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Recrystallization of Cold Spray-Fabricated CP Titanium Structures

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Cold gas dynamic spray (cold spray) is a promising rapid deposition technology in which particles deposit at supersonic velocities. The effect of isothermal annealing on recrystallization and mechanical properties of commercial purity (CP) titanium structures that were directly fabricated through cold spray deposition is studied. The optimized cold spray parameters led to a dense cold spray structure. Results show that annealing improves ductility of the cold-sprayed CP titanium structure. The mechanism for softening is the nucleation and growth of equiaxed grains, which include an ultrafine grain structure. A physical-based model for recrystallization of the cold spray CP titanium is proposed. The results show that recrystallization does not eliminate preferred orientation inherited from the cold spray material.

Keywords cold spray, heat treatment, recrystallization, titanium, ultrafine grain

1. Introduction

The unique properties that titanium provides such as high strength-to-weight ratio, excellent corrosion resistance, and bio-compatibility have made this material a favorable option for many applications in aerospace, implants, and corrosive environments (Ref 1-4). However, the high oxygen affinity of titanium limits the affordability of this material due to expensive production processes that require a controlled atmosphere such as vacuum arc and cold hearth melting (Ref 5). It seems, however, that the absence of oxidation through cold gas-dynamic spray (cold spray) process makes this technology a cost-effective alternative in direct fabrication of titanium products from powder. This is confirmed by, an earlier report by Karthikeyan (Ref 6), which reveals that cold spray fabrication leads to reduction in material input, elimination of mold and melting cost, and reduction of rework and finishing for titanium products, thus making titanium an affordable choice for wider industrial applications.

Cold spray is a deposition process in which small particles in the solid state accelerate to high velocities (normally above 500 m/s) in a supersonic gas jet and deposit on the substrate material. The kinetic energy of the particles is used to obtain bonding through plastic deformation upon impact with the substrate. This provides a unique advantage for cold spray to be exploited for temperature-sensitive, oxygen-sensitive, phase-sensitive, amorphous, and nanostructure materials. The mechanism for metallic bonding achieved through cold spray has been proposed to be involved with the rupture of thin films on the particle's surface generating a direct interface (Ref 7, 8).

For successful fabrication of titanium parts via cold spray, a critical particle velocity is required (Ref 9, 10). This velocity is achieved through optimization of cold spray parameters such as deposition gas (temperature, pressure, and type of the gas), stand off (the distance between the tip of the nozzle and substrate), powder size, and powder feeding rate. Generally, successful supersonic deposition results in the formation of a dense material with limited ductility that constitutes largely deformed particles known as splats (Ref 11, 12).

The splat formation in cold spray deposition is a complicated thermomechanical event that generally leads to formation of dislocations and imperfections in the microstructure limiting plastic deformation. Recrystallization, which involves nucleation and growth of new dislocation-free grains from the deformed structure, improves ductility. Earlier studies (Ref 13) have shown such improvement for cold spray CP titanium with, however, limited attention to microstructural evolution. The aim of this study is to examine the influence of isothermal heat treatment on cold spray CP titanium structures.

The results show that limited work hardening in cold spray CP titanium provides the driving force for sluggish static recrystallization. Static recrystallization occurs through a nucleation and growth process where new strain-free nuclei form and grow into new grains at the expense of the deformed material (Ref 14). Isothermal heat treatment of cold spray CP titanium led to formation of ultrafine (<5 μm) grains in the material. X-ray diffraction results reveal that recrystallized structure of cold spray CP titanium exhibits preferred orientation, which is most likely inherited from cold spray-fabricated material.

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2. Experimental

A commercially available CP titanium, grade 4, powder with composition presented in Table 1 was chosen for this study. The powder was sourced from Xian deBaode Metallurgy Pty Ltd. and was produced using hydride-dehydride method. The average particle size was 27 μm with powder size distribution and particle morphology as shown in Fig. 1. A cold spray system (CGT™ KINETIKS® 3000) was used for direct fabrication (deposition) of the material from powder. Helium at elevated pressure was introduced to a gas heater and powder feeding vessel (Fig. 2). Heating of the pressurized gas was established electrically. The high pressure and high temperature gas was introduced into a converging/diverging (de Laval) nozzle that was attached to a robot.

Compression of the gas through the nozzle throat followed by expansion to atmospheric pressure resulted in supersonic flow conditions. Temperature of the gas was measured using a thermocouple located in the converging (stagnation) section of the nozzle. Similarly, a pressure sensor recorded the gas pressure in the stagnation zone of the spray nozzle. Cold spray parameters shown in Table 2 were optimized in such a way that maximum velocity for particles was achieved from the cold spray system. This was important to eliminate porosity and achieve a dense material.

