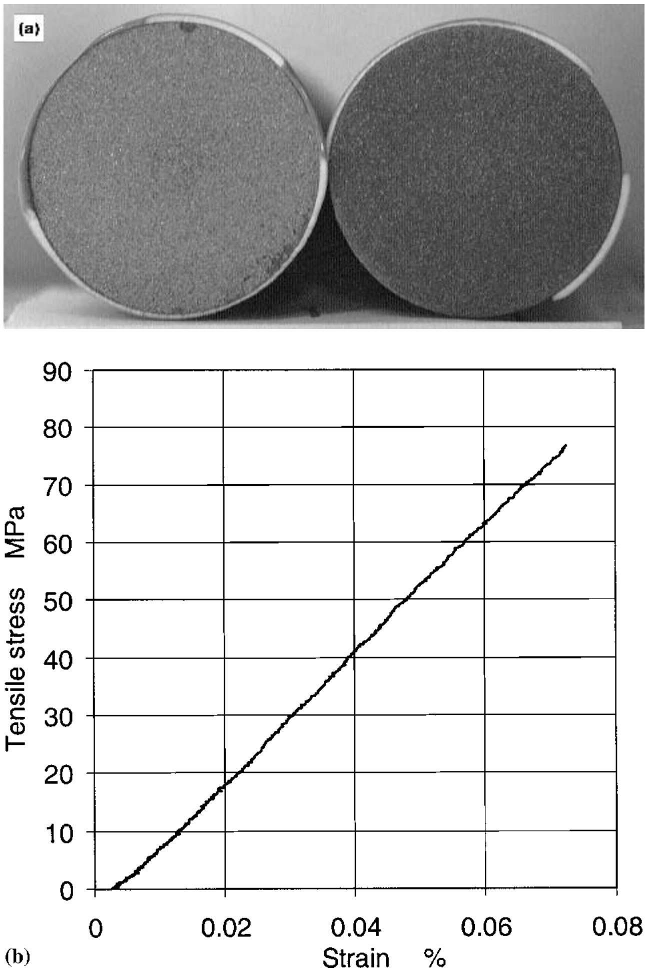

Fig. 5 **(a)** Photograph of complete fracture surface of specimen sprayed after heating to 650 °C; **(b)** corresponding tensile strength/strain curve

Test specimens were heated by clamping them in a copper heater block (120 × 80 × 70 mm) in which three 150 W cartridge heaters were inserted. The copper block was nickel-plated to prevent oxidation and wrapped with ceramic fiber insulation to reduce heat loss. It was designed to hold two test samples simultaneously (Fig. 4), and a temperature controller was used to keep them at the required temperature (up to a maximum of 750 °C) while they were being sprayed. The temperature of each specimen was monitored with a J-type thermocouple attached to its side, 3 mm below the exposed upper surface. The temperature at the center of the specimen was measured and found to be at most 10 °C below that at its periphery. The temperature of the two coupons differed by less than 5 °C during tests.

During an experiment, two test specimens were inserted in the block heater, heated up to the desired temperature, and sprayed with the plasma gun while keeping particle impact conditions constant (measured with the DPV 2000). Spraying was done with a powder feed rate of 16 g/min until the coating thickness was about 0.3-0.4 mm. It took approximately 2 min to coat the surface. After spraying was complete, the test coupons were removed from the copper block heater and allowed to cool to room temperature. The roughness of the coated substrate was

