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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.msea.2011.09.083>

Materials Science and Engineering A, 530, pp. 253-265, 2011-09-29

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Mechanical behavior of Ti cold spray coatings determined by a multi-scale indentation method

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ARTICLE INFO

Article history:

Received 24 March 2011

Received in revised form 24 August 2011

Accepted 20 September 2011

Available online 29 September 2011

Keywords:

Titanium

Hardness measurement

Nanoindentation

Mechanical characterization

Powder metallurgy

ABSTRACT

The effect of the indentation load on the hardness measurements on cold spray Ti coatings was evaluated. Varied load indentation was carried out with nanoindentation at loads between 1 and 20 mN and microindentation at loads between 0.1 and 5 N. Nanoindentation measurements showed an indentation size effect and were fit to the Nix–Gao model for strain gradient plasticity. The microindentation measurements depended on the indentation size in a manner different from the Nix–Gao model and were strongly affected by the material porosity and cohesive strength between cold sprayed particles. By comparing results from the two indentation techniques, a hardness loss parameter was formulated that helped explain the mechanical behavior at all length scales and its relation to the various defects within the coating. Comparisons of the hardness loss parameter between cold spray coatings and a bulk Ti plate showed that this new parameter provided a good measure of when the mechanical behavior of the cold spray coatings approached that of a traditionally manufactured material. Evaluation of the hardness loss parameter of coatings and the bulk material, combined with microstructural characterization before and after indentation, was used to examine the relationships between processing conditions, coating microstructure and mechanical behavior for coatings fabricated with spherical and non-spherical Ti powders.

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1. Introduction

For well over a hundred years, hardness testing has provided scientists and engineers a quick measure of the mechanical properties of a material or coating [1]. However, the technique has also been fraught with potential artifacts, many of which are related to a phenomenon known as the “indentation size effect” [2–11]. This typically refers to the simple observation that the hardness measured by an indentation test is often not constant, but instead changes with applied load. The explanation of this effect has changed over the years as sample preparation, indenter manufacture and testing apparatus have become more sophisticated. Initially, the size effect was most often tied to sample problems (e.g. roughness, work hardening, contamination), indenter problems (e.g. bluntness, roughness or simply poorly characterized geometry), or testing problems (e.g. poor calibration) [12,13]. With modern hardness testing most, if not all, of these problems have been addressed and there is now the opportunity to explore and use

the indentation size effect as a means to characterize the mechanical properties of materials [8,14–16].

Modern versions of indentation size effect generally result from the fact that as the indent size changes, its interaction with defects within the material changes. For metals and alloys tested at very low indentation loads, there is generally a hardness increase with decreasing indent size. This version of the indentation size effect has been shown to take place due to an increase in strain gradients tied to the geometrically necessary dislocations that form below the indenter. A strain gradient plasticity model, commonly called the Nix–Gao model [8], has been used extensively in the literature, where the model allows one to determine a true material hardness independent of load or indent size. For ceramics and other brittle materials, such as intermetallic compounds, there is an indentation size effect due to the extent of fracture of the material [6,15–17]. Depending on what one wishes to learn about the material, low load indentations can be used to explore the yield strength [17] or the high load limit can be applied to examine a hardness under conditions of extreme fracture [6,15,16].

The examples in the previous paragraph for useful versions of the indentation size effect are for engineering materials manufactured by traditional methods that have a relatively constant and

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homogenous distribution of defects. The problem presented here is for a material manufactured by cold spray [18–20], a young material processing technology that consolidates metallic powders by propelling them to supersonic velocities. The powders impact onto a substrate and build up a coating. Many complex phenomena take place during deposition, including: work hardening, formation of adiabatic shear instabilities and recrystallization [21–24]. The plastic deformation and formation of the adiabatic shear instability are believed to contribute to the bonding [25–28] for both particle to substrate (i.e. coating adhesion) and particle to particle (i.e. coating cohesion). Also, cold sprayed coatings demonstrate regions of high dislocation density and grain refinement [22] and have varying amounts of large scale defects such as porosity and particle boundaries [29,30]. The extent and character of the defects within cold sprayed materials is very dependent on the processing conditions and will not necessarily be constant within a given coating. Thus, this is a challenging material for hardness testing where analysis of the indentation size effect is necessary and was shown to reveal significant additional information compared to a single load analysis for the hardness [30].

In this paper, nanoindentation and microindentation techniques were used for varied load indentation on Ti cold spray coatings and bulk Ti plate. The mechanical response of the coatings and the bulk Ti plate to the indentation load was evaluated by a measure of the hardness but also by post-examination of indents. The coating hardness at varied indentation loads was explained through the formulation of a hardness loss parameter that was correlated to coating porosity, cohesive strength and work hardening.

2. Procedure

2.1. Sample preparation

Cold spray coatings were produced from commercially pure titanium powders, including a spherical commercial purity (CP) Ti powder obtained from Raymore Industries (Raymore Inc., Boisbriand, QC, Canada) and a non-spherical (irregular) CP-Ti powder, obtained from H.C. Starck (HC Starck GmbH, Goslar, Germany). The size and morphology of the powders were reported previously [31]. The average particle diameters of the powders were 29 μm for the spherical powder and 63 μm for the non-spherical. Substrates were either a mild steel (for coatings) or a CP-Ti plate (for single splats). For coatings, the substrate was grit blasted with 24 grit Al_2O_3 , while for splats, the substrate was left with a milled finish. The microstructure of the bulk Ti plate and feedstock Ti powder, shown in Fig. 1(a and b), was acicular with an equiaxed colony diameter of $10 \pm 6 \mu\text{m}$ in bulk Ti plate and estimated colony size of 5–10 μm in feedstock Ti powder. Steel substrates were not characterized.

