Near-Net-Shape Molybdenum Parts Produced by Plasma Spray Forming

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Abstract

Complex and thin-walled refractory metallic parts including molybdenum (Mo) rocket nozzle and crucible were fabricated using plasma spray forming (PSF) followed by hot isostatic pressing (HIPing). Optical microscope (OM), scanning electron microscope (SEM), Archimedes method, Vickers hardness and tensile tests have been employed to study microstructure, density, micro-hardness and mechanical properties of the parts. A lamellar structure consisting of vertical columnar grains, micron-sized pores, partially melted particles and rough interlaminar contacts with gaps of sub-micron sizes between lamellae were found in PSF Mo deposits. Relative density, micro-hardness and ultimate tensile strength (UTS) of the deposits were about 89%, 150 HV0.025 and 44 MPa, respectively. After low-pressure and two-step HIPing, those changed up to about 92%, 250~400 HV0.025 (interior ~ exterior layers), 93 MPa, and 97%, 325 HV0.025 and 170 MPa, respectively. Moreover, a four-stage mechanism of HIPing for PSF parts including heating up, recrystallization, lamellae movement, plastic yielding and creep has been proposed and discussed in detail. [doi:10.2320/matertrans.M2010340]

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1. Introduction

Mo and Mo-based alloys are refractory materials of high melting point, high temperature strength, good thermal properties, and high ablation resistance. Parts of near-net-shape refractory materials such as heating element, crucible and rocket nozzle etc. have found wide applications in chemical processing, electrical and mechanical engineering, airplane and aerospace industries. However, due to its ultra-high melting point (2623°C) and high ductile-to-brittle transition temperature (around room temperature), it is difficult to fabricate large-scale or thin-walled Mo parts with complex shape by conventional industrial methods such as powder metallurgy (PM) and chemical vapor deposition (CVD). People have long wished to develop new and effective fabrication methods to produce refractory metallic parts of desired shapes and density. Capability of making high quality near-net-shape parts, PSF has then come into play as one such potential fabrication method of choice for Mo and Mo-based alloys.

Differing from PM and CVD, PSF sprays refractory metallic powders directly onto a predesigned mandrel. Almost any feedstock can be sprayed onto the mandrel in a controllable manner to provide a compact of desired shape and wall thickness with benefits of simplifying fabrication process and cost reduction. Recently, researches on fabrication refractory metallic tungsten (W) or W-based products by PSF have been reported by Wu et al.10 and Rea et al.11 The former10 presented the technique of PSF method to make large-scale W tubular heating elements, while the latter11 explored and characterized vacuum plasma spray formed W alloy parts reinforced by nanoscale HfC particles. In addition, Chwa et al.12 reported that Mo-Cu composites fabricated by vacuum plasma spraying.

In addition to partially melted large particles and splashing of droplets, variation in processing parameters such as powder feed rate, spraying cross-head speed and spraying distance may cause inherent defects including voids and/or inclusions in the deposits. Consequently, poor adhesion among lamellae has always been formed in plasma sprayed deposits.13 In order to reduce these defects, applying HIPing to further densify the deposits (including ceramics, intermetallics and high-temperature metallic alloys) has been reported by several groups.10,11,14,15 Those early works showed that HIPing played great influence on microstructure changes and physical properties of plasma sprayed deposits. However, to our knowledge, there is no work on the relation between microstructure and mechanical property of PSF Mo parts before and after HIPing treatment. In addition, the densification mechanism of HIPed deposits made by PSF method is still not well understood yet. It is then the objective of current work to establish the relationship among microstructure and mechanical properties, and to study the densification mechanism of HIPing of PSF Mo parts.

