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Abstract (Doctor)

Title of Thesis	Influence of Substrate Properties on Bonding Mechanism of Cold Sprayed Titanium Dioxide Coating

Approx. 800 words

Cold spraying is an emerging technique in which spray material particles ranging from 1 to 50μm are stimulated by a stream of supersonic gas at a temperature below the materials melting point an d leading to the production of the coating formation from the solid state particles. In term of the bonding mechanism for cold sprayed metal coating, the manifestation at the interface of adiabatic shear instability represents the most accepted bonding mechanism theory. Meanwhile, bonding mechanism for cold sprayed pure ceramic materials is still unclear yet.

The substrate surface plays a crucial role in achieving the high-strength adhesiveness of coatings that are cold sprayed because their adhesive strength is specifically determined by the bonding of the first layer of TiO_2 particles with the outermost surface of the substrate. In addition, substrate surface plays an important role in the deposition because it can provide chemical affinities during the particle interaction after impact or plastic deformation or thin layer remaining oxide. Literature on bonding mechanism of cold sprayed TiO_2 onto metal substrate has focused almost exclusively on TiO_2 powder properties and to date, no systematic investigation has considered from substrate properties perspective. The aim of this thesis is to study the factors and understand the bonding mechanism that contributed from substrate hardness, substrate oxide surface roughness and substrate oxidation in term of composition and thickness. Substrate hardness have influenced toward substrate deformation when cold sprayed TiO_2 impacts the substrate surface with a high impact velocity. Substrate deformation will lead to mechanical anchoring which is one of the bonding mechanisms in cold spraying process. Roughness of the oxide surface can provide bonding mechanism through mechanical interlocking. As metal is used as substrate, a passive oxide layer with a thickness of a few nanometers will often make up the outermost surface. The increased temperature of the annealed substrate also indicated thicker surface oxide on the surface of the substrate, and changes in the composition of the substrate. Bonding mechanism by atomic intermixing at a thin amorphous layer remaining about a few nanometers along the interface TiO_2 particle/newly form substrate surface due to chemical forces may also be the bonding mechanism involved in the cold spraying of titanium dioxide on metal surface. Thicker passive oxide on the surface of the substrate indicate a more inactive area to form the bonding between TiO_2 coating/newly formed surface of the substrate if thicker passive oxide remains on the substrate surface after cold sprayed TiO_2 impacting. One of the bonding mechanisms is chemical reaction at the oxide-free interface

between particles or particle/substrate that known as metallurgical bonding.

I performed an experiment involving 5 types of materials as substrate, pure copper (C1020), pure aluminum (Al 1050), stainless steel (SUS304), pure chromium (Cr) and structural steel (SS400). Selection of pure copper and pure aluminum substrate because comprehensive analysis of cold sprayed on copper substrate and aluminum substrate over a decade. This was basic understanding to study bonding mechanism of cold sprayed TiO_2 onto metal substrates. Our research group`s previous study showed that when cold sprayed TiO_2 onto preheating or annealing stainless steel alloy, the adhesion strength of TiO_2 coating showed an increased trend but this value was still low compared to metal cold sprayed. To increase the adhesion strength of TiO_2 coating, bonding mechanism involved must be understood. Selection of stainless steel, SUS 304 to clarify bonding mechanism involved, in order to increase the coating adhesion strength. Selection of pure chromium substrate to further understand the influence of chromium element in stainless steel substrate toward bonding mechanism involved. Moreover, selection of structural steel, SS400 to study the influence of ferum element in stainless steel substrate.

My research findings show that the adhesion strength of cold sprayed TiO_2 coating on soft and pure annealed materials, C1020 and Al 1050, showed a decreasing trend as the annealed substrate increased from room temperature to 400°C. SUS 304 showed increasing trend of cold sprayed TiO_2 coating as the temperature of the annealed substrate increased from room temperature to 1000°C. For pure Cr, adhesion strength of TiO_2 coating showed an increasing trend from room temperature to 700°C and decreased at 1000°C. Meanwhile, the SS 400 showed steadily an increased trend in the adhesion strength of TiO_2 coating from room temperature to annealed 400°C but no successful coating on annealed 700°C SS 400.

Soft and pure annealed materials, C1020 and Al 1050 from room temperature to 400°C, decrease in hardness is pronounced at 400°C due to recrystallisation. FIB result shows substrate plastic deformation occurs on both pure material at 400°C but at this temperature the adhesion strength of the TiO_2 coating is lowest. This suggests that the bonding mechanism involved here is not mechanical anchoring. The TEM result showed a remaining thin amorphous approximately 10nm layer along the interface TiO_2/metal substrate. As the temperature of the annealed substrate increases, thicker surface oxide on the surface of the substrate but the particle velocity is constant in all experiment condition. Therefore, it contributes to more inactive area and it could prevent cold sprayed TiO_2 coating from forming bonding with newly free metal substrate oxide surface. Metallurgical bonding is pronounced as bonding mechanism for both annealed soft and pure materials.

In the case of annealed hard and alloys material SUS 304; annealed substrate hardness showed a decrease trend from room temperature to 1000°C. The FIB result confirmed substrate deformation occur on annealed 1000°C SUS 304 after been impacted by high velocity cold sprayed TiO_2. TEM findings showed a remaining thin amorphous layer approximately 10nm along the interface TiO_2/newly formed metal substrate for annealed 1000°C SUS304. Higher temperature, such as 1000°C, mechanical and chemical factor affected the bonding mechanism by substrate deformation and atomic intermixing. Moreover, SUS 304 from room temperature to annealed 700°C showed higher annealed substrate hardness and no substrate deformation present. The only factor that influenced bonding mechanism is oxide layer on substrate surface. SUS 304 have oxide layer consist of Fe_2O_3 and Cr_2O_3. Referring to result of pure chromium substrate showed steady increased of coating adhesion strength from RT to annealed 700°C but structural steel, SS 400 on annealed 700°C, no successful coating on this annealed substrate temperature. Therefore, Cr_2O_3 have major influence to bonding mechanism of cold sprayed TiO_2 on stainless steel by mixed oxide bonding since our TiO_2 powder feedstock have oxygen defective, TiO_{2-x}. During the cold spraying process, the agglomerated powder of TiO_2 in nano-scale primary particles, which also contained nanoporosity, was fractured, leaving an unstable surface with a dangling bond structure.The unstable surface TiO_{2-x} with defective oxygen and a dangling bond structure in the nano-scale primary particle, preferentially to form the chemical mixed-oxide bonding of TiO_2–Fe_2O_3+Cr_2O_3. Kinetic spraying processes, including warm spray or cold spray, the particle– substrate or particle–particle interface is exposed to high temperature below the melting point and high compressive stress exceeding 1–2 GPa at the impacted region. The combination of a thin amorphous phase of oxide, high temperature and pressure, and strong reactivity of titanium with oxygen could induce particle–particle bonding.

To sum up, our research had led us to substantial progress in clarifying the bonding mechanism associated with cold sprayed ceramic materials. The present findings may help to clarify the role of remaining substrate oxide to bonding mechanism of cold sprayed TiO_2.