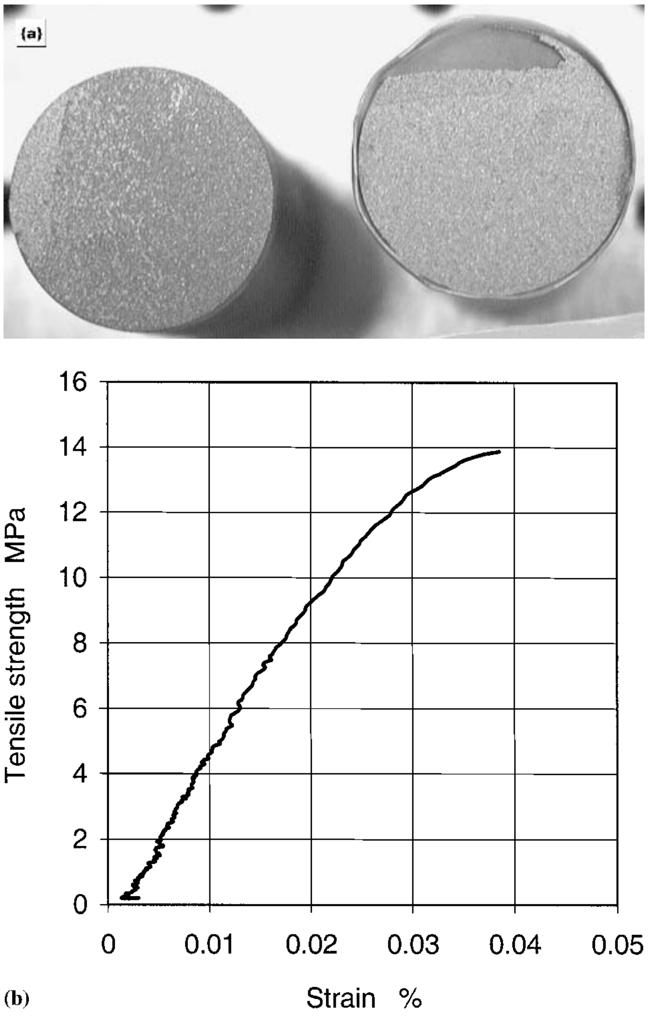

Fig. 6 **(a)** Photograph of partial fracture surface of specimen sprayed after heating to 250 °C; **(b)** corresponding tensile strength/strain curve

measured to be about 7-10 µm. Six specimens were coated at each substrate temperature.

Coating adhesion measurements were performed in accordance with the widely used ASTM C633-79 test.[12] Following the recommendations of the standard, the coated surface of the cylindrical sample was glued to another identical cylinder using epoxy adhesive film (FM 1000, Cytec Industries, West Paterson, NJ) with a tensile strength of 90 MPa. The glued cylinders were mounted in a tensile test machine (model MTS 810, MTS System Corp., Eden Prairie, MN) equipped with a self-aligning fixture and pulled apart until the coating failed. An 8-bit data acquisition system continuously recorded the tensile load exerted by the machine and the coating strain.

Cross-sections through the coatings were polished and examined under a scanning electron microscope. Coating porosity was measured using a mercury intrusion porosimeter (Autopore 9400 Micrometrics, Norcross, GA), which measures the volume of mercury forced under high pressure into a sample of the coating.

The composition and depth of oxide layers on the test surfaces after heating was determined using x-ray photoelectron spectroscopy (XPS) combined with argon-ion sputtering using a PHI 5500 system (Physical Electronics, Eden Prairie, MN). The XPS system produces monochromatic x-rays to excite atoms on the surface of a test specimen and uses an electron spectrometer to measure the energy of photoelectrons emitted in response by the specimen. Since photoelectron energy depends on the structure of atoms they are emitted from, peaks in the XPS spectrum can be used to characterize surface composition. The thickness of oxide was measured using an argon ion beam to erode the surface. The rate of removal of oxide being known, the thickness of the surface film was calculated from the time required to completely eliminate it and expose bare metal.

