Hydrophobic / icephobic coatings based on thermal sprayed metallic layers with subsequent surface functionalization

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Abstract

Hydrophobic / icephobic coatings have been fabricated using a combination of thermal sprayed metallic MCrAlY (M = Ni, Co) coatings with a subsequent deposition process using 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS). The MCrAlY coatings provide the desirable surface roughness feature for hydrophobicity, and water contact angle of 135° was directly obtained after aged in the atmosphere for 1 week. However, it was found that the hydrophobicity of MCrAlY was not stable under water impinging due to unstable hydrocarbon absorption. Better hydrophobicity with water contact angle of 154° and improved durability have been achieved by further modification using POTS vapour on the rough MCrAlY coatings. X-ray photoelectron spectroscopy results revealed that replacement of absorption of hydrocarbon by functional C-F groups played important role in the improvement of hydrophobicity and durability. The ice adhesion test confirmed that lower ice adhesion strength of MCrAlY based coatings have been obtained compared with the threshold for icephobicity which is desirable to be applied as icephobic coatings for aircraft. The electro-thermal heating de-icing test showed an energy saving of 28.6% for de-icing with the two-step MCrAlY based coatings. The combination of strong metallic MCrAlY rough layers and the subsequent functionalization enables a new approach for the fabrication of durable hydrophobic / icephobic coatings.

Key Words: Hydrophobic, icephobic, MCrAlY, thermal spray

1. Introduction

A hydrophobic surface is a kind of water-repellent surface with water contact angle of greater than 90° and it is widely believed to enable water droplet bouncing off from the surface, delay ice formation and reduce ice adhesion strength [1-3], which is also known as icephobicity. Development of durable hydrophobic / icephobic surface has attracted great interest in the past decades due to the desires for self-cleaning, anti-icing, de-icing, fog-resistance for various industrial applications especially in aircraft. The modern aircraft are equipped with the de-icing system using heating methods which will build up weight, increase fuel consumption and add complexity to the aircraft system [4]. Therefore, a layer of durable hydrophobic / icephobic coatings on the leading edge of the aircraft wings is an ideal solution to reduce ice adhesion on the aircraft surface and improve the energy efficiency during the de-icing process.

Currently, the widely reported hydrophobic / icephobic materials are mainly based on low surface energy polymers such as poly(dimethylsiloxane) or polytetrafluoroethylene [5-11]. However, the main disadvantages of these polymer-based hydrophobic / icephobic surfaces are the frangibility due to weak mechanical performance, abrasion resistance and degradation of polymers. Recently, ceramic and metallic based hydrophobic coatings have shown promising improvement on the mechanical performance [12, 13]. However, the mechanism of the hydrophobicity of ceramics and metallic materials has remained controversial and it is critical for further improvement.

Thermal spraying is a popular approach to fabricate metallic coatings from melted metal particles [14-18]. After re-solidification of the melted and partially melted particles, coatings with good bonding and mechanical strength can be obtained [14, 19]. Therefore, thermal spraying has been widely used to fabricate coatings such as thermal barrier coatings with strong mechanical performance applied in combustion chambers for aircraft engines [20, 21]. But the thermal sprayed metallic coatings without surface modification tend to be hydrophilic because of a large number of polar sites on their surfaces [16, 22-25].

Thermal sprayed MCrAlY (M = Ni, Co) coatings have been proved to provide good bonding on metal substrates [26]. Besides, the rough surface morphology makes it a desirable candidate to be further functionalized by low surface energy materials, e.g. 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS) aiming for hydrophobic and icephobic applications. In this work, metallic MCrAlY coatings have been fabricated by thermal spray methods and showed a surprising hydrophobicity although the stability remains an issue. Better hydrophobicity and improved durability have been obtained after further modification vapour deposition of POTS with low surface energy onto the rough structure. The two-step MCrAlY based coatings also demonstrate lower ice adhesion strength which is also desirable to be used as passive ice protection for aircraft.