Coatings studied here were prepared with a Kinetiks 4000 cold spray gun (CGT GmbH, Ampfing, Germany) with either a MOC 24 nozzle (CGT, GmbH, Ampfing, Germany) for nitrogen or a VH70 nozzle (ASB Industries, USA) for helium. Many of the general aspects of deposition and starting materials, including measurements of velocity, the size, morphology, composition and microstructure of the powders were previously published [31,32]. Briefly summarizing sample preparation, coatings prepared with nitrogen had gas pressures from 2 MPa to 4 MPa and gas preheat temperatures ranging from 300 °C to 800 °C. The Ti powders were fed at a rate of 20 g/min at a gun standoff distance of 4 cm. The in-flight particle velocity was measured in a free jet with DPV2000 system (Tecnar Automation, St-Bruno, QC, Canada). One coating was prepared with spherical powder and He as the propelling gas. The gas pressure was maintained at 4 MPa and the gas was preheated to 350 °C. The gun standoff distance and powder feeding rate were 8 cm and 20 g/min.

Cold sprayed splats were prepared from spherical powder with nitrogen and helium gases under the same gas temperature, gas pressure and gun stand-off distance as the cold spray coatings. Single splats were deposited by increasing the gun traverse speed to 1 m/s and by decreasing the powder feeding rate to 1–5 g/min in the same manner as previously reported [28]. The splats deposited with nitrogen gas were produced at a different time frame than coatings and the in-flight particle velocity was re-measured prior to sample preparation.

2.2. Microstructural characterization

All cold spray coatings were sectioned across the coating thickness and mounted in cross-section in a cold mount epoxy. The mounted specimens were polished with metallographic procedures designed to minimize polishing damage (specifically for examination by electron backscatter diffraction) with a final step of 0.05 μm colloidal silica. No chemical etching was carried out prior to indentation as it can create surface roughness that would adversely influence nanoindentation measurements. The same was also true for specimens examined for porosity measurements.

A variable pressure scanning electron microscope (Hitachi VP-SEM, Japan) was operated in high vacuum and images were acquired in backscattered mode. For each coating, a total of ten micrographs were collected at 500 $\times$ magnification, from which an average porosity was calculated. It should be noted that the porosity and microstructural characterization carried out was for the same coatings, but for cross-sections a few millimeters away from the cross-sections in previous reports [31]. Porosity was measured across the coating thickness (approximately 50 μm away from the coating – substrate interface and the coating surface regions) using a commercially available image analysis software (Clemex Vision

Fig. 1. Etched images (LOM) of (a) bulk Ti plate and (b) feedstock Ti powder. Acicular Ti microstructure was observed in feedstock powder and in the bulk Ti plate.

Professional 5.0, Clemex Technology Inc., Longueuil, QC, Canada) where the grayscale was used to differentiate the number of pixels tied to the porosity. The porosity of a commercially pure Ti plate of 3 mm thickness (McMaster-Carr, Aurora, OH) was measured in the same manner as described above.

VP-SEM was also used to characterize the interface between the splats and Ti substrate. The splats were mounted into a conductive cold mount epoxy and polished to a final step of 0.05 μm colloidal silica across the splat cross-section. The samples were then etched with Kroll reagent (3 ml HNO_3 , 2 ml HF and distilled water) to reveal the bonded interface between splats and the substrate.

2.3. Nanoindentation testing

Nanoindentation testing was carried out using Ubi3 instrumented indenter (Hysitron Incorporated, Minneapolis, MN, USA) with a diamond Berkovich tip. Indentation of coatings was carried out by two methods. A survey of the coating hardness was carried out with a line profile of 50 indents across the coating thickness with an indent spacing of 10–20 μm . The load function had a 1 mN peak load with 1 s hold time and 0.2 mN/s loading and unloading rates. For the second method, the indentation size effect was explored by varying the indentation load from 1 mN to 20 mN with loading and unloading time segments of 5 s and a hold time of 1 s. Five matrices of 8 indents at varying peak loads and spaced at 10 μm apart were performed. The five matrices were performed in random locations in the coatings, distant from both the substrate-coating interface and the free surface.

The hardness was calculated from the unloading curves using the method described by Oliver and Pharr [33] and according to Eq. (1). In Eq. (1), the hardness is measured from the peak load, P (which was assigned), and the Berkovich indenter projected area, A_p , that is a function of the indentation contact depth, h_c , as described in Eq. (2). In Eq. (2), $C_0 = 24.5$ for an ideal Berkovich tip while C_1 , C_2 and C_3 are the constants that are used to describe the area function of the tip, accounting for roughness and tip defects.

$$H = \frac{P(N)}{A_p(\text{m}^2)} \quad (1)$$

$$A_p = C_0 h_c + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} \dots \quad (2)$$

The tip area function for the Berkovich indenter, as per Eq. (2), and frame compliance of the instrument were calibrated on a fused quartz standard, with these results being periodically checked during the indentation testing.

In Eq. (2), indenter contact depth, h_c , is calculated from the load/unload curves according to Eq. (3). The contact depth is a function of the indenter penetration depth at the maximum load, h_f , load, P , and material stiffness, S , which is a slope of the unloading segment of the indentation load versus indentation depth curve [33]. The indenter shape geometry is taken into account by the ε geometry factor. For a Berkovich indenter, geometry factor, ε , is 0.72 [33].

$$h_c = h_f - \varepsilon \left(\frac{P}{S} \right) \quad (3)$$

The nanoindentation hardness reported in this paper is measured according to Eq. (1) and will be referred to as nanohardness. Topographical images of the sample regions tested were taken before and after nanoindentation with a piezoelectric scanner system (i.e. similar to an atomic force microscope) mounted on the Ubi3 system and using the nanoindentation tip for imaging. Indentation load vs. indentation depth curves in combination with topographical imaging were used to identify and remove any indents affected by coating porosity or particle de-bonding.