Table 1 Composition of CP titanium powder

Ti	C, %	Fe, ppm	H, %	N, %	O, %	Si, %	Other, %
Balance	0.12	160	0.03	0.01	0.35	0.9	0.4 max

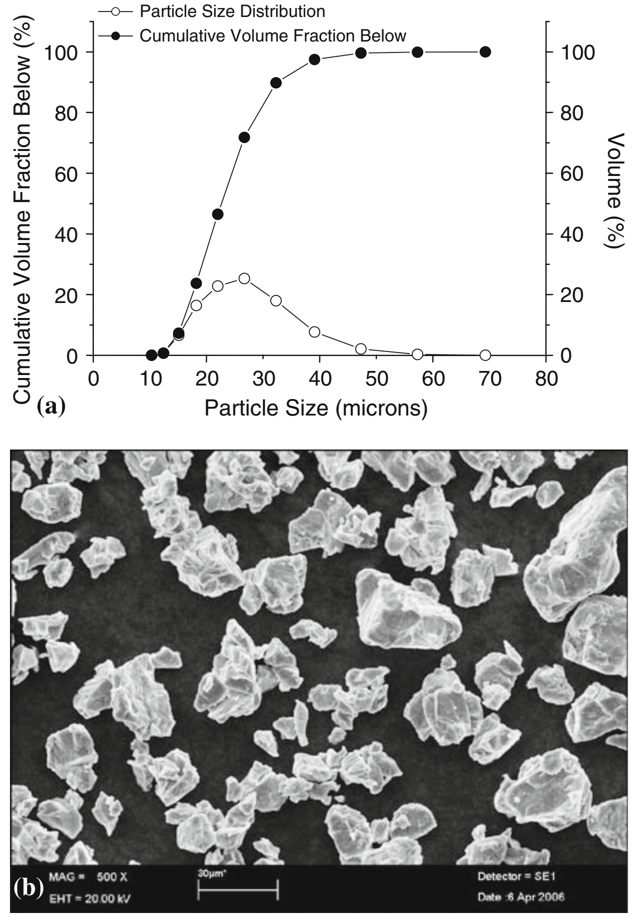

Fig. 1 (a) Size distribution and (b) scanning electron micrograph of the CP titanium powder used in this study

Electrical Discharge Machining (EDM) was used to prepare samples (10 × 10 × 10 mm) from the CP titanium block in the deposition direction. Specimens were annealed isothermally at 350, 450, and 550 °C in air. Utilization of air instead of controlled atmosphere appears to be a cost-effective practice for CP titanium in many industrial applications. Annealing temperature and time were chosen to establish softening curves under the condition that oxidation was minimized, and the results were comparable with cold-rolled and annealed CP titanium studies available in literature (Ref 15, 16).

Hardness of some specimens under Vickers indentation load of 300 g was measured after grinding with 240- and 1200-mesh SiC papers. To examine improvement of mechanical properties after isothermal annealing, subsize tensile samples were machined, according to ASTM E8M standard, from the fabricated block normal to the deposition direction (Fig. 3). The gage length for tensile samples was 10 mm. Two samples were tested for each experiment, and the results were averaged for a loading rate of 0.5 mm min^{-1}.

Some specimens were mounted for microstructural observations. Samples were polished with 1200-, 2000-, and 4000-mesh sand papers for 2 min. This was followed by 15, 3, and 1 μm diamond polishing. A small force (12 Newton) was applied to prevent particle (splat) ejection from cold spray specimen surface. An Olympus PMG3™ microscope was used for microstructural observation. Some specimens were etched in a modified Kroll's titanium etching solution (3cc HF, 30cc HNO_3, and 67cc water). Five drops of surfactant were added to reduce surface tension of the solution and to improve grain boundary etching. The average linear intercept grain size was measured using computer-aided image analysis. The numbers of intercepts were measured for at least 10 random fields, from which the average intercept length was derived.

A Bruker GADDS X-ray micro-diffractometer using Cu Kα radiation monochromated with crossed coupled Gobel mirrors operating at 40 kV and 40 mA was employed to determine the X-ray diffraction patterns. The X-ray beam was collimated to a spot size of 800 μm with a Bruker pinhole collimator, and a count time of 120 s was used in each case. Diffraction patterns were produced by Chi-integration around the intersected Debye cones to give a scan over the 2-theta range 23.7 to 57.1° with a step size of 0.02°. Analyses were performed on the collected X-ray data using the Bruker XRD search match program EVA™. Crystalline phases were identified using the ICDD-JCPDS powder diffraction database.