2. Experimental Procedures

Roughly spherical feedstock with average particle size of 59 μm and purity of 99.95 mass% Mo produced by spray drying was shown in Fig. 1(a). At high magnification, we can see the porous morphology of each powder which is agglomeration of many tiny Mo particles (see Fig. 1(b)). The feedstock was dried in an electric oven at 100 ± 5°C for 1 h to mitigate clogging and agglomeration for better ability of injection in feeding hose during plasma spraying. Graphite mandrels were prepared and fixed on turnplate at rotating speed of 60 rpm in an airtight chamber of Ф1300 × 1700 mm. The chamber was first evacuated and then filled by Ar at 1.01 × 10⁻¹ MPa. The feedstock was sprayed onto the graphite mandrel using a DH-1080 plasma system (max. 80 kW). The deposition parameters used are given in Table 1.

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After plasma spraying, graphite mandrels were removed from spray-formed deposits by machining. The deposits were then HIPed without encapsulation with parameters listed in Table 2. Note, the heating rate was set at 10°C/min.

Finally, these parts were cooled to room temperature in furnace.

Densities of PSF parts before and after HIPing were measured by Archimedes method [accuracy of ±1.6%]. The relative density was calculated as actual density divided by theoretical density. Micro-hardness was measured by Buehler 5410 Vickers hardness Tester. A load of 25 g was applied for a dwell time of 15 s and 10 indents were measured along a straight line (from exterior to inner layers of cross section of each Mo part) [accuracy of ±2.0%]. The tensile specimens with gauge length of 25 mm, width of 4.8 mm, and thickness of 5.0 mm were prepared by wire electrical discharge machining (EDM). Tensile strength of PSF and HIPed deposits were measured using Instron3369 machine at a displacement rate of 1.0 mm/min. Samples for metallographic study were prepared according to common practice of grinding on emery papers and mechanical polishing by rough (4–8 μm) and fine (0.5–1 μm) diamond pastes, respectively. Mixture of ammonia water (NH₃/H₂O) and hydrogen peroxide (H₂O₂) of volume ratio of 1:2 was used as etchant. Microstructures of etched samples were investigated by optical microscope. A scanning electron microscope (JEOL JSM-6360LV) equipped with energy dispersive X-ray spectroscopy (EDS) and back scattered electrons (BSE) was used to characterize microstructure changes of PSF and HIPed parts.

3. Results and Discussion

3.1 Microstructures of PSF deposits

Near-net-shape Mo nozzle and crucible are shown in Fig. 2.

Microstructures in cross section and surface layer of Mo parts fabricated according to parameters listed in Table 1 (a) nozzle, and (b) crucible.
are depicted in Fig. 3. Figure 3(a) shows elongated splats forming a curved lamellar structure which is typical phenomena of thermal spray coatings.\textsuperscript{16} The thickness of the lamellae is ranged from 5 to 10\,\mu m. Rough interlamellar contacts with tiny pores and gaps can be found between the splats due to incompleteness of coalescence of impacting particles with pre-consolidated surface layers. Some partially melted Mo particles can be observed in local region as one shown in Fig. 3(b). Ideal pancake-like depositions with smooth surface (see Fig. 3(c)) reveal the fact that spraying temperature is high enough to melt most of the Mo feedstock. In addition, we observed the formation of micro-cracks (see Fig. 3(d)) in the deposit owing to tensile stress resulting from rapid cooling of molten film on top of pre-solidified particles during plasma spraying.

### 3.2 Influences of HIPing on microstructures of Mo parts

Microstructures of cross section of HIPed Mo parts are depicted in Fig. 4. After low-pressure HIPing (10\,MPa and 1600\,\degree C for 1\,h), microstructures of exterior layers and those of inner ones are different as pointed out by a transition line in Fig. 4(a). Although most gaps being eliminated and disappeared, tiny pores are still retained as shown in higher-magnification image for the exterior layers (see Fig. 4(b)). Differ from those of exterior layers, many gaps and micro-pores are still remained in inner layers (see Fig. 4(c)). We believed that exterior layers are much denser than those of inner ones due possible to insufficient HIPing pressure and time. After two-step HIPing ((low-pressure HIPed (10\,MPa and 1600\,\degree C for 1\,h) parts were undergone high-pressure HIPing (150\,MPa and 1600\,\degree C for 2\,h)), the transition line (see Fig. 4(a)) has been disappeared with tiny pores left as shown in Fig. 4(d). Comparing with exterior layers of low-pressure HIPed parts (see Fig. 4(b)), the total number of micro-sized pores were decreased (see Fig. 4(e)). In addition, further densification took place in inner layers whereas large gaps and pores being eliminated or mitigated (see Fig. 4(c) and (f)). As a result, we were able to achieve much higher density for the deposits through two-step HIPing.