2.4. Microindentation testing

Microindentation was performed with Clark Microhardness Tester CM-1000AT with a Vickers diamond indenter. The indentation loads of 0.1–5 N were used. Five indents, spaced at three indent spacings, were performed at a given load. Indent diagonals were measured by optical means with a magnification of 500 $\times$. The difference between the two diagonals was typically very small (0–7% difference), but in cases where indents interacted strongly with coating defects (e.g. porosity) the difference was as large as 17%. Vickers hardness, VH , was calculated by dividing the applied force (in kg) by the indent surface area (in mm^2) [5] in the standard manner. However, for a comparison between the nanohardness, the Vickers hardness were converted to the units of GPa and a hardness, H_{micro} , based on a projected contact area of the Vickers indenter [5,17,34,35]:

$$H_{\text{micro}}(\text{GPa}) = \frac{VH \times 9.8 \text{ m/s}^2}{1000 \times \sin 68^\circ} \quad (4)$$

Microindentation hardness values reported in this paper were calculated with Eq. (4) and are referred to as “microhardness.” Provided hardness is consistently reported in the same units and with the area calculated in the same manner, measurements made with Berkovich and Vickers indenters are found to have quite good agreement, largely due to the fact that both indenters are self-similar with a nearly identical relationship between projected area and indentation depth [5,34,35].

The indentation depth, h_{micro} , was calculated using Eq. (5), from the Vickers projected area, A_p^{Vickers} , which is a function of the indenter diagonals d and b [34]:

$$h_{\text{micro}} = \sqrt{\frac{A_p^{\text{Vickers}}}{24.5}} = \sqrt{\frac{d \times b}{2 \times 24.5}} \quad (5)$$

2.5. Splat adhesion strength testing

Splat adhesion strength testing was performed on individual Ti splats deposited by cold spray onto commercially pure Ti plates of 3 mm thickness (McMaster-Carr, Aurora, OH). The splats were deposited under same spray conditions as described above for full Ti coatings. The splat adhesion strength of cold sprayed Ti splats was tested using a Micro-Combi Scratch Tester (CSM Instruments, Inc., Needham, MA). A previously published splat adhesion strength testing procedure was used [28].

3. Results and discussion

3.1. Cold spray deposition and coating characterization

By changing process conditions, changes in the in-flight velocity of cold sprayed particles were realized. Fig. 2 is a plot of measured particle velocity versus gas pre-heat temperature, with gas pressure also noted as labels on the graph. Average deposition velocities ranging from 608 to 805 m/s were obtained for spherical coatings and from 652 to 859 m/s for non-spherical coatings. The higher average velocity obtained for non-spherical powder compared to spherical powder is typically explained by the higher drag forces experienced by the irregular powder [31,36]. For one coating sprayed with He and spherical powder, the deposition velocity reached 1173 m/s.

The results in Fig. 2 were all measured within the same time frame of spraying the coatings studied here. Splats were sprayed some time after the coatings were prepared with identical temperature and pressure conditions. In all instances, a 6–10% increase in the average velocity was measured for identical process

Fig. 2. Effect of the carrier gas preheat temperature and pressure on the spherical and non-spherical particle deposition velocity. The deposition velocity increased with gas preheat temperature and with gas pressure. Higher deposition velocities were measured with helium gas as opposed to nitrogen gas.

conditions. The increase in velocity was attributed to small changes in the cold spray system that resulted in a more stable gas flow. Comparisons between material properties for splats sprayed at different conditions are expected to still be useful in comparison to the coatings as the velocity increase was a systematic change for all spray conditions.

The extent of individual splat deformation (see Fig. 3) and quality of the cold sprayed coatings (see Fig. 4) changed as a function of deposition velocity. Top view and cross-sectional micrographs of splats are shown in Fig. 3. The etched cross-section of splats deposited at low deposition velocity showed non-continuous bonding between the splat and Ti substrate. The appearance of the splat–substrate interface became more continuous with increase in deposition velocity. Along with this indication of increased bonding, the splats became more deformed and pan-caked. While these observations are for Ti onto Ti, similar observations have been made for Ti deposited on mild steel [28].

As deposition velocity increased, coating microstructure was also modified for spraying with either the spherical [c.f. Fig. 4(a–c)] or non-spherical powders [c.f. Fig. 4(d–f)]. In both cases, an increase in deposition velocity translated into a more fully dense coating. This effect was even more pronounced when spraying with He. Fig. 5 shows a coating cross-section for the one specimen of spherical powder sprayed with He. This coating showed no obvious porosity at this magnification.

Porosity measurements are plotted versus deposition velocity in Fig. 6. The coatings deposited with non-spherical powder showed a higher porosity than coatings deposited with spherical powder. For both powders, an increase in the deposition velocity led to a decrease in coating porosity. For spherical powders, the coating porosity approached that of the bulk Ti plate for deposition velocities above 750 m/s. For non-spherical powders, the highest deposition condition, with a velocity of 859 m/s, led to low porosity of about 2%. One other condition, with a velocity of 762 m/s, led to a low porosity. It was not clear why this spray condition led to a more favorable porosity while others with higher velocities did not.

3.2. Splat adhesion strength

Changes in the deposition velocity also resulted in changes in the splat adhesion strength. In Fig. 7, the splat adhesion strength is plotted as a function of deposition velocity for Ti splats deposited from spherical Ti powder onto a CP Ti plate. As deposition velocity increases, the splat bond strength increases and approaches the bulk shear strength of Ti. For most splats deposited with nitrogen, the splat de-bonded at the splat–substrate interface. For the splats deposited with He, most were partially embedded in the substrate and failed within the particle itself. Thus, the splat adhesion strength for splats with He are expected to be a lower limit for the strength of the bonded interface. As particles impact, deformation and the formation of an adiabatic shear instability are the main mechanisms for metallurgical bonding of cold sprayed material [18,20,27], measurements of splat adhesion strength may provide useful comparisons to the indentation load response of coatings, which is reflective of cohesion strength between sprayed particles.

Fig. 3. SEM images of top view and etched cross-section of cold spray splats deposited at (a and b) 625 m/s (N₂ at 300°C 3 MPa) (c and d) 825 m/s (N₂ at 800°C 4 MPa) and (e and f) 1173 m/s (He at 350°C 4 MPa) particle velocity, gas preheat temperature and pressure conditions. A more pronounced bonding was observed at the splat and the substrate interface for splats deposited at a higher deposition velocity.

Fig. 4. Micrographs acquired by SEM for spherical (a–c) and non-spherical (d–f) Ti coatings deposited with nitrogen gas with a deposition velocity and gas conditions of: (a) 608 m/s (N_2 at 300 °C, 3 MPa), (b) 648 m/s (N_2 at 500 °C 3 MPa), (c) 805 m/s (N_2 at 800 °C 4 MPa), (d) 652 m/s (N_2 at 300 °C 3 MPa), (e) 725 m/s (N_2 at 500 °C 3 MPa) and (f) 859 m/s (N_2 at 800 °C 4 MPa).