2. Experimental details

2.1 Fabrication of MCrAlY (M = Ni, Co) coatings

Durable hydrophobic / icephobic coatings based on metallic MCrAlY materials were fabricated by high-velocity oxygen fuel (HVOF) thermal spray system on aluminium alloy substrates with the size of 20 mm × 40 mm. To improve the adhesion between the substrates and the coatings, the aluminium substrates were sandblasted by Saftigrit white 180/220 grit following by cleaning under compressed air. The substrates were attached to the sample holders and fastened to the carousel which can rotate at a constant speed of 186 rpm. The MCrAlY powders (Ni-191-4 supplied from Praxair Surface Technologies) containing nickel, cobalt, chromium, aluminium and yttrium were placed in the powder feeder and delivered to the spray gun by nitrogen gas with a pressure of 4 bar and flow rate of 11 L/min after passing a flame heating area. The spray gun installed in a vertical axis robot arm can move from upper position to lower position to realize uniform coatings.

2.2 The second step modification

The second step to improve the hydrophobicity / icephobicity and durability is to deposit a low surface energy material POTS onto the rough surface of MCrAlY coatings using chemical vapour evaporation method [3]. Briefly, a small amount of POTS was placed into a container with the MCrAlY coating samples and heated to 180 °C in a chamber furnace with ventilation for 3 hours.

2.3 Characterization of morphology, composition and hydrophobicity

The cross-section and top view morphology were investigated by a JEOL 6490LV scanning electron microscope (SEM). The binding energies of elements for the MCrAlY coating after aged in the atmosphere for 1 week were characterized by a VG Scientific ESCALAB Mark II X-ray photoelectron spectroscopy (XPS) using Al Kα X-ray as the radiation source with a wavelength of 1486.6 eV. Static water contact angle, advancing water contact angle, receding contact angle and contact angle hysteresis of the coatings were characterized using a First Ten Angstroms, Inc., FTA200 contact angle goniometer.

2.4 Durability test

To evaluate the durability, erosion tests under pressurized water impinging using an atomiser with a gas pressure of 15 psi, the velocity of 35 ~ 37 m/s and liquid flow rate of 72 mL/min were performed. Pressurized water with the droplet size of 12.7 microns (Sauter Mean Diameter) was sprayed onto the coated samples using a stainless nozzle (PNR UK Ltd) for the duration of 90 minutes. The water contact angle was measured before and after the erosion test.

2.5 Electro-thermal heating test for energy consumption

The electro-thermal heating tests were performed using a home-made testing facility on a cold plate with a setting temperature of -30 °C. The samples were held downward on a stand with a distance of 5.5 cm from the surface of the cold plate. The ice blocks with the weight of 8 g were frozen on the samples. A heating element driven by a power supply with a voltage of 15 V and a current of 0.09 A started to heat once the temperature reached -5 °C. The ice blocks would drop when the ice melted at the interface. The duration of heating prior to ice dropping was recorded and the overall energy consumption for de-icing can be calculated accordingly.

2.6 Ice adhesion strength test

Ice adhesion tests were performed using a home-made testing rig based on a centrifuge method. A glaze ice block (mass of 1.3 g) in a mould was frozen on the surface of the coating at -10 °C in an environmental chamber overnight before the test. The samples were fixed on a carbon fibre reinforced polymer rotor which could be driven by a servo motor (MOOG G403-2053A) in the environmental chamber at a setting temperature of -5 °C. During the test, the ice detached from the coating surface under centrifugal force when the rotor was driven at a steady acceleration of 30 rpm/s. Using the rotation speed at the moment of the detachment of the glaze ice block, the centrifugal force F (N) can be calculated using equation [27]:

$$F = mr\varpi^2 \qquad (1)$$

where *m* is the mass of ice block (kg), *r* is the radius of the beam (m) and ϖ is the speed of rotation (rad/s). From the centrifugal force, the shear stress can be determined:

$$\tau = \frac{F}{A} \qquad (2)$$

where A is the ice area (m^2), τ is the shear stress (Pa). Four MCrAlY based coating samples were measured for better accuracy.