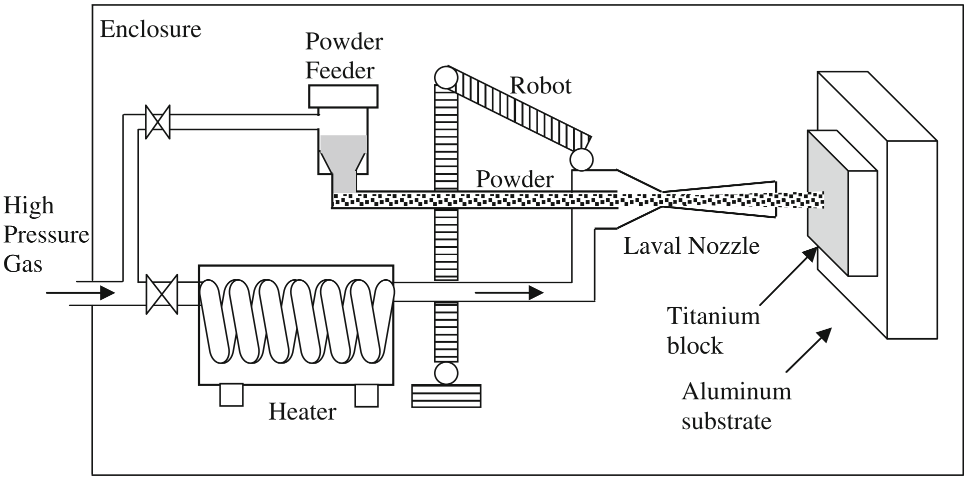

Fig. 2 Schematic representation of cold spray system utilized in this study for deposition of CP titanium

Table 2 Cold spray parameters for deposition of CP titanium

Deposition gas	Temp., °C	Pressure, MPa (×10 bar)	Feeding rate, g/min	Stand off, mm
Helium	600	1.5	18	30

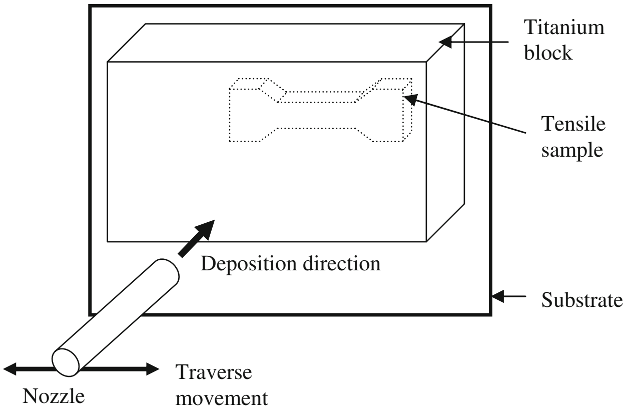

Fig. 3 Schematic representation of the samples machined from the directly fabricated cold-sprayed CP titanium block

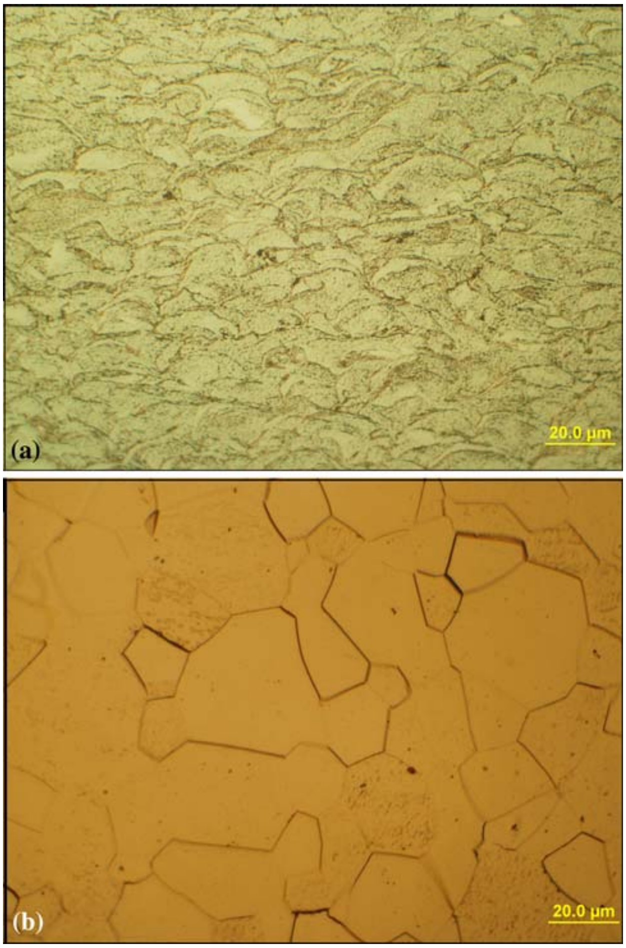

Fig. 4 (a) Micrograph of the cold-sprayed CP titanium and (b) a typical equi-axed grain structure of CP titanium