Fig. 5. Micrograph acquired by SEM for a spherical Ti coating deposited at deposition velocity of 1173 m/s (He at 350 °C 4 MPa).

Fig. 6. Coating porosity with respect to deposition velocity. The spherical coatings deposited with nitrogen are plotted as closed circles while the spherical coating deposited with helium gas is plotted as an open circle.

3.3. Nanohardness and microhardness results and comparison

Results from nanoindentation testing (at a constant peak load of 1 mN and indenting across the coating) are presented in Fig. 8(a) as average nanohardness versus deposition velocity. No significant variation in nanohardness was observed as a function of position within the coatings. This trend has been observed previously [24,37], where nanoindentation provided hardness associated with material with minimal influence of porosity and other macroscopic defects. The nanohardness of the coatings was higher compared to the bulk material and the starting powders (all plotted at 0 m/s in Fig. 8(a)). Also, coatings prepared with non-spherical powders were marginally harder than those prepared with spherical powders. Lastly, at this indentation load, the starting powders and bulk Ti plate all had similar hardness.

Fig. 7. Splat adhesion strength for Ti splats on a commercially pure Ti plate. The data points in black represent the adhesion strength of splats deposited with nitrogen gas. The data point in open circle represents the adhesion strength of splat deposited with helium gas. The adhesion strength of splats increased with increase in the deposition velocity. The horizontal line is the shear strength of grade 2 bulk Ti and is provided in Ref. [48].

Fig. 8. Cold spray coatings (a) nanohardness at 1 mN load and (b) microhardness at 0.1 N load. Higher nanohardness was measured for the cold spray coatings when compared to the nanohardness of the feedstock powder and bulk Ti plate. The nanohardness was higher for the non-spherical coatings and lower for the spherical cold spray coatings. On the other hand, no difference between the microhardness of the cold sprayed coatings and microhardness of the bulk Ti plate was measured.

In Fig. 8(b), microhardness of spherical and non-spherical coatings is plotted with respect the deposition velocity. The hardness of the feedstock powder was not measured using a microindentation technique because, even for low loads, the indent size approached the size of the particles. The microhardness values for spherical and non-spherical coatings were similar to each other for all spray conditions and not significantly higher or lower than the hardness of the bulk Ti plate.

From examination of Fig. 8, different conclusions can be made about the relative hardness of the coatings, powders and substrate, depending on whether nanohardness results (c.f. Fig. 8(a)) or microhardness results (c.f. Fig. 8(b)) are used. A number of parameters affect the hardness measurements in the nanoindentation and in the microindentation regimes. Reduction in grain size or increase in material work hardening and dislocation density are often associated with the increase in the hardness [13]. On the other hand, a decrease in the hardness can be tied to material defects such as porosity and in the case of coatings to the particle de-bonding [13,29,38]. The degree to which these parameters affect the hardness measurements depends on the indentation load and size. Thus, for materials such as cold sprayed coatings, which have different amounts of work hardening, porosity and particle bonding strength, it becomes critical to explore the indentation size effect in detail to determine a best method that explains the hardness response of all materials consistently.

3.4. Nanoindentation size effect on hardness

Matrix nanoindentation with indents at varying load was performed in random locations in the coatings. An example of a matrix of indents imaged in the SEM is shown in Fig. 9. As can be seen in Fig. 9(a), the indent #1, which encountered porosity, demonstrated an uncharacteristic increase in the indentation depth (c.f. Fig. 9(b)) compared to other indents that did not encounter porosity. In some instances, indentation in a coating with poor cohesive strength could result in particle de-bonding similar to one observed with indent #3 and possibly indent #2 in Fig. 9(a). Like the porosity interaction, particle de-bonding induced an uncharacteristic increase in the indentation depth for a given indentation load as can be seen in Fig. 9(b). Other indents for this matrix were acceptably similar to one another within typical experimental error encountered for nanoindentation. These indents also were found to be far away from porosity and particle boundaries (c.f. Fig. 9(a)). By the examination of the indentation load–depth curves coupled with topographical imaging of residual indents, a systematic data filtering was carried out on each indent to limit the effect of the coating porosity and particle de-bonding on the nanohardness measurements. Indents that appeared to be affected by defects, from significant deviations in the load–displacement data, observation of defect interaction in AFM images or both, were discarded and not included in the final results reported here.

Fig. 9. (a) SEM image of 1–20 mN load nanoindentation indents in spherical coating deposited at 608 m/s (N_2 at 300 °C 3 MPa) and (b) corresponding indentation load vs. indentation depth curves. A more pronounced decrease in the indentation depth was measured for the indents affected by the coating porosity (indent 1) and particle de-bonding (indents 2 and 3).

Fig. 10. Nanohardness data and the result from fitting to Eq. (6) for (a) spherical cold spray coatings, (b) non spherical cold spray coatings and the bulk Ti plate (shown in both (a) and (b)).

The average nanohardness at eight different loads ranging from 1 to 20 mN is plotted in Fig. 10 as a function of the contact depth for the bulk Ti plate and all of the coatings. For every dataset, the qualitative trend is the same: with increasing indentation depth the nanohardness decreases. Due to the nature of the method used, where larger scale defects were avoided, the variation in hardness seen in Fig. 10 is likely due to the version of the indentation size effect due to geometrically necessary dislocations, often referred to as the Nix–Gao model [8]. This model, using the law of strain gradient plasticity and dislocation density distribution, is governed by Eq. (6),

$$H = H_0 \sqrt{1 + \frac{h^*}{h}} \quad (6)$$

where H is the nanohardness, h is the indentation depth, H_0 is a material hardness at infinite indentation depth, and h^* is a characteristic length scale.