3. Results and discussion

3.1 Surface morphology and hydrophobicity of the unmodified MCrAlY coatings

The cross-section and top view morphology of the MCrAlY coating were characterized by scanning electron microscope as shown in Fig. 1 and Fig. 2. The SEM images show that typical rough coatings with partially melted particles and open porosity were formed onto the substrates by a thermal spray process. The rough surface was created by the metallic particles after melting or partially melting and re-solidification process which would benefit strong mechanical performance. The rough morphology would create air pockets and benefit hydrophobic surfaces. The open porosity will also allow POTS vapour to diffuse and be deposited into the porous structure of MCrAlY coatings in the subsequent functionalization process.

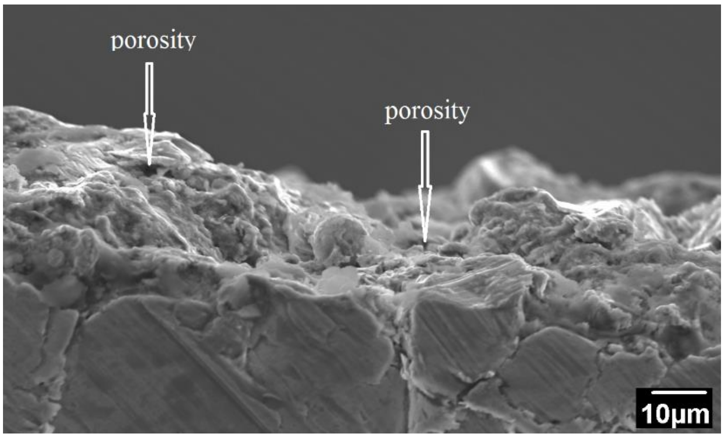

Fig.1. Cross-section scanning electron microscope image of the MCrAlY coatings fabricated by thermal spray.

It was widely believed that common metals tend to be hydrophilic because of a large number of polar sites on their surfaces owing to coordinative unsaturation [22-25]. However, it was surprising to find that the surface of MCrAlY coatings was hydrophobic with water contact angle of 135° after aged in the atmosphere for 1 week (shown in the inset of Fig. 2(a)) although the as-sprayed coating was hydrophilic. To evaluate the durability of the hydrophobicity and explore the suitability for applications as icephobic coatings in aircraft, erosion test by water impinging was performed. After erosion test for 90 minutes, the water contact angle shown in the inset of Fig. 2(b) dropped to 29° indicating that the unmodified MCrAlY coatings are not suitable for practical applications due to low stability. By comparing the surface morphology of MCrAlY coating before erosion test (Fig. 2(a)) and after erosion test (Fig. 2(b)), it can be found that the erosion test did not destroy the surface of the MCrAlY coating which is expected due to the strong mechanical performance of the thermal sprayed metallic coating. By excluding the damaging of the surface morphology as the main reason for the unstable hydrophobicity, it is very reasonable to infer that the surface chemistry changed during the erosion test.