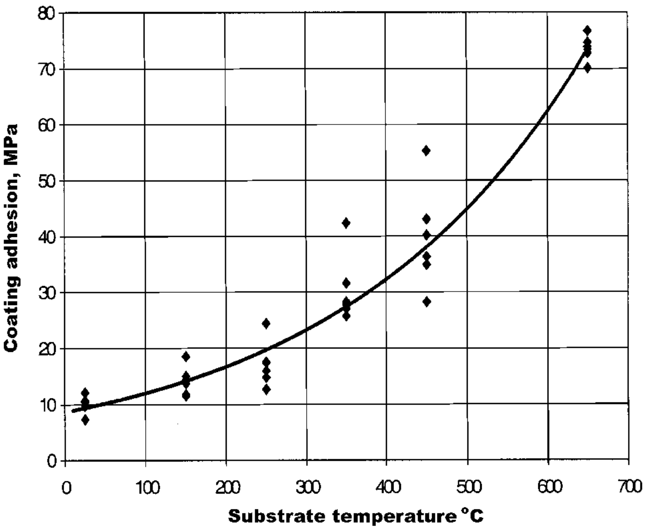

Fig. 7 Adhesion strength of nickel coatings plasma sprayed on stainless steel substrates at varying temperatures

3. Results and Discussion

Figure 5(a) shows a photograph of the fractured surfaces of a specimen after it was pulled apart in the tensile test machine. In this case the stainless steel substrate was heated to 650 °C during spraying. The coating failed at the substrate-coating interface while remaining attached to the adhesive. The corresponding stress-strain curve is given in Fig. 5(b); it is linear, demonstrating that failure was brittle. The maximum tensile stress—in this case 77 MPa—was recorded as the adhesive strength of the coating.

In a few, seemingly random, cases the entire coating did not completely detach from the substrate when it was pulled apart and a small portion of it remained on the surface. Figure 6(a) shows such a failure in a test where the stainless steel substrate was heated to 250 °C. In this case the stress-strain curve (Fig. 6b) became nonlinear, showing ductile failure at the glue-coating interface.

Figure 7 shows the variation of adhesive strength with substrate temperature. Each data point in the graph represents a different specimen. Coating adhesion strength is seen to increase with substrate temperature. Tensile strength increase was small when substrate temperatures rose from room temperature to 250 °C, ranging from an average of 10 MPa at room temperature