3. Results and Discussion

The cold spray CP titanium microstructure (Fig. 4a) represented a structure that consists of highly deformed particles (splats), which is different from a typical annealed CP titanium structure originated from nucleation and growth of equiaxed grains (Fig. 4b). The absence of porosity and largely deformed splat structure in Fig. 4(a) confirms that cold spray parameters (Table 2) were optimized correctly to achieve a dense material. The results in Fig. 5 show that the hardness of cold spray CP titanium sharply declines from 320 HV to 210 HV after 30 min of isothermal annealing at 550 °C. This rapid decline in hardness indicates that the material is in the static recrystallization stage of the softening process. However, an increase in time for isothermal treatments results in a

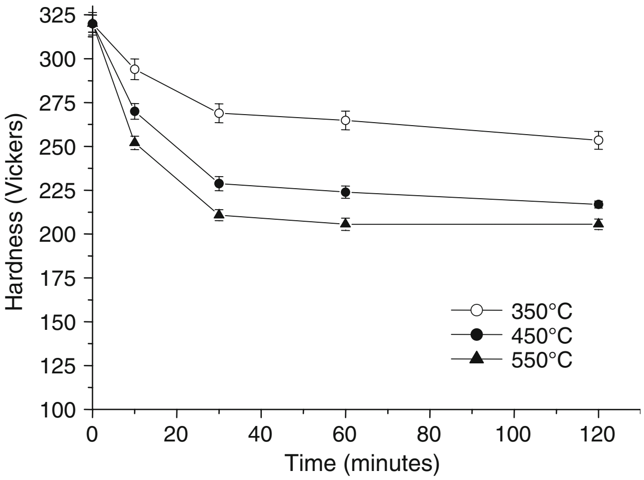

Fig. 5 Softening curves corresponding to cold spray CP titanium annealed at 350, 450, and 550 °C

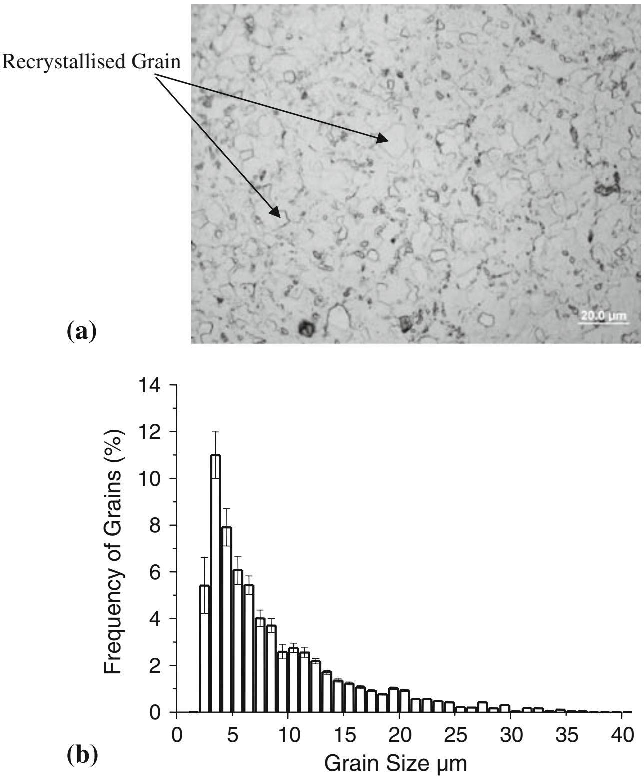

Fig. 6 (a) Microstructure of the heat-treated cold spray CP titanium held at 550 °C for 2 h and (b) normalized grain size distribution of the recrystallized material

steady state region with a slight decline in hardness, which corresponds to grain growth stage.

The results show that a recovery region, which generally initiates before recrystallization, with a slower rate of softening, was absent for cold spray CP titanium of this study. This observation was similar to studies for cold-worked CP titanium (Ref 16). The annealed material at 550 °C for 2 h represented an equiaxed microstructure that constitutes a mixture of fine and coarse grains (Fig. 6a). Figure 6(b) shows grain size distribution in the recrystallized material with grain size frequency normalized in respect to 100 grains. The figure reveals that the material contained 25% ultrafine grains (<5 µm) with average grain size of 7 µm.

