Porosity Prediction of Porous Materials Deposited by Semi-Molten Spraying Particles

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Abstract: To determine the relationship between the deposition characteristics of semi-molten particles and the porosity of porous materials prepared by flame spraying, metal powders of Mo and 316L were used and the melting degree of deposition particles was controlled. Based on the experimental observations, a three-dimensional, random-stacking model was established by introducing the slipping characteristics of semi-molten particles, which could help predict the porosity of the generated porous metal materials. The results show that the maximum porosity of porous materials deposited by semi-molten particles was about 82%. A one-to-one relationship was observed between the melting degree of particles and the porosity of deposited samples. The three-dimensional random model could successfully predict the porosity of porous materials by combining the melting degree and slipping characteristics of spray particles, and the predicted values were consistent with the experimental results. The results of this study are useful to control the pore structure of porous materials deposited by semi-molten spraying particles.

Keywords: flame spraying; melting degree; porosity; random stacking; simulation

1. Introduction

Porous metal not only has the properties of the metal itself, but also has several special properties, such as high energy absorption, large specific surface area and high permeability, due to its pore structure [1,2]. In recent years, thermal-spraying methods, such as plasma spraying, flame spraying and cold spraying, have been used to prepare porous materials with different metals and pore structures by utilizing the non-compactness of particle-accumulation deposition or the volatilization characteristics of composite powders [3–5]. Due to its simplicity, rapidity and wide range of applications, thermal spraying has attracted wide attention from researchers. It is generally believed that solid particles are difficult to deposit due to collision and rebound during thermal spraying. Recently, the author has found that effective deposition of micro-melt or partially melted particles can be achieved by controlling the melting degree of particles by low-speed (10–30 m/s) flame spraying [6,7]. However, the deposition of porous materials by semi-molten spraying particles has not been reported yet.

In the thermal-spraying process, the melting state of particles is the main factor that determines the characteristics of particle deposition. At present, the particle-melting degree is mainly characterized through numerical simulation [8,9], while the experimental method for quantitative characterization of the particle-melting degree is rarely reported. Besides, there have been few studies on porosity prediction of porous materials based on the melting degree of spraying particles. In addition, it has been reported that the spraying angle has a significant influence on the deposition morphology and geometric size of particles [10–12]. As the spraying angle increases, the porosity of the deposited coating increases significantly [13,14]. However, the influence of the deposition characteristics of semi-molten particles on the pore structure of deposited porous materials is not clear. A simple two-dimensional model can predict the relationship between the collision
bonding angle of particles and the porosity of porous materials deposited by particle accumulation [15]. In the two-dimensional model, all the particles are surface-molten and deposited on the former particles with the same connection angle and direction. Then, the porosity is defined as the ratio of the shielded area to the total area of the particle-pore system from the two-dimensional view. However, as the calculation only considers the bonding angle of the two-dimensional plane [15], a more realistic three-dimensional model is needed to reveal the relationship between particle-deposition characteristics and porosity of deposited porous materials.

In this study, metal powders with significantly different melting points were used as research objects (316L with m.pt. of 1850 °C, and Mo with m.pt. of 2610 °C). According to the experimental phenomena and results, a three-dimensional, random-stacking model was used to simulate the corresponding relationship between the melting degree of semi-molten particles and porosity. By combining the slipping characteristics of semi-molten spraying particles with different melting degrees into the three-dimensional, random-stacking model, the porosity of porous materials deposited by semi-molten particles can be well predicted by simulation calculation.

2. Materials and Methods
2.1. Deposition of Porous Materials

Mo (purity of 99.9%) and 316 stainless-steel powders were used as the starting materials and were obtained from the powder manufacturer (Beijing General Research Institute of Mining and Metallurgy (BGRIMM) Technology Group, Beijing, China). The morphologies of Mo and 316 stainless-steel powders are shown in Figure 1a,b, and their nominal size ranges were 50–75 µm and 75–79 µm, respectively. The powders were screened over a narrow range before spraying to obtain particles with the same melting degree.

Figure 1. Morphology of (a) Mo and (b) 316L stainless-steel sprayed powders.

2.2. Preparation of Deposits

To ensure the same melting degree of the spray particles, a homemade flame torch was used to generate semi-molten particles for deposition of isolated particles or porous samples. The acetylene flow rates of 100 to 300 L/h, and spray distances from 20 to 70 mm were employed to provide particles with a range of melting degrees and porous Mo and 316L with different porosities. The pressures of C2H2 and O2 were fixed at 0.1 and 0.4 MPa, respectively. During the spraying process, the powder-feed rate was set to 10 g/min. Isolated particles were deposited from 15° to 90°, and the spray angle was set equal to the particle impact angle.

2.3. Characterization of Samples

The morphology of the samples was characterized by scanning electron microscopy (SEM, FEI QUANTA600 FEG; FEI Company, Hillsboro, OR, USA; VEGA II-XMU TSCAN, Brno, Czech Republic). The isolated particles were characterized by both SEM and three-dimensional (3D) confocal-laser-scanning microscopy (VK-9710, Keyence, Osaka, Japan).
The porosity of the samples was determined from SEM cross-sectional images by image analysis software (Image J, DT200: National Institutes of Health, Bethesda, MD, USA).