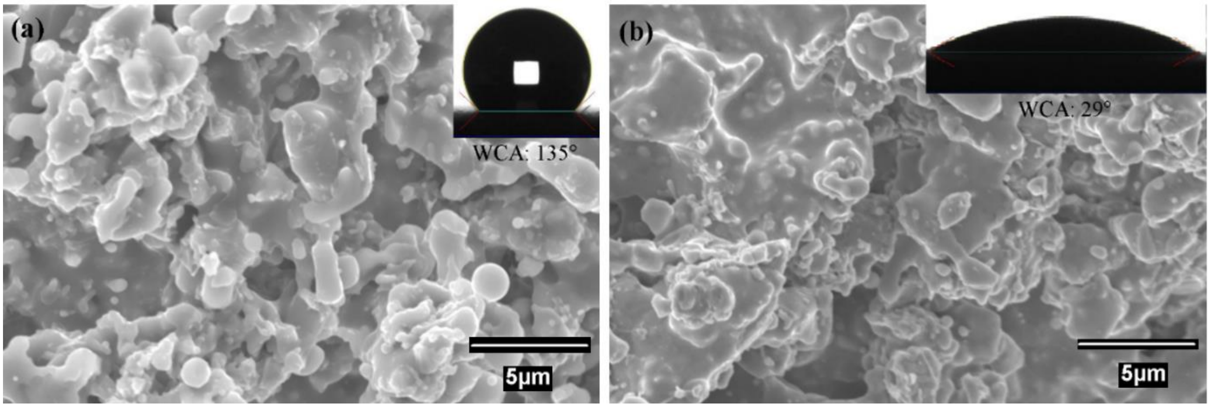

Fig. 2. Top view scanning electron microscope image of the MCrAlY coatings aged in the atmosphere for 1 week (a) before erosion test; (b) after erosion test. The inset shows the water contact angle before erosion test and after erosion test.

To improve the hydrophobicity durability of MCrAlY coatings, it is very important to find out the underlying mechanism of the hydrophobicity. Previous experiments confirmed that hydrophobicity of metal materials could be achieved by hydrocarbon absorption [28-30] and the idea has been extended for various materials such as ceramic oxides [31] and graphene [32]. XPS characterization for the MCrAlY coating aged in the atmosphere for 1 week was performed to investigate the possibility of hydrocarbon absorption. Fig. 3 shows the carbon peak, often referred to as the "adventitious carbon" peak, which is believed to be indicative of hydrocarbons adsorption onto the surface although hydrogen cannot be explicitly detected [33]. Similar results were also reported by Preston [34], Khorsand [35] and Ohtsu [36]. However, as explained in the previous section, hydrophobicity achieved by hydrocarbon absorption is not stable as the absorption can be easily removed by water impinging.

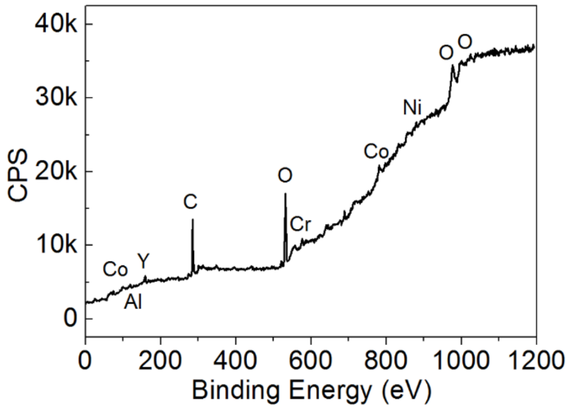

Fig. 3. X-ray photoelectron spectroscopy result for the unmodified MCrAlY coatings after aged in the atmosphere for 1 week.

3.2 Improvement of the hydrophobicity and durability by subsequent functionalization

The second step treatment was performed by the deposition of POTS onto the rough surface of the MCrAlY coatings. A combination of thermal sprayed metallic coatings with subsequent surface functionalization is promising to improve the hydrophobicity and durability due to the better mechanical performance of the metallic coatings comparing. Fig. 4(a) shows the top view SEM image of MCrAlY coating after the second step modification indicating very similar surface morphology with that before modification as the POTS layer is too thin to be detected by SEM. Fig. 4(b) shows the surface profile of the MCrAlY coatings with hydrophobic POTS layer. The inset shows the water contact angle of 154° indicating improved hydrophobicity by the deposition of POTS vapour. The advancing contact angle, receding contact angle and contact angle hysteresis of the MCrAlY coatings before the surface modification and after modification are shown in Table 1. It can be seen that the contact angle hysteresis reduced from 16° to 2° after surface modification indicating better mobility of water droplets which may benefit the anti-icing function of the coatings by allowing water rolling off from the surface [37-39].