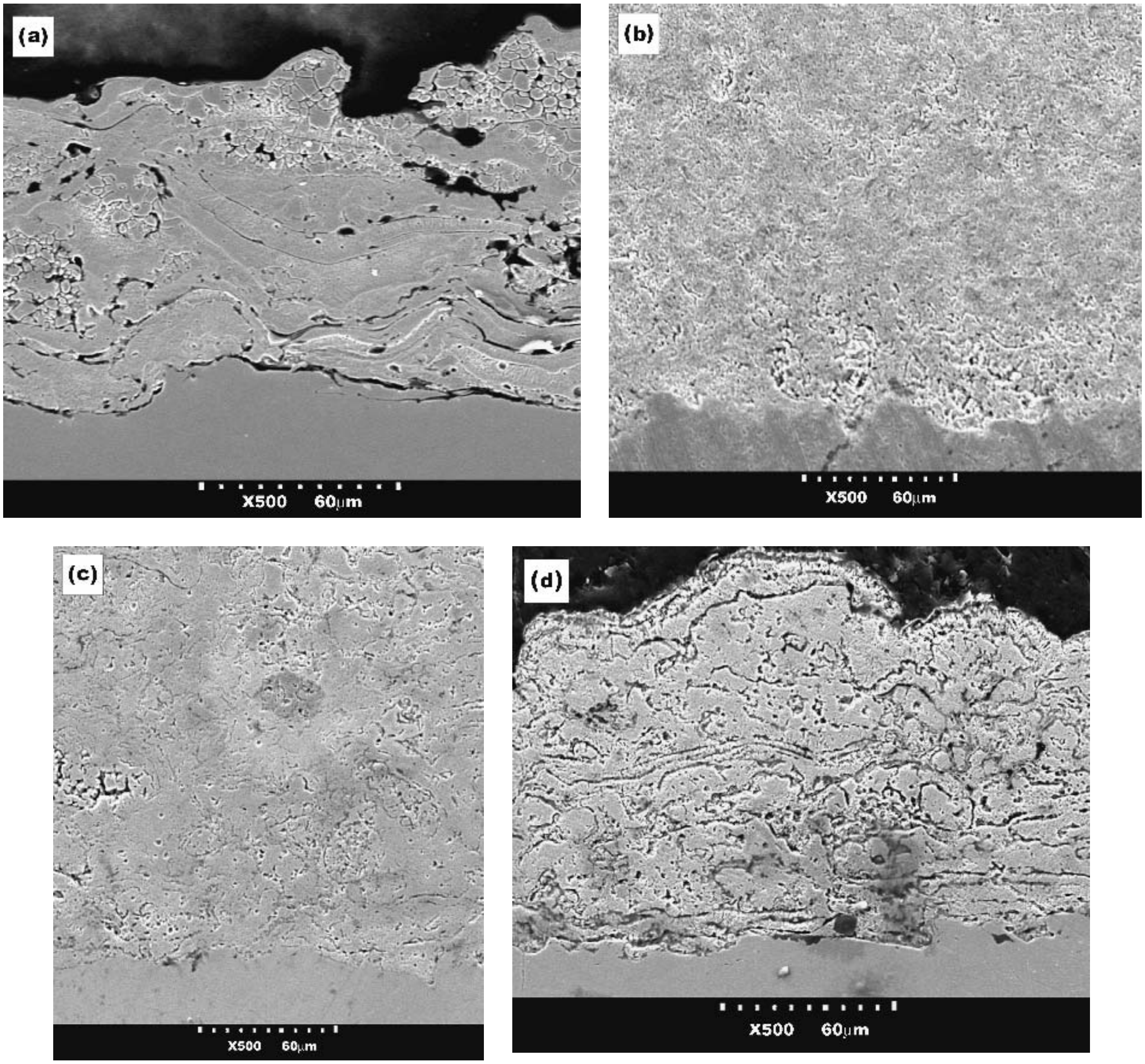

Fig. 8 Microstructure (etched) of nickel coatings deposited on stainless steel substrates at temperatures of **(a)** 25 °C, **(b)** 350 °C, **(c)** 450 °C, and **(d)** 650 °C

to 17 MPa at 250 °C. Above 300 °C, average tensile strength increased rapidly from 30 MPa at 350 °C to 74 MPa at 650 °C.

Coatings applied on heated substrates had a denser microstructure than those applied on a surface at room temperature. Figure 8 shows SEM micrographs of cross-sections through coatings applied on stainless steel substrates at 25 °C (Fig. 8a), 350 °C (Fig. 8b), 450 °C (Fig. 8c), and 650 °C (Fig. 8d), respectively. At the lowest temperature 25 °C, there were large pores in the coating, and voids were visible along the coating-substrate interface (Fig. 8a). Higher temperatures yielded much denser coatings with fewer pores (Fig. 8b-d).

Measurements with a mercury intrusion porosimeter confirmed that heating the coupons reduced coating porosity. Figure 9 shows the variation of coating porosity with substrate temperature. Coatings deposited at temperatures above 300 °C have significantly lower porosity than those sprayed on colder substrates. Also, the average pore size diminishes with increasing temperature, with a much greater fraction of pores being smaller than 1 μm when the substrate temperature was increased from 250-520 °C (Fig. 10).

The increase in adhesion strength and decrease in porosity when the substrate temperature was raised above 300 °C corresponds to the change in splat morphology we previously saw when nickel particles were sprayed on a stainless steel surface.[7] Particles deposited on a surface below 300 °C were irregular in shape, whereas those deposited on a hotter surface were disk shaped. Disk splats provide better contact with the substrate and therefore greater adhesion strength. Computer simulations showed that the most important reason for a change in splat shape was increased thermal contact resistance due to an oxide layer.[9]

The thickness of the oxide film of a surface depends on the heating time. Table 1 shows the time taken to heat the surface to each of the temperatures used in experiments.