2.4. The Random Model

The experimental results show that the accumulative deposition of semi-molten particles by flame spraying had a remarkably random character. The particles were joined by a neck formed by the melted parts of the particles, as shown in Figure 2. According to this observation, the experimental powder was formed into small balls, and small balls of a certain diameter were randomly placed into a given space. The volume fraction of the particles was calculated according to the number of small balls that were held in a given space to obtain the porosity. In the simulation process, the following assumptions were made: (1) The diameter of the ball represents the diameter of the solid core of the particle. The spheres with different diameters represented particles with different degrees of melting; (2) The influence of velocity on particle deposition was ignored; (3) Particles did not bounce or deform; (4) The contact point of random collision between particles was the coordinate of particle deposition; and (5) Particles were connected to each other to form a porous skeleton. It was assumed that the molten part was filled between particles to form a bonding neck, and the influence of the molten liquid phase on particle coordinates was ignored. In the simulation process, the distance between the small balls was calculated to determine whether they had collision contact.

3. Results and Discussion

3.1. Typical Morphology of Porous Sample Deposited by Semi-Molten Spray Particles

Figure 3a–d present the surface morphology and cross-sectional microstructure of typical porous Mo and 316L deposited by semi-molten spray particles with an acetylene flow rate of 150 L/h and a spray distance of 40 mm. The pores were formed by stacking of near-spherical particles, indicating that spray particles were in a semi-molten period during deposition. The bonding neck was formed by the melting-liquid fraction of the spray particles, then the particles joined to form a connected pore structure. Therefore, with the increase in melting degree of the spray particles, the intergranular bonding was strengthened and the bonding-neck size increased. The particles deposited first had a shading effect on the particles deposited later. Thus, the space shielded by the particles formed pores. Due to the different angles of impact and bonding between particles, the pore size formed by the shading effect varied from several microns to hundreds of microns. This indicated that the uniformity of the particle-melting degree influenced the pore structure of porous deposit. In addition, the impact angle also had a significant effect on the pore structure and porosity of porous deposit.
3.2. Porosity Prediction by Random Simulation with Melting Degree

3.2.1. Maximum Porosity by Simulation

When the melting degree was very small, the deposition process was equivalent to the random stacking of rigid spheres. Therefore, the simulated porosity using rigid spheres approximated the maximum porosity of the porous material deposited by semi-molten particles. A space of $10,000 \times 10,000 \times 10,000$ was selected as the deposition unit, and deposition particle diameters of 50, 60, 70, 80, and 90 µm were used. The simulation results show that, when the melting degree was small enough that the material was regarded as a rigid ball, the maximum porosity of the porous material deposited by semi-molten particles was about 82%. When the particle diameter was changed, the porosity of the obtained porous material remained unchanged, as shown in Figure 4. Hence, it was concluded that the powder-particle size had little effect on the porosity of porous materials deposited by semi-molten spray particles. The semi-molten spray particles must have a certain degree of melting to allow the molten liquid to form a bonding neck between the particles. Consequently, the porosity of porous material deposited by semi-molten particles was always smaller than the maximum simulated value of rigid spheres.
3.2.2. Effect of Melting Degree on Porosity

Assuming that the original diameter of the particles was 100 µm, the size of the unmelted core of particles decreased as the melting degree increased. Small balls with diameters of 100, 90, 80, 70 and 60 µm, respectively, were used for the three-dimensional, random-stacking simulation, which represented the diameters of particles without melted cores at different melting degrees. The number of particles accommodated in the space was obtained, and the total particle volume was calculated to predict the porosity of the deposition unit. The simulation results of porosity at different melting degrees were obtained. The melting degree under different spraying conditions was calculated using the values from 3D profiles of single particles. The height of a deposited particle was measured using 3D profiles, as shown in Figure 5. The height of a deposited particle was assumed to be the diameter of the solid core within a semi-molten particle. Then, the melting degree was determined by the original particle size and the diameter of the solid core of semi-molten particles. The porosity under different spraying conditions was calculated by analyzing SEM cross-sectional images with image analysis software (Image J, DT200, National Institutes of Health, Bethesda, MD, USA).

Figure 4. Simulation results of rigid-sphere stacking.

Figure 5. Single-particle, three-dimensional morphology of 316L deposit obtained by flame spraying with acetylene flow rate of 150 L/h and spray distance of 40 mm.