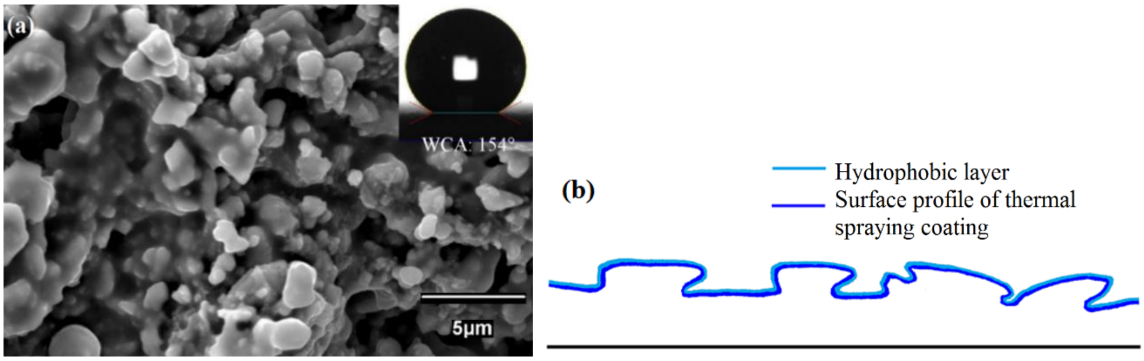

Fig. 4. (a) Top view scanning electron microscope image of the MCrAlY coatings after surface modification. The inset shows the water contact angle after surface modification; (b) the schematic diagram of the surface modification by low energy materials onto MCrAlY coatings.

Table 1 Advancing contact angle, receding contact angle and contact angle hysteresis of the MCrAlY coating before and after surface modification.

	Advancing contact angle (°)	Receding contact angle (°)	Contact angle hysteresis (°)
MCrAlY before surface modification	99	83	16
MCrAlY after surface modification	144	142	2

To evaluate the durability, erosion tests under pressurized water impinging were performed on samples after the second step modification using the same conditions with the unmodified MCrAlY coatings. It can be seen from Fig. 5, the water contact angle after POTS treatment dropped to 149° from 154° while the water contact angle before POTS treatment dropped to 29° from 135° indicating a significant improvement of durability. From the durability improvement, it is reasonable to infer better bonding has been obtained between MCrAlY/POTS comparing with MCrAlY/hydrocarbons. To reveal the surface status, XPS scan was performed for MCrAlY before and after modification.

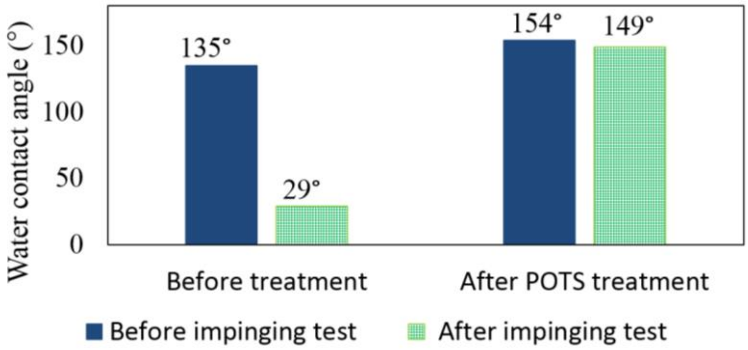

Fig. 5. Durability test results for MCrAlY based coatings before POTS treatment and after POTS treatment.

3.3 The mechanism of improvement of hydrophobicity and durability

Fig. 6(a) shows the wide scan survey spectrum of the F 1s photoelectron line and F KLL Auger peaks of MCrAlY samples before and after modification. It can be clearly seen that there is an F 1s peak centred at 688.31 eV and F KLL peaks centred at 833.31 and 860.31 eV for the MCrAlY coating after POTS treatment, while there is not any F peak for the unmodified MCrAlY coating [40, 41]. In the scan for C 1s region shown in Fig. 6(b), C-F peak centred at 291.31 eV appears after POTS treatment while there is no C-F peak before treatment [40, 41]. The XPS results confirm that after the modification the surface of the thermal sprayed MCrAlY coating was grafted by POTS hydrophobic layer with C-F groups which play an important role for improved hydrophobicity and durability.