It is speculated that a mixture of ultrafine grains and grains larger than 5 µm is beneficial for improved mechanical properties of CP titanium. This is because of the fact that ultrafine grains provide the strength, without addition of alloying elements, and coarse grains offer ductility for the material (Ref 17, 18). However, to achieve an ultrafine-grained structure, complicated thermomechanical events such as Equal Channel Angular Processing (ECAP), High Pressure Torsion (HPT), and Accumulative Roll Bonding (ARB) are required, which can be difficult to control and are costly processes (Ref 19, 20). It seems that cold spray processing has the potential to be exploited as a cost-effective method to manufacture the precursor structure for formation of ultrafine-grained CP titanium directly from powder.

A decrease in annealing temperature from 550 to 450 °C led to a decline in recrystallization rate of cold spray material with the lowest recrystallization rate at 350 °C (Fig. 5). This is in agreement with the finding in other studies that a decrease in temperature leads to a sluggish recrystallization in CP titanium (Ref 15, 16). It is worth noting that, to some extent, the annealed cold spray CP titanium resembles cold-worked material that is recrystallized. For instance, Güçlü et al.'s study (Ref 16) shows that a grade 2 CP titanium at 550 °C which is 50% cold worked reaches steady stage region of softening with 30% decline in hardness. A similar result in Fig. 5 shows that annealing at 550 °C results in 33% softening for cold spray CP titanium. However, the time to reach the steady state condition (grain growth) for cold spray is about 60 min compared with 20 min for cold-worked CP titanium in Güçlü et al.'s study (Ref 16).

This extended time for recrystallization suggests that most possibly the driving force for recrystallization and strain energy in cold spray material is lower than that in the cold deformed structure. To clarify this, recrystallization kinetics of cold spray CP titanium is established assuming, similar to cold-worked material (Ref 16), recrystallization follows an Arrhenius type equation;

$$\frac{1}{t_{50}} = A \exp\left(\frac{-Q}{RT}\right) \tag{Eq 1}$$

where t_{50} is the time for 50% static recrystallization, A is constant, Q is the activation energy for recrystallization, R is the gas constant (8.314 J/mol K), and T is the absolute temperature. The value for t_{50} is estimated from the time corresponding to the average value of the hardness for sprayed material and the minimum hardness value in Fig. 5.

The activation energy, Q, for recrystallization of the cold spray CP titanium was estimated to be 13 kJ/mol from a plot of ln t_{50} versus $1/T$ (Arrhenius plot) in Fig. 7. This

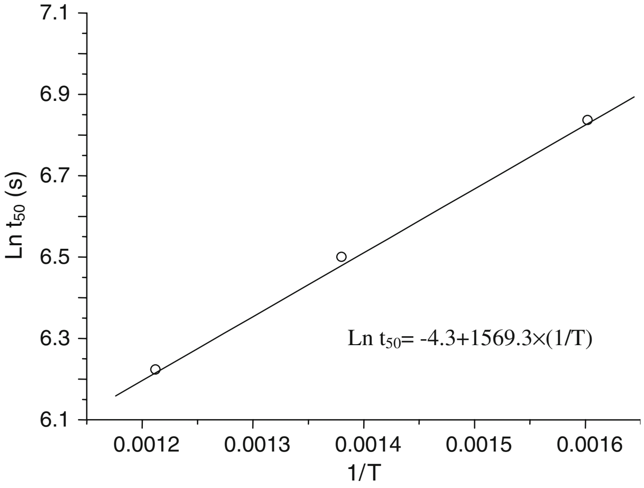

Fig. 7 Arrhenius plot for annealed cold spray CP titanium

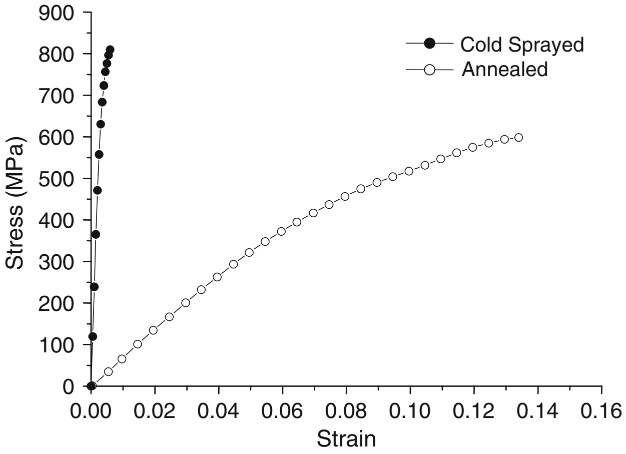

Fig. 8 Comparison of the tensile properties for (a) cold spray CP titanium and (b) annealed cold spray material at 550 °C for 2 h

energy, 13 kJ/mol, is significantly lower than 96 kJ/mol, which is the activation energy for the diffusion of cold-deformed titanium in hexagonal closed packed structure (Ref 21). Similarly, the activation energy of cold spray CP titanium is considerably smaller than the activation energy reported by Güçlü et al. (Ref 16) for 23, 35, and 50% cold-worked CP titanium with 64, 66, and 88 kJ/mol, respectively.