The relationship between melting degree and porosity of porous 316L and porous Mo obtained by experiment was compared with the simulation results, as shown in Figure 6. It can be seen that in the same space, with the decrease in particle diameter, the number of spheres accommodated in the random-stacking simulation gradually increased, and the calculated result of porosity gradually decreased. Although the simulated melting degree under the above assumptions was consistent with the trend of porosity, the simulated porosity was much larger than the experimental porosity in the melting degree range from 0% to 77%. The simulation value agreed well with the experimental results only when the melting degree of particles ranged from 77% to 90%. The analysis suggests that this was mainly because the simulation was based on the premise that particles of any melting
degree have the same deposition behavior. When the particles impact, they are assumed to be deposited in situ without deforming. However, in the actual deposition process, when the semi-molten particles impacted with the pre-deposited particles, there was always a certain angle of collision between the particles, and the particles slipped significantly at a certain angle (as shown in Figure 7). The slipping distance is marked by the arrow in Figure 7a. It is evident that the slipping distance increased with the decrease in impact angle from about 30° (as Figure 7a) to 15° (as Figure 7b). Therefore, the collision point was no longer the deposition point, and the particle slip changed the deposition position, filled the pores, and increased the number of particles accommodated in a given space.

Figure 6. Relationship between melting degree of spray particles and porosity of the porous deposits.

Figure 7. Slipping distance of 316L particles at impact angles of (a) 30° and (b) 15° deposited by flame spraying with acetylene flow rate of 150 L/h and spray distance of 40 mm.

3.3. Slipping Characteristics of Deposition Particles

It has been shown that the collision angle has a very significant effect on the deposition of particles [15–17]. Previous experiments found that when semi-molten particles were deposited at different collision angles, the non-molten core of the particles slipped significantly [18]. During these experiments, when two particles collided, they collided with a spherical surface. Hence, the two particles always collided at a certain angle and the slip phenomenon was not negligible. In the simulated collision process, due to the vertical incidence of the particle, it was assumed that the particle slipped along the arc of the particle being touched in the direction of the z axis after the collision. Thus, the maximum distance the particle may slip is a quarter arc length; otherwise, the particle passes over the particle being touched. Moreover, the maximum slip distance allowed by particle theory is also related to the collision angle between particles (Figure 8). In this paper, a single particle was deposited under different melting degrees and collision angles, and the slip distance was calculated by the SEM images (as shown in Figure 7). The
comparison between the maximum slip distance allowed by particle theory and the actual slip distance of particles at different collision angles is shown in Figure 9. In the simulation process, when the maximum slip distance allowed by the particle theory was larger than the actual slip distance of the particle, the actual slip distance was substituted into the calculation. On the contrary, the particles passing over a collision had a second collision. The coordinates at the end of particle slip or collision were recorded. The porosity then was calculated according to the number of balls accommodated in a given space after slipping. Obviously, the number of the balls that were accommodated in the space increased due to the slipping, and the corresponding porosity decreased.

Figure 8. Schematic of slipping deposition of semi-molten particles.

Figure 9. Slipping distance of solid core of spray particles at different impact angles through experimental conversion and theoretical calculation.

3.4. Simulation Results with Slipping Characteristics

According to the simulated calculation with the slip distance of Mo and 316L particles at different melting degrees obtained from the experiment, the corresponding relationship between the melting degree of Mo and 316L particles and porosity was obtained respectively, and it was compared with the results obtained by the experiment [18]. The results are shown in Figure 10. It can be seen that the simulation results were less than the experimental results. When the melting degree was low, the simulation results were in good agreement with the experimental results, with a deviation of less than 10%. The reasons mainly include the following aspects: (1) The melting degree and the corresponding slip distance of particles considered in the simulation calculation were obtained by statistical measurement, so certain errors existed; (2) The hypothetical conditions in the simulation process, such as no deformation of the particle, were unavoidable during the actual deposition process. In the process of collision deposition, the particle deformation was more significant because the melting point of 316L is about 1850 °C, lower than the temperature of oxyacetylene flame. Hence, the experimental result was significantly smaller than the simulation result. (3) The rebound of particles was ignored in the simulation process,
and it was assumed that particles with a large amount of slippage will have secondary collision deposition over the collided particles. This assumption led to an increase in the number of particles that may be deposited, resulting in a decrease in simulated porosity. By comparison, it was found that the simulated results of the two powders had a high coincidence degree at a low melting degree. Particularly, the melting degree was low during this experiment, as the melting point of Mo is about 2610 °C. Therefore, the experimental results of Mo porosity were larger than the simulation results. However, the experimental results of 316L porosity were smaller than the simulation results at a low melting degree. This indicates that the actual slip distance was smaller than the measured value on the plate because the slip surface was a curved surface, which was the surface of deposited particles. Thus, the three-dimensional stochastic model showed better applicability at a low melting degree.

Figure 10. Simulation value with slipping distance.

4. Conclusions

The relationship between the melting degree of semi-molten spray particles and the porosity of porous materials prepared by flame spraying was investigated through experiments and a three-dimensional random model. The results show that the maximum porosity of porous materials deposited by semi-molten particles was about 82% during flame spraying. The experimental results indicate that the melting degree showed a one-to-one correlation with the porosity of the deposited samples. As the slip phenomenon was not negligible, the slip distance was added in the three-dimensional random model. The results show that the simulated results of the two powders had a high coincidence degree at a low melting degree. It was because the actual slip distance was smaller than the measured value on the plate substrate. The actual slip surface was a curved surface, which was the surface of deposited particles. The above results indicate that the three-dimensional stochastic model has better applicability at a low melting degree.

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