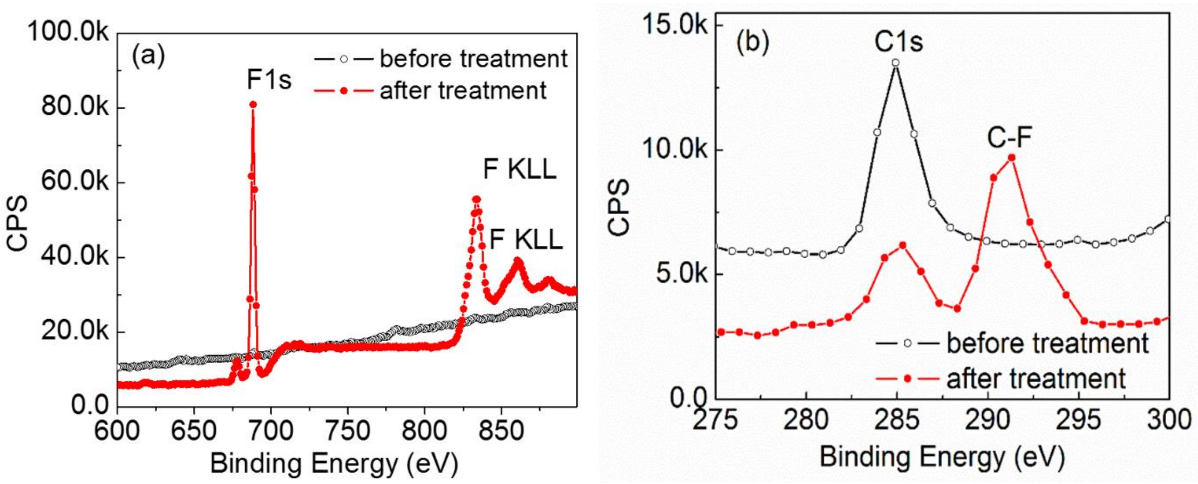

Fig. 6. X-ray photoelectron spectroscopy results for F1s (a) and C − F (b) of MCrAlY coatings before treatment and after modification by the penetration of POTS.

3.4 Energy consumption in the de-icing test

Aiming for applications as icephobic coatings in aircraft, a single hydrophobic coating to prevent or delay ice formation is not likely to be accepted considering strict safety reasons in the aerospace industry. An integration between the electro-thermal de-icing system with the icephobic coatings will have a better chance to be used in aircraft for reduction of energy consumption during electro-thermal heating to remove ice [42, 43]. Therefore, an electro-thermal heating test rig was applied to evaluate the energy consumption during heating until the ice block detached from the surface of the samples. In table 2, the test results show that an average of 329.0 Joules consumed to detach the ice block for aluminium substrate and an average of 234.9 Joules consumed for MCrAlY samples with POTS coatings indicating 28.6% of energy can be saved during de-icing process.

Table 2 Energy consumption during de-icing of metallic coatings

Sample	Melting duration (second)	Energy input (Joules)	Energy saved
Average of Al substrates	243.7±16%	329.0±16%	N/A
Average of MCrAlY based coating	174.0±3.4%	234.9±3.4%	28.6%

It is very easy to understand that better thermal conductivity will benefit higher energy efficiency during the de-icing process due to the higher thermal exchange rate between the heating element and the ice block. The thermal conductivity of the aluminium substrates is 205 W/(m·K) and the thermal conductivity of the MCrAlY coating is 7.2 W/(m·K) [44]. The thermal conductivity of the coated sample calculated according to the resistance in series of the aluminium substrate and the MCrAlY coating is 59 W/(m·K). By insertion of the MCrAlY coating between the aluminium substrates and the ice block, the thermal exchange rate will be slowed down due to the lower thermal conductivity. However, the thermal conductivity of MCrAlY is still much higher than that of most polymers which are normally less than 0.5 W/(m·K) indicating promising applications as an alternative approach of polymer hydrophobic coatings. Another important parameter for the hydrophobic surface, work of adhesion which is a measure of the strength of the contact between two phases, may compensate the slower thermal exchange rate of MCrAlY based coatings and play more roles on the energy efficiency during de-icing. The work of adhesion, W, can be calculated according to the Young-Dupré equation [45]:

$$W=\sigma(1+\cos\theta) \tag{3}$$

where σ stands for the surface tension and θ stands for the water contact angle. By using the 154° as water contact angle of MCrAlY based coatings and 83° as the water contact angle of aluminium substrates, the work of adhesion on aluminium substrates is 11.1 times of that on