The above results suggest that work hardening in cold spray material (which may be sourced from twins, dislocation pile up, and imperfections induced during deposition) provides limited driving force for recrystallization. The stored energy in deposited structure is mostly sources from splat formation during the deposition of CP titanium particles at supersonic speeds. Splat formation is a complicated thermomechanical event in which deformation of particles occurs under supersonic shock load and adiabatic shear instability (Ref 10). This, however, is dissimilar to the cold-worked structure that is the result of highly deformed grains that are formed under significantly lower pressure and more homogeneous stress distribution.

Tensile property of the cold spray CP titanium was examined, as an example, to quantify improvement of mechanical properties after isothermal annealing. The stress (σ) versus strain (ε) curves of the cold spray CP titanium before and after isothermal annealing are shown in Fig. 8. The cold spray material achieves 800 MPa before failure. This is significantly higher than the tensile stress of 10 MPa reported in earlier studies by Papyrin et al. (Ref 13) for cold spray CP titanium. In the same study, Papyrin et al. (Ref 13) reported 9% porosity in their deposited CP titanium structure, which is most likely the reason for reduction in tensile strength. Porosity in cold spray deposits is generally formed because of inadequate deformation of particles due to insufficient velocity.

Furthermore, the tensile strength, 800 MPa, for cold spray CP titanium is 160% higher than the strength of 310 MPa for coarse grain, 15 μm, CP titanium (Ref 17). However, improvement in the strength of cold spray CP titanium consequently leads to a significant reduction in plastic deformation to 0.02%. The rational for increase in strength and reduction of ductility for cold spray CP titanium structure is complicated and seems to be related to work hardening, preferred orientation (texture), deformation mode, and splat size of the deposit all of which require further study.

Stress-strain behavior of the cold spray CP titanium annealed at 550 °C shows 8% elongation, which is a significant improvement in ductility compared with as-sprayed material (Fig. 8). The strength of the annealed CP titanium is 600 MPa, which shows a decrease of 200 MPa from the strength of the material before heat treatment. However, the strength of the annealed cold spray CP titanium, 600 MPa, is significantly higher than the 28 MPa reported in earlier studies by Papyrin et al. (Ref 13). In Papyrin's study, cold spray CP titanium was heat-treated at 840 °C in argon for 4 h. The significant reduction in the strength of annealed cold spray titanium in Ref 13 is most likely related to the presence of 9% porosity in deposited titanium, which is detrimental for mechanical properties.

It is worth noting that Fig. 8 represents a decrease in the strength of the cold spray CP titanium after heat treatment as expected. However, Papyrin's (Ref 13) study does not provide explanation on why heat treatment improves the strength of cold spray material from 10 to 28 MPa. It is speculated that this anomaly is due to the fact that heat treatment may improve the bonding between the splats that have not been strongly connected in the cold spray structure. A weak bonding between splats is mostly sourced from insufficient velocity of the particles that may contribute to formation of porosity in the cold spray deposits (Ref 12, 22).

Qualitative X-ray analysis in Fig. 9 reveals development of preferred orientation in cold spray and heat-treated material. The results for CP titanium powder in Fig. 9(a) revealed X-ray diffraction peaks in respect to $(10\bar{1}0)$, (0002), $(10\bar{1}1)$, and $(10\bar{1}2)$ planes, which are consistent with standard CP titanium. Figure 9(b) shows a