The nanohardness measurements presented in Fig. 10 were fit to Eq. (6) and the results of the fits are summarized in Table 1. The best fit curves are also included in Fig. 10. In general the Nix–Gao model provided a confident fit to the nanohardness measurements. However, the most confident fit was obtained for the bulk Ti plate. Fits to the data for cold spray coatings were in some cases not as confident and generally occurred for cases where the coating had high porosity. Thus, despite the data filtering to remove suspect indents, there may be some small influence of porosity and particle de-bonding on the nanohardness results that leads to a small departure from the Nix–Gao model.

The parameter H_0 in Eq. (6) is an indication of a “true” material hardness at a condition where only statistically stored dislocations influence the hardness (independent of load or depth) and there is no effect from larger scale defects. In Fig. 11, H_0 is plotted as a function of deposition velocity. The spherical and non-spherical cold spray coatings demonstrate higher hardness when compared to the bulk Ti plate, plotted at 0 m/s. While no direct comparison for H_0 can

Fig. 11. True hardness, H_0 , of the bulk Ti, spherical and non-spherical cold spray coatings vs. deposition velocity. The spherical coating deposited with helium gas is plotted in an open circle.

be made for the feedstock powders, the comparison to the Ti plate, which had similar hardness to the powders at a load of 1 mN, provides evidence that the cold sprayed particles become harder upon impact. Higher hardness measurements in the cold spray coatings is likely a result of high impact stresses and strain induced by the cold spray deposition process, but perhaps also grain refinement as previously reported by Kim et al. [22,37]. Trends for the true hardness, H_0 , versus deposition velocity for both the spherical and non-spherical coatings were found to be rather weak. For spherical coatings, the true hardness stayed constant within the error on the measurements. For non-spherical coatings, there was a slight decrease in hardness with increasing velocity. Ti has a hexagonal closed packed structure and plastic deformation in the material is limited. It is possible that after the initial plastic deformation, the remainder of the impact stress is converted to heat and no further

Table 1
Strain gradient plasticity fit parameters for spherical and non-spherical coatings.

Spherical Coatings	h^* (nm)	H_0 (GPa)	Non-spherical coatings	h^* (nm)	H_0 (GPa)
608 m/s (N ₂ at 300 °C 3 MPa)	39 ± 15	2.92 ± 0.12	652 m/s (N ₂ at 300 °C 3 MPa)	34 ± 14	3.36 ± 0.14
648 m/s (N ₂ at 500 °C 3 MPa)	64 ± 20	2.86 ± 0.13	725 m/s (N ₂ at 500 °C 3 MPa)	27 ± 13	3.62 ± 0.14
688 m/s (N ₂ at 600 °C 3 MPa)	37 ± 9	3.06 ± 0.07	762 m/s (N ₂ at 600 °C 3 MPa)	63 ± 9	3.16 ± 0.07
785 m/s (N ₂ at 750 °C 4 MPa)	85 ± 31	3.15 ± 0.20	844 m/s (N ₂ at 750 °C 4 MPa)	54 ± 13	3.23 ± 0.11
805 m/s (N ₂ at 800 °C 4 MPa)	36 ± 12	2.98 ± 0.10	859 m/s (N ₂ at 800 °C 4 MPa)	80 ± 25	2.86 ± 0.16
1173 m/s (He at 350 °C 4 MPa)	144 ± 20	2.60 ± 0.08	–	–	–
Bulk Ti	84 ± 11	2.19 ± 0.04	–	–	–

Fig. 12. Microindentation hardness as a function of the indentation depth for (a) spherical and (b) non-spherical cold spray coating. The microhardness decreased with increase in the indentation depth for coatings deposited at low deposition velocity. A plateau hardness for all coatings was eventually reached.

work hardening takes place [21,39–42]. For both spherical and non-spherical coatings, the true hardness was nearly constant over all deposition conditions with the averages being $H_0 = 2.85 \pm 0.23$ GPa for spherical coatings and $H_0 = 3.25 \pm 0.28$ GPa for non-spherical coatings. The difference in the true hardness between coatings prepared with the different powders may be due to differences in the starting powders and the way they deform upon impact. A higher oxygen content in the non-spherical powder [31] compared to the spherical powder may explain some of the increase in hardness. Another consideration is the size of the particles. For the smaller, spherical particles, it was previously shown that the impact site has an increase in hardness while regions that undergo jetting can have thermal softening [24]. One may consider that only a small portion of the larger, non-spherical particles undergo jetting, while the rest of the particle is free to work harden upon impact and due to impact from other particles.

3.5. Microindentation size effect on hardness

Microindentation measurements also revealed a size effect, but in a different manner than nanoindentation measurements. For coatings prepared with spherical powder, two types of general behavior of microhardness versus indentation depth were observed (see Fig. 12(a)). For the two spherical coatings, prepared at low deposition conditions (i.e. deposition velocities of 608 and 648 m/s), the microhardness decreased with indentation depth up to approximately 5 μm and then became constant. All other spherical coatings, with higher deposition conditions, revealed a relatively constant and stable microhardness, the same trend observed for the bulk Ti plate.

Coatings prepared with non-spherical powder had a similar demarcation between high and low deposition conditions, but also slightly different trends (see Fig. 12(b)). For the two non-spherical coatings prepared at low deposition conditions (same conditions as for spherical but with velocities of 652 and 725 m/s), the hardness was relatively constant at depths up to 5–7 μm and then dropped above these depths. For non-spherical coatings prepared with higher deposition velocity, the hardness was stable (i.e. no rising or falling), but was also somewhat scattered. All of the observations on microindentation trends of hardness with depth are summarized in Table 2.

Differences between the spherical and non-spherical coatings for their trends of microhardness versus indentation depth are likely due to the significant difference in particle size. At low loads, diagonals of Vickers indentations were on the order of 10 μm , large enough to interact strongly with particle boundaries for the spherical coatings, but not necessarily for the non-spherical coatings with larger powder size. At higher loads, the diagonals for the Vickers indents reach 60–100 μm , a size that certainly provides interactions with particle boundaries for both spherical and non-spherical coatings.