MCrAlY based coatings which can explain the less energy consumption of MCrAlY based coatings during the de-icing process by electro-thermal heating.

3.5 Ice adhesion strength

Besides the work of adhesion, ice adhesion strength is also correlated with the wettability. It was revealed that the average ice adhesion strength is linearly correlated with 1 + cosθe, with *θe* standing for the estimated equilibrium contact angle which implies that a low ice adhesion strength can be obtained from the hydrophobic MCrAlY based coatings [45]. In this experiment, the centrifuge adhesion tests were performed to evaluate the ice adhesion strength of MCrAlY based coatings [46]. There are some variations in the testing values due to the mechanical vibration of the carbon fibre bar during acceleration or the uneven temperature distribution caused by the atmosphere disturbance in the environmental chamber. Therefore, four samples were fabricated and tested using the same conditions. From Fig. 7, it can be seen that all the measured shear stresses between the coated samples and glaze ice block was remarkably less than the shear stresses between the Al substrates and glaze ice block. The shear stresses between the ice and the MCrAlY based coatings are all lower than 100 kPa which is the threshold for icephobicity [47]. The lower ice adhesion strength will facilitate ice removal which is another advantage to be applied as passive ice protection for aircraft.

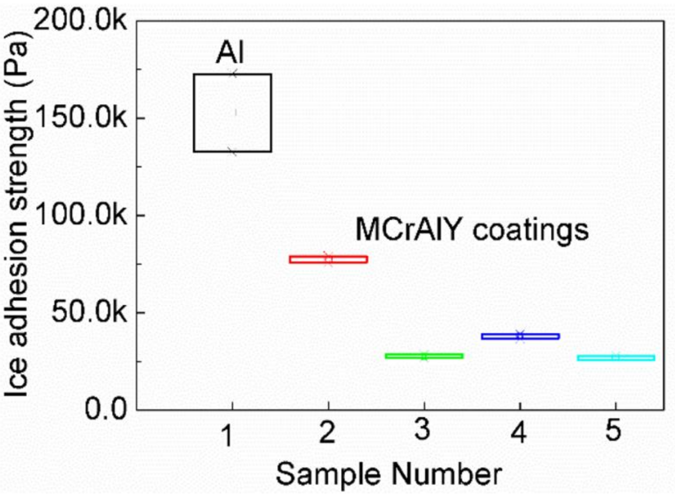

Fig. 7. Ice adhesion strength of Al substrates and MCrAlY based coatings.

4. Conclusions

Hydrophobic / icephobic coatings have been fabricated using a combination of thermal sprayed MCrAlY (M = Ni, Co) layers and further functionalization of POTS deposition onto the rough surface of MCrAlY. The sprayed MCrAlY coatings after aged in the atmosphere for 1 week provide the desirable surface roughness feature for hydrophobicity, and water contact angle of 135° was directly obtained. However, the unmodified MCrAlY coatings showed unstable hydrophobicity which dropped to 29° after water impinging. The second step modification using POTS deposition significantly improved the hydrophobicity and durability by replacement of the absorption of hydrocarbons by C-F groups. Lower ice adhesion strength of MCrAlY based coatings than the threshold of icephobicity has been obtained which will facilitate ice removal. Reduced energy consumption in the de-icing process by the two-step MCrAlY based coatings has been demonstrated. The combination of rough MCrAlY coatings and the subsequent modification with POTS enable a new approach to fabricate durable hydrophobic / icephobic coatings.

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