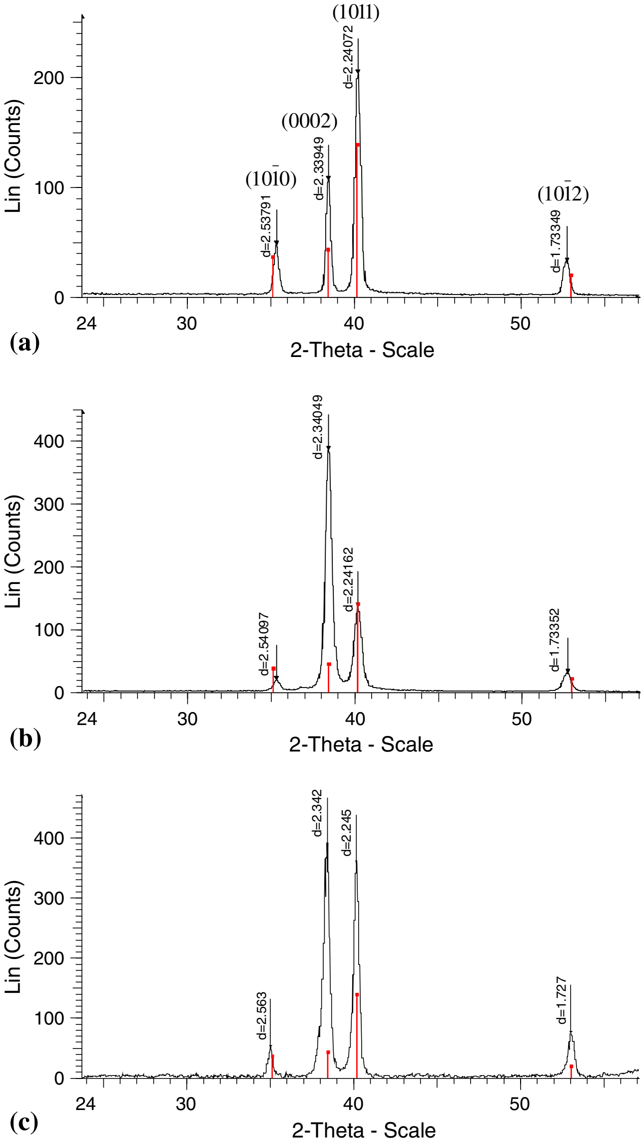

Fig. 9 X-ray diffraction pattern for (a) titanium powder, (b) cold spray CP titanium, and (c) heat-treated cold spray CP titanium at 550 °C for 2 h

significant increase in the intensity and formation of texture for (0002) at 38.4° compared with CP titanium powder. Annealing at 550 °C for 2 h did not eliminate the preferred orientation for (0002) compared with cold spray material (Fig. 9b and c). However, the intensity was increased in respect to $(10\bar{1}0)$, $(10\bar{1}1)$, and $(10\bar{1}2)$ planes (Fig. 9b and c).

Earlier studies by Nourbakhsh and O'Brien (Ref 23) on texture formation in cold-rolled and annealed CP titanium suggest a complicated transition in texture in respect to the rolling strain. For instance, development of texture in cold-rolled CP titanium, i.e. {0002} poles, emerges in such a way that at first a split rolling direction texture forms. This texture then rapidly transforms to a split transverse direction texture with an increase in straining. It is most likely that such complicated transition exists for cold spray CP titanium, which requires further investigation.

X-ray peaks corresponding to oxygen, as second phase in CP titanium structure such as TiO and TiO_2, were absent in Fig. 9. This is with respect to the fact that oxygen during thermal treatment could form an oxygen diffusion zone in CP titanium (Ref 16). A qualitative assessment of Fig. 9(c) reveals that heat treatment did not increase oxygen to a detectable concentration of 0.5% by X-ray (Fig. 9c). Fukai et al. (Ref 24) have demonstrated that the presence of 0.3% oxygen has relatively small effect on the flow stress and static recrystallization of titanium. Knowing this, it is reasonable to consider that 0.35% oxygen content for CP titanium of this study (Table 1) demonstrates a similar effect on the static recrystallization and tensile properties. This, however, requires additional quantitative study of recrystallization kinetics in respect to oxygen concentration in cold spray-fabricated titanium.

4. Conclusions

Annealing led to recrystallization and improvements in ductility of cold spray fabricated CP titanium. A physical-based model was proposed for kinetics of recrystallization in cold spray CP titanium. The results confirm that the activation energy for recrystallization for cold spray structure is lower than that for self-diffusion for titanium, with lower strain energy available for recrystallization compared with cold-rolled CP titanium structures. The recrystallized structure of this study constitutes an ultra-fine grain structure mixed with coarse grains that posses preferred orientation. Recrystallization does not eliminate texture that CP titanium inherits from precursor cold spray fabrication process.