For higher deposition velocity, spherical coatings had a very stable and constant microhardness, while the non-spherical coatings had a stable but scattered microhardness. This trend may also be due to the differences in average particle sizes, but could be also due to differences in deposition velocity and the fact that the non-spherical coating had, on average, more porosity. Another consideration is that the non-spherical powders have an irregular shape. Upon arrival, a metallurgical bond is developed at the

Table 2
Summary of plateau hardness and behavior of hardness versus indentation depth for microindentation results. For comparison, porosity and adhesion strength measurements are presented as well.

Spherical powders	Coating porosity (%)	Splat adhesion strength	General behavior of H vs. h	H_{plateau} (GPa)	Non-spherical powders	Coating porosity (%)	General behavior of H vs. h	H_{plateau} (GPa)
N ₂ at 300 °C 3 MPa	High	32 ± 52	1	1.14 ± 0.03	N ₂ at 300 °C 3 MPa	High	3	1.01 ± 0.36
N ₂ at 500 °C 3 MPa	Low	92 ± 51	1	1.32 ± 0.09	N ₂ at 500 °C 3 MPa	High	3	1.41 ± 0.23
N ₂ at 600 °C 3 MPa	Low	128 ± 86	2	1.85 ± 0.04	N ₂ at 600 °C 3 MPa	Low	4	1.83 ± 0.20
N ₂ at 750 °C 4 MPa	Low	152 ± 16	2	2.21 ± 0.08	N ₂ at 750 °C 4 MPa	High	4	2.30 ± 0.29
N ₂ at 800 °C 4 MPa	Low	238 ± 33	2	2.15 ± 0.35	N ₂ at 800 °C 4 MPa	Low	4	2.41 ± 0.26
He at 350 °C 4 MPa	Low	254 ± 21	2	2.57 ± 0.04	–	–	–	–
Ti plate	Low	–	2	1.97 ± 0.06	–	–	–	–

* A porosity of less than 3% was marked as low while greater than 5% was marked as high. 1 – hardness drops “early,” plateaus above 5 μm . 2 – no hardness drop, stable. 3 – hardness drops “late,” above 7.5 μm . 4 – no drop, hardness is stable but scattered.

Fig. 13. Optical images of 0.1 N and 5 N indents in (a and b) bulk Ti plate, spherical Ti coatings deposited at (c and d) 608 m/s (N_2 at 300 °C 3 MPa), (e and f) 805 m/s (N_2 at 800 °C 4 MPa) and g-h) 1173 m/s (He at 350 °C 4 MPa) particle deposition velocity, gas preheat temperature and gas pressure. Indenter interaction with coating porosity and particle de-bonding in the indentation site were observed.

impact site but if a significant portion of the particle does not participate strongly to the impact event, the bonding strength may be reduced. Thus, one would expect a higher degree of variability of the cohesive strength when using irregular powders. Despite differences in the general behavior of microhardness versus

depth, all of the coatings exhibited a constant microhardness at the highest loads where there is the most significant interaction with defects such as particle boundaries and porosity. Thus, to provide a simple characterization of the microhardness for comparison between coatings, the values for the highest three loads

Fig. 14. Optical images of 98 mN and 4900 mN indents: in non-spherical deposited at (a and b) 652 m/s (N_2 at 300 °C 3 MPa) and at (c and d) 859 m/s (N_2 at 800 °C 4 MPa) particle deposition velocity, gas preheat temperature and gas pressure.

were averaged. These results are presented in Table 2 as “plateau hardness”.

Trends in microhardness identified in Fig. 12 and summarized in Table 2 were correlated with features observed in optical micrographs of residual indents. Fig. 12 is a collection of optical micrographs for the bulk Ti plate (c.f. Fig. 13(a–b)), coatings sprayed with nitrogen with velocities of 608 m/s (c.f. Fig. 13(c–d)) and 805 m/s (c.f. Fig. 13(e–f)), and the coating sprayed with helium (c.f. Fig. 13(g–h)). In each case, an image is provided for a residual indent at the lowest load (0.1 N) and the highest load (5 N). For the residual indents on the Ti plate, a deviation from a perfect diamond shape was observed (see Fig. 13(b)). This is due to plastic anisotropy that has been previously observed for CP Ti [43]. Otherwise, the indents were well behaved with no obvious interaction with defects.

In contrast, the indents on the coatings deposited at low deposition velocity of 608 m/s exhibited evidence of particle de-bonding and interaction with porosity. Comparing the plateau hardness of the Ti plate to this coating (c.f. Table 2), these defects led to a distinct reduction in the hardness. The two coatings prepared at higher velocity conditions with nitrogen (c.f. Fig. 13(e–f)) and helium (c.f. Fig. 13(g–h)), showed residual indents that were much similar to those on the bulk Ti plate. Some particle de-bonding and interaction with porosity was observed, but not nearly as much as for the lower deposition velocity conditions. These observations are consistent with trends identified in Table 2 where the high deposition velocity condition coatings have the same trend of microhardness with depth as the bulk Ti and have plateau hardness as high or higher than the bulk Ti plate.

Optical micrographs of residual indents in non-spherical coatings provided similar information. For a coating with lower deposition velocity of 652 m/s, there is evidence of extensive defect interaction (c.f. Fig. 14(a–b)), while for high deposition velocity of 859 m/s, there is not nearly as much defect interaction (c.f.

Fig. 14(c–d)). These differences in defect interaction with the indenter were reflected in differences in the plateau hardness for the two non-spherical coatings (c.f. Table 2). Observation of residual indents for the other spherical and non-spherical coatings, while not shown here, showed information consistent with data in Table 2 and the observations discussed here.

3.6. Formulation of a hardness loss parameter

As discussed in Section 3.3, indentation at only one load, whether it be with nanoindentation or microindentation, provides an incomplete and potentially incorrect comparisons for the mechanical properties of cold sprayed materials. An exploration of two distinctly different versions of an indentation size effect for nanoindentation (c.f. Section 3.4) and microindentation (c.f. Section 3.5) provided valuable information on the mechanisms for changes in the measured hardness. As can be seen in Fig. 10, in the nanoindentation regime, the hardness drops with indentation load following the strain gradient plasticity model of Nix and Gao [8]. Thus, with nanoindentation performed in regions least affected by porosity and particle boundaries, the dominant mechanism for the hardness changes (i.e. indentation size effect) in Fig. 10 must be variation in the density of geometrically necessary dislocations beneath the indenter. This version of the indentation size effect becomes less pronounced at higher indentation loads and the nanohardness eventually converged to a constant hardness value, H_0 , which is independent of the indentation depth. This parameter, H_0 , is the “true” material hardness, which is dependent on the statistically stored dislocation density in the material and could be also tied to the material grain size, work hardening and recrystallization linked to cold spray deposition process [22,24,29,37,44]. In a fully dense material, H_0 should correlate well with indentation at higher loads and greater indentation depth (e.g. the microhardness measured here).