The microstructures of HIPed parts after etching are depicted in Fig. 5. The characteristic lamellar structure of plasma sprayed deposits was retained in Mo parts after low-pressure HIPing (see Fig. 5(a)). After two-step HIPing, the lamellar structure has been transformed into granular structure with larger grain sizes (see Fig. 5(b)). Similar to the work of Khor \textit{et al.},\textsuperscript{15} the lamellar structure of plasma sprayed deposits faded away with HIPing pressure and time due to fast diffusion of elements. In order to control grain growth and improve mechanical properties including micro-hardness and UTS, Re, HfC and ZrC etc. have been added as reinforcements through solid-solution and/or dispersion strengthening.\textsuperscript{17,18}

### 3.3 Mechanical properties and fracture surface analysis

Influences of HIPing conditions on micro-hardness of PSF Mo parts are shown in Fig. 6. Owing to the existence of
pores, micro-cracks and gaps, relative density of PSF Mo parts was approached only to 89%. Consequently, their micro-hardness is much lower (150 HV$_{0.025}$) possible due to incompletion of densification. In addition, micro-hardness was similar from exterior to inner layers. After low-pressure HIPing, relative density of deposits was increased up to 92% due to reduction in number and size of pores and gaps with denser exterior layers (see Fig. 4(a)). As a result, micro-hardness of exterior layers (more than 400 HV$_{0.025}$) is much higher than that of inner ones (about 250 HV$_{0.025}$) as if there is one transition line in Fig. 4(a). After two-step HIPing, the relative density of deposits was increased up to 97% owing to further diffusion, unification and equilibration. To our surprise, instead of uniform increase in micro-hardness, we found there are ups and downs, i.e., the micro-hardness of inner layers increased (from 250 to 325 HV$_{0.025}$) while that of exterior layers dropped (from 400 to 325 HV$_{0.025}$). There are at least two major factors responsible for such results, one is density increase inside inner layers, one is grain growth occurred in exterior layers. Consequently, the difference of micro-hardness for those two distinct regions becomes negligible (within error limit) and approaches an average of 325 HV$_{0.025}$. To further increase micro-hardness, proper reinforcements should be used according to Fujitsuka et al.\textsuperscript{17} and Zhang et al.\textsuperscript{18} and more work is in progress.

Fig. 4 SEM images of (a) cross section, (b) magnificated exterior and (c) inner layers of low-pressure HIPed deposits, and (d) cross section, (e) magnificated exterior and (f) inner layers of two-step HIPed deposits.
Average UTS of PSF parts measured from 6 samples up to break was about 44 MPa. Vertical columnar grains can be discerned within layers of fracture surface of PSF parts as shown in Fig. 7(a). This observation suggested that the solidification is completed immediately upon molten droplets and/or partially melted particles impacted on the surface of the deposit. Following droplets spread on pre-deposited splats whereas nucleation and solidification taking place layer by layer to finally form a columnar dominated structure.20,21) One of primary detriments to mechanical properties of PSF parts is their incomplete densification (only 89%). Moreover, rupture could occur at interfaces between layers of lamellas for their inferior coalescence.22,23) In addition, the existence of granular particles (see Fig. 3(b)) is responsible for the weakness of part. Once crack encountering a granule, detachment occurs rapidly along particle-matrix interface and lowers the strength of the part.24)