References

1. M.J. Donachie, Jr., *Titanium: A Technical Guide*, 2nd ed., ASM Int., OH, 2000, p 2-3
2. O.E.M. Pohler, Unalloyed Titanium for Implants in Bone Surgery, Injury, *Int. J. Care Injured*, 2000, **31**, S-D7-13
3. M. Niinomi, Mechanical Properties of Biomedical Titanium Alloys, *Mater. Sci. Eng. A*, 1998, **A234**, p 231-236
4. R.R. Boyer, An Overview on the Use of Titanium in the Aerospace Industry, *Mater. Sci. Eng. A*, 1996, **A213**, p 103-114
5. G. Lutjering and J.C. Williams, *Titanium*, Springer-Verlag, Berlin, Heidelberg, Germany, 2003, p 57-66
6. J. Karthikeyan, Cold Spray Technology: International Status and USA Efforts, Report from "ASB Industries Inc., 1031 Lambert Street, Barbeton, OH 44203", 2004, p 1-14
7. A.P. Alkhimov, A.N. Papyrin, V.P. Dosarev, N.J. Nesterovich, and M.M. Shuspanov, Gas-Dynamic Spray Method for Applying a Coating, U. S. Patent 5,302,414, 12 Apr 1994
8. R.C. McCune, A.N. Papyrin, J.N. Hall, W.L. Riggs II, and P.H. Zajchowski, An Exploration of the Cold Gas-Dynamic Spray Method for Several Materials Systems, *Advances in Thermal Spray Science & Technology*, C.C. Berndt and S. Sampath, Eds., Sept 11-15 1995 (Houston, TX), ASM International, 1995, p 774
9. D.L. Gilmore, R.C. Dykhuizen, R.A. Neiser, T.J. Roemer, and M.F. Smith, Particle Velocity and Deposition Efficiency in the Cold Spray Process, *J. Therm. Spray Technol.*, 1999, **8**(4), p 576-582

10. H. Assadi, F. Gärtner, T. Stoltenhoff, and H. Kreye, Bonding Mechanism in Cold Gas Spraying, *Acta Mater.*, 2003, **51**, p 4379-4394
11. J. Karthikeyan, C.M. Kay, J. Lindeman, R.S. Lima, and C.C. Berndt, Cold Spray Processing of Titanium Powder, *Proceedings, 1st International Thermal Spray Conference (ITSC 2000)*, May 8-11 2000 (Montreal, Quebec, Canada), p 255-262
12. C.J. Li and W.Y. Li, Deposition Characteristics of Titanium Coating in Cold Spraying, *Surf. Coat. Technol.*, 2003, **167**, p 278-283
13. A. Apayrin, V. Kosarev, S. Klinkov, A. Alkimov, and V. Fomin, Cold Spray Technology, 1st ed., Elsevier, 2007, p 229-231
14. C.M. Sellars, J.J. Jonas, Symp.: Thermomechanical Processing of Steel, S. Yue and E. Es-sadiqi, Eds., 2000, p 3
15. M. Hayashi, H. Yoshimura, M. Ishii, and H. Hrada, Recrystallization Behaviour of Commercially Pure Titanium During Hot Rolling, Nippon Steel Technical Report No. 62, July 1994, p 64-68
16. F.M. Güçlü, H. Çimenoğlu, and E.S. Kayalı, The Recrystallization and Thermal Oxidation Behaviour of CP-Titanium, *Mater. Sci. Eng. C*, 2006, **26**, p 1367-1372
17. Y.G. Ko, D.H. Shin, K.T. Park, and C.S. Lee, An Analysis of The Strain Hardening Behaviour of Ultra-Fine Grain Pure Titanium, *Scripta Mater.*, 2006, **54**, p 1785-1789
18. A.V. Sergueeva, V.V. Stolyarov, R.Z. Valiev, and A.K. Mukherjee, Advanced Mechanical Properties of Pure Titanium with Ultrafine Grained Structure, *Scripta Mater.*, 2001, **45**, p 747-752
19. A.A. Popov, I.Yu. Pyshmintsev, S.L. Demakov, A.G. Illarionov, T.C. Lowe, A.V. Segeyeva, and R.Z. Valiev, Structural, Mechanical Properties of Nanocrystalline Titanium Processed by Severe Plastic Deformation, *Scripta Mater.*, 1997, **37**, p 1089-1094
20. D. Terada, S. Inoue, and N. Tsuji, Microstructure and Mechanical Properties of Commercial Purity Titanium Severely Deformed by ARB Process, *J. Mater. Sci.*, 2007, **42**, p 1673-1681
21. D.A. Askeland, *The Science and Engineering of Materials*. Chapman and Hall, London, 1990, p 123
22. S.H. Zahiri, D. Fraser, S. Gulizia, and M. Jahedi, Effect of Processing Conditions on Porosity Formation in Cold Gas Dynamic Spraying of Copper, *J. Therm. Spray Technol.*, 2006, **15**(3), p 422-430
23. S. Nourbakhsh and T.D. O'Brien, Texture Formation and Transition in Cold-Rolled Titanium, *Mater. Sci. Eng.*, 1988, **100**, p 109-114
24. H. Fukai, K. Minakawa, and C. Ouchi, Dynamic and Static Restoration Processes in the α Region of Commercially Pure Titanium and Effect of Oxygen and Iron on These Processes, *J. Iron Steel Inst. Jpn.*, 2005, **91**(8), p 676-684