Fig. 15. Indentation size effect on nanohardness and microhardness measurements in spherical cold spray coating deposited at 608 m/s (N_2 at 300 °C 3 MPa). The difference between true hardness – H_0 and plateau hardness – $H_{plateau}$ is measured in terms of “hardness loss”.

In the cold spray process, there is significant evidence that near fully dense materials can be fabricated [19]. However, very little research has been done to quantify the extent to which a coating with very low porosity will behave mechanically in the same manner as the material prepared by traditional bulk manufacturing methods. Other factors besides porosity come into play, such as the cohesion between cold sprayed particles. In this study, these additional defects caused the coating microhardness to drop and, in cases where there was significant indenter–defect interaction, to vary with indentation depth (see Fig. 12). The plateau hardness, taken from the highest three loads, is representative of a microhardness that has significant interaction with porosity and particle boundaries near the indentation site.

With these two important hardness parameters defined and tied to specific types of defects in the coatings: “true” material hardness, H_0 , tied to dislocations, and the plateau hardness, $H_{plateau}$, tied to porosity and particle boundaries, we now formulate the concept of a “hardness loss.” Our microhardness measurements were consistently lower than H_0 , which can be seen by comparing Figs. 10 and 12, or values of H_0 and $H_{plateau}$ in Tables 1 and 2. Also, Fig. 15 provides an example dataset of both nanohardness and microhardness for one of the spherical cold spray coatings. The difference between H_0 and $H_{plateau}$ is the “hardness loss” related to the presence of porosity and incomplete particle bonding within the coating. As the “true” hardness of the materials studied here also varies slightly from coating to coating due to differences in initial dislocation density and small variations in microstructure due to recrystallization, the hardness loss was best taken as a percent difference by the following equation:

$$\text{Hardness loss(\%)} = \frac{H_0(\text{GPa}) - H_{plateau}(\text{GPa})}{H_0(\text{GPa})} \quad (7)$$

The hardness loss was calculated for all the cold spray coatings and bulk Ti with Eq. (7) and the H_0 and $H_{plateau}$ values from Tables 1 and 2. A decrease in the hardness loss was observed with increase in the deposition velocity, as shown in Fig. 16. A hardness loss reaching 0% was measured for the coating deposited with He gas at 1173 m/s. Interestingly, the hardness loss in the bulk material was not zero (~10%) and was likely due to the asymmetric nature of some of the indents, as seen in Fig. 13(b). Other defects may have led to hardness loss for the bulk material such as porosity, or grain boundary sliding or microcracking. Some part of the hardness loss may also be related to the small differences between the Berkovich and Vickers indenters [5,35].

The dependence of the hardness loss parameter on porosity revealed a direct relationship for both spherical (see Fig. 17(a))

Fig. 16. Percent hardness loss in (a) spherical and (b) non-spherical cold spray coatings plotted as a function of deposition velocity. A linear regression fit for the hardness loss of spherical and non spherical cold spray coatings is shown. The spherical coating deposited with helium gas is plotted in an open circle.

and non-spherical coatings (see Fig. 17(b)). However, as noted in Table 2, the coatings fit into two groups of low porosity (<3%) and high porosity (>5%). For spherical coatings with low porosity, there were significant differences in hardness loss despite similar porosity. Similarly, for high or low porosity non-spherical coatings, there are significant differences in hardness loss within each group. Thus, the apparent direct relationship seen in both Fig. 17(a and b) is somewhat deceptive. Other mechanisms for hardness loss must be at play.

Other than porosity, the other mechanism for hardness loss, seen in Figs. 13 and 14, was particle de-bonding. This mechanism is somewhat complex and is a function of the inter-splat bonding strength (i.e. cohesive strength). The cohesive strength of a cold spray coating depends on the formation of the adiabatic shear instability, which is believed to become significant above the critical velocity for a given material. For Ti, the critical velocity has been found to be anywhere from 700 m/s to 900 m/s [20]. For the spherical particles of similar size to those sprayed here, the critical velocity is expected to be between 700 and 750 m/s [20,31,37]. For the non-spherical Ti powder, the critical velocity has been measured previously to be 690–880 m/s [45]. The extent of metallurgical bonding will still vary as a function of particle velocity, particle impact angle, the in flight particle temperature, heat input from the particle impact and a corresponding temperature rise of the coating during deposition. Many of these phenomena are difficult to measure experimentally, especially the in-flight particle temperature. Computer simulations can successfully predict the heat input from the gas and particle impact with the substrate [27,46].

As a first step in understanding the relationship between the hardness loss parameter and cohesive strength, we consider the correspondence between hardness loss and the splat adhesion strength (see Fig. 18). Despite the complexity associated with cohesive strength as discussed in the previous paragraph, the relationship between Ti splat adhesion strength and hardness loss parameter was good. Thus, the basic mechanism of splat impact leading to adiabatic shear instability and metallurgical bonding seems to translate quite well to hardness loss due to particle cohesive strength.