The thickness and composition of the oxide layer was measured using XPS analysis combined with argon ion sputtering. The scale on the surface of heated stainless steel specimens was determined to be a combination of iron and chromium oxides. It had a layered structure with the upper layer made up mostly of iron oxide (Fe_2O_3), whereas the lower layer adjacent to the metal substrate consisted largely of chromium oxide (Cr_2O_3). The ratio between the two oxides gradually changed with depth across the film. Pech et al. previously reported finding such a layered scale structure on heated stainless steel surfaces.[13] Figure 11 shows the thickness of the chromium and iron oxide rich layers on substrates preheated to 150, 350, and 650 °C. The total oxide layer thicknesses were 60, 180, and 288 nm, respectively, for the three cases. There was no measurable change in surface roughness due to oxidation.

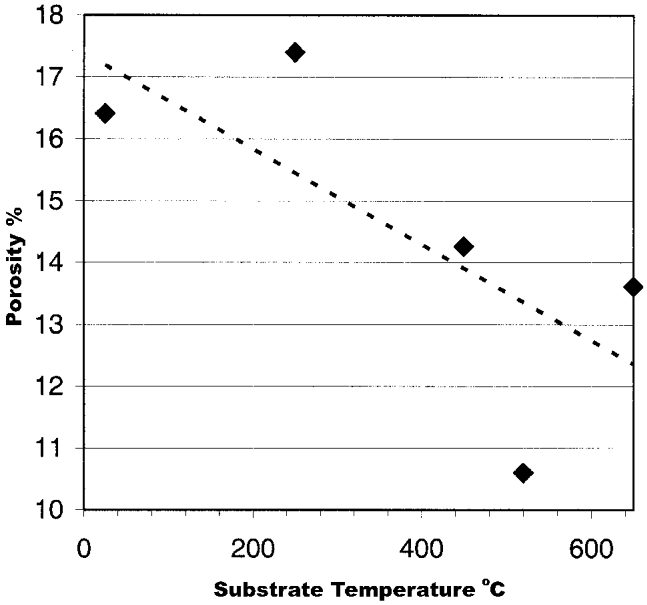

Fig. 9 Variation of coating porosity with substrate temperature during coating

To separate the effects of the oxide layer and substrate temperature on coating adhesion, a set of six stainless steel specimens was heated to 650 °C, held at that temperature for 2 min, and then cooled down; the entire cycle taking about 50 min. After they had cooled, the specimens were coated, and the adhesion strength of the coating measured. Coatings on these oxidized surfaces had average adhesion strength 13.5 MPa, which was 34% higher than those on nonoxidized surfaces (average adhesion strength 10.1 MPa). However, this increase was not as large as that observed when spraying on surfaces held at 650 °C (Fig. 7) where an average adhesion strength of 74 MPa was recorded. Therefore, the large enhancement of adhesion strength was not due to the oxide layer alone but also required higher surface temperature.

Finally, a few coating adhesion tests were done with coupons made of cobalt alloy L605, which is much less susceptible to oxidation than stainless steel. The surface scale was not layered in this case but consisted of a uniform mixture of cobalt and chromium oxides. The scale thickness was 20 nm on an unheated surface and increased to 150 nm on a coupon heated to 500 °C. Though the oxide films were much thinner than those on stainless steel surfaces, coatings still showed improved adhesion with increasing surface temperature. The adhesion strength of nickel coatings averaged 16 MPa at room temperature and increased to 55 MPa on surfaces preheated to 500 °C.

Our experiments have shown that heating the substrate while applying a plasma spray coating can significantly increase adhesion strength and reduce porosity. These improvements cannot be attributed entirely to surface oxidation and changes in

Table 1 Time Required to Heat Specimens to Different Temperatures

Substrate Temperature, °C	Heating Time, min
150	8
250	14
350	18
450	20
550	22
650	25

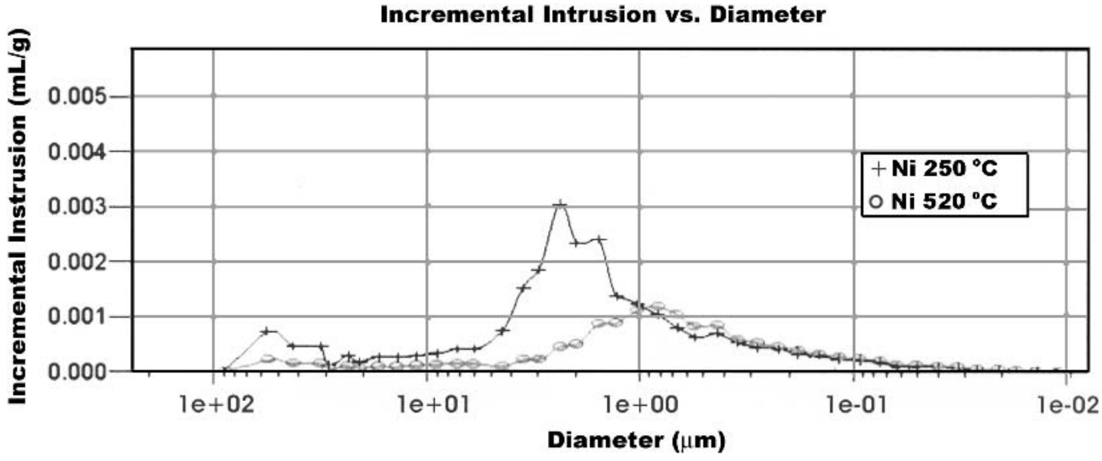

Fig. 10 Pore size distribution

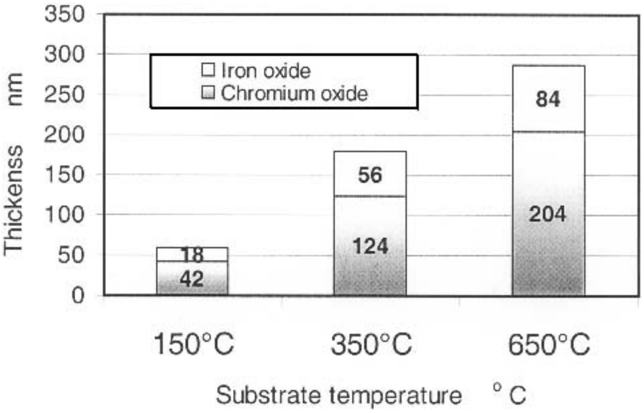

Fig. 11 Thickness of oxide layers formed on stainless steel substrates after heating to various temperatures

splat shape due to increased surface thermal contact resistance. Heating the substrate can influence impact and solidification of molten particles in several other ways. It can

1) Reduce the cooling rate of particles impinging on the surface, giving them more time to flow into surface cavities and form stronger bonds.
2) Form an oxide layer on the surface. This thereby reduces droplet solidification rates that promote diffusion at the droplet-substrate interface, and improve adhesion. The oxide layer can also change the surface crystal structure and increase its micro roughness and wettability of the surface.[13]
3) Evaporate moisture and other volatile contaminants on the surface, allowing better contact between impacting particles and the substrate.

It is likely that all of these factors contributed to improved coating adhesion.

4. Conclusions

We measured the adhesion strength of plasma-sprayed nickel coatings applied on heated stainless steel and cobalt alloy substrates. Adhesion strength on stainless steel coupons increased by almost an order of magnitude—from 10-74 MPa—when substrate temperature was raised from 25-650 °C. Coating porosity decreased with increasing substrate temperature. There was a marked increase in coating strength and drop in porosity for substrates heated above 300 °C.

When stainless steel coupons are heated, oxide films form on their surface, which act as a thermal barrier and reduce the cooling rates of impinging droplets, suppressing splashing and droplet break-up. However, surface oxidation alone did not explain the increase in adhesion strength. 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. Cobalt alloy coupons, which oxidize less than stainless steel when heated, also showed improved coating adhesion with heating. Heating the substrate removes moisture and other volatile contaminants on the surface. It also slows the solidification rate of deposited particles, allowing them to enter surface cavities before freezing. High surface temperatures enhance diffusion between the coating and substrate; all those factors contribute to improved adhesion. This work is in progress to determine the effect of each factor on coatings adhesion.

Acknowledgments

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