Comparisons between the hardness loss of the cold spray coatings and the bulk Ti can provide a new understanding for optimization of the cold spray process to obtain a near fully dense material with similar mechanical response to materials fabricated by more traditional methods. The fits provided in Fig. 16 are

Fig. 17. Percent hardness loss vs. (a) spherical and (b) non spherical coating porosity. An increase in the hardness loss is measured with increase in the coating porosity for spherical and non spherical Ti coatings. The spherical coating deposited with helium gas is plotted in an open circle.

linear regressions to the data for both the spherical and non-spherical coatings prepared with nitrogen. The intercept at 0% hardness loss is indicative of the material behaving in an ideal bulk-like manner with no particle de-bonding and porosity and with no other significant mechanisms for indentation size effect other than the geometrically necessary dislocations of the Nix–Gao model. Such behavior was only observed for the coating deposited with He at deposition velocity of 1173 m/s. Coatings deposited with nitrogen all had deposition velocities below 850 m/s and also exhibited particle de-bonding at least to some small extent. Thus, considering these observations and using the intercepts at zero hardness loss from Fig. 16, the minimum recommended deposition velocities in order to achieve ‘bulk like’ properties for the spherical and non-spherical Ti powders deposited with nitrogen gas are 910 m/s and 950 m/s, respectively. However, to define zero hardness loss as the necessary condition for a quality coating is perhaps too strict. The hardness loss for the Ti plate was roughly 10%, and considering the error bars, coatings with a hardness loss on the order of 15% behaved in a similar manner. One would need to fully explore the effect of variation in cohesive strength in these coatings on the bulk behavior, perhaps in a tensile testing configuration [47].

It is important to note that higher gas temperature, when compared to Helium coating, is used to deposit nitrogen coatings. The

gas temperature has been previously shown to have an effect on particle adhesion and can affect the hardness loss parameter [28]. Separate study is required to define the intercept velocity for coatings deposited with He. It would also be interesting to explore the effect of other process conditions, such as feed stock power temperature and the substrate temperature, on the hardness loss parameter and whether these changes can provide a significant reduction in the intercept velocity from Fig. 16.

The hardness loss technique explored here has implications for hardness testing in general, but especially for materials fabricated by powder consolidation. To simply measure hardness at one load, whether it is large or small will not provide a complete picture of the mechanical response of the material. The technique developed and reviewed here, with combined nanohardness and microhardness and development of the hardness loss parameter, provides a relatively simple alternative that will give a more complete picture of the mechanical integrity of a material made by cold spray or other powder consolidation techniques.

4. Conclusions

The mechanical behavior of Ti cold spray coatings, prepared with both spherical and non-spherical powders, was examined by indentation methods. Single load indentation testing was found to be insufficient and led to potentially erroneous comparisons among the coatings fabricated. Instead, a method using many indentation loads was used to explore the indentation size effect in both the nanoindentation and microindentation regimes. In combination with observation of the residual indents, a hardness loss parameter was formulated that uses both data from nanoindentation, which was representative of dislocation based indentation size effect (i.e. the Nix–Gao model), and from microindentation, which was representative of indentation size effect related to porosity and poor particle adhesion. Using the multiple load indentation method developed here and a number of other experimental techniques, the following conclusions were made:

- (1) Based on the hardness measurements and the true hardness calculated from the Nix–Gao fits to nanoindentation data, the cold spray Ti coatings were harder than the starting powders and harder than the annealed bulk Ti specimen, likely due to work hardening that takes place upon particle impact.
- (2) All of the cold spray coatings prepared with nitrogen as the propelling gas exhibited a microhardness, H_{plateau} that was lower than the true hardness, H_0 , obtained from the Nix–Gao fits to

Fig. 18. Percent hardness loss of spherical coatings as a function of cold spray sputter adhesion strength on a bulk Ti plate. A decrease in hardness loss was measured with increase in the sputter adhesion strength. Shear strength of a grade 2 Ti [48] was used when plotting data for the bulk Ti plate.

nanoindentation data. This hardness loss was due to interaction of the indenter with particle boundaries and porosity.

- (3) A hardness loss parameter was developed that described the extent to which porosity and poor cohesion strength affects the mechanical behavior of the cold spray coatings. The hardness loss decreased as deposition velocity increased. For the lowest spray condition, the hardness loss was 61% for spherical coatings and 70% for non-spherical coatings. For the highest spray condition with nitrogen propelling gas, the hardness loss was 28% for spherical coatings and 16% for non-spherical coatings.
- (4) Adhesion strength was measured between Ti splats on a bulk Ti plate. The adhesion strength increased as a function of deposition velocity. Also, as the adhesion strength increased, the hardness loss decreased, indicating the measurements of splat adhesion can provide some indication of cohesive strength within a coating sprayed with the same conditions.
- (5) Based on trends of hardness loss with porosity and adhesion strength and examination of images of residual indents, the main mechanism for hardness loss was found to be particle de-bonding (i.e. poor cohesive strength). While porosity did influence the hardness loss, the effect of particle de-bonding was more obvious as a range of cohesive strength was realized in the coatings studied here while only a narrow range of porosity was observed.
- (6) For the coating prepared with helium as the propelling gas, the hardness loss was close to zero (1%). At the same time, the splat adhesion strength was high and no evidence of particle de-bonding in residual indents was observed.
- (7) The hardness loss parameter was used to compare cold sprayed material to a bulk Ti plate prepared by traditional manufacturing methods. This led to a recommended minimum deposition velocity for fully dense Ti coatings with “bulk-like” behavior (i.e. no particle de-bonding or significant porosity effects). For the powders sprayed here, the minimum velocity was 910 m/s for spherical powders and 950 m/s for non-spherical powders.
- (8) The technique of multiple load indentation and use of the hardness loss parameter was found to adequately explain the mechanical behavior in cold spray coatings that have a wide range of defects. In comparison to single load indentation methods, the new technique provided a more complete description of the mechanical behavior and the ability to make meaningful comparisons between coatings.

Acknowledgements

The authors gratefully acknowledge the financial support from the Canadian Foundation for Innovation; CFI, project No. 8246, for the cold spray equipment, CFI, Leader's Opportunity Fund, project No. 13029 for the nanoindentation equipment and Natural Sciences and Engineering Research Council (NSERC) Strategic Grants Program for the operational funding of this project. The authors thank Michael Shockley, Ahmad Rezaeian, Bernard Harvey, Mario Lamontagne and Frederic Belval for their technical assistance. Finally, the authors acknowledge the staff in the Functional Coatings and Surface Engineering Laboratory (FCSEL) at Ecole Polytechnique de Montreal for providing access to the instrument used for splat adhesion testing.

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