UTS of low-pressure HIPed parts has been changed up to 93 MPa as their relative density increased. The fracture surfaces of exterior and inner layers of tensile samples are depicted as Fig. 7(b) and 7(c), respectively. After low-pressure HIPing, lamellar structure was retained in the deposits with columnar grains transforming into fine recrystal grains. Similar to the work of Khor et al.,15) Mo grains of PSF parts recrystallized and grew up within each lamella. We found out that the fracture surface of exterior layers is dominated by intergranular rupture of Mo grains and detachment of lamellas as shown in Fig. 7(b). In addition to abovementioned characteristics of exterior layers, more gaps and pores could be found in fracture surface of inner ones (see Fig. 7(c) and refer to Fig. 4(c)). After two-step HIPing, Mo grains underwent distinctly coarsening with fracture surfaces of exterior layers were mixing of transgranular and intergranular ruptures (see Fig. 7(d)), while those of inner ones were dominated by intergranular rupture (see Fig. 7(e)). From abovementioned analysis, microstructures of exterior and inner layers of low-pressure HIPed parts are different with relative density of the former higher than that of the latter. During subsequent high-pressure HIPing, both exterior and inner layers of low-pressure HIPed deposits went through further densification. Comparing with low-pressure HIPing, the relative density of exterior layers after two-step HIPing will still be, with less degree, higher than that of inner ones. Although the difference of micro-hardness for exterior and inner layers, after two-step HIPing, becomes negligible, the former will be stronger than the latter. Consequently, there is observable difference appeared in fracture modes. UTS of two-step HIPed Mo parts was further increased (up to 170 MPa) with relative density. It should be noted that recrystal grains changed into polyhedral shape by transferring of grain boundary owing to self-diffusion of Mo. In addition, the lamellar structure was not distinctly shown in fracture surface, indicating larger driving force for diffusion occurred at 1600°C and 150 MPa.

3.4 Mechanisms of HIPing

Differing from granular structure of powder metallurgy, typical PSF Mo parts take lamellar structure. Thus, mechanism of HIPing is believed to differ and worth further discussions. We here propose a four-stage mechanism for PSF parts.

1) Heating up: During early stage of HIPing, vertical columnar grains dominated lamellar structure with pores and gaps retained in the deposits.

2) Recrystallization: During low-pressure HIPing, recrystallization only occurred inside the lamellae with shape changing from columnar into polyhedral. During subsequent high-pressure HIPing, recrystallized grains went further coarsening, which could eventually break through the restriction of lamellae (as recrystal grains are larger than...
thickness of lamellae). As a result, recrystallization and grain growth are two controlling factors for PSF parts to transform from lamellar into granular structure.

(3) Lamellae movement: High temperature together with stress field applied caused interlamellar diffusion such that diffusion from particles to voids enabling the lamellae to move closer together and, finally, to erase micro-pores or gaps. At the end of this stage, recrystal grains of adjacent lamellae will start to contact with each other.

(4) Plastic yielding and creep: If external pressure is high enough, the flow strength of the deposit can exceed its yield strength locally once particles touching to each other. Consequently, yielding takes place with plastic deformation occurred among adjacent grains and elimination of micro-pores. During densification, the number and total surface of contact areas increase continuously which leading to the drop of effective pressure per unit area. As a result, the velocity of densification decreases gradually with time. Then contact regions continue to creep such that the density of parts increases further owing to shrinking of remnant closed-pores. Finally, under high pressure, Mo parts transform from lamellar into granular structure owing to recrystallization and distinct grain growth. A few remnant closed-pores can be found in the deposits. Similar to the works of Khor et al., plastic yielding and creep, brought about by high pressures, appeared to be the dominant influences in the increase in density of Mo parts.

According to the typical results of cold-pressed green compacts from conventional PM, HIPing-mechanism diagrams containing three models (plastic yielding, power-law
creeping and diffusional densification) have been proposed by Wilkinson and Ashby,27) and Arzt et al.28) While in the work of Swinkels et al.,29) the dominant mechanisms of densification are plastic yielding and power-law creeping. Except abovementioned three densification models, two more mechanisms have been proposed by Helles et al.30)

From detailedly comparison, we consider that there are two different characters between our four-stage mechanisms and those presented in Refs. 27–30). First, PSF Mo parts (at early stages of HIPing) will go through heating up, recrystallization and lamellae movement owing to their typical lamellar structure. They will eventually transform from lamellar into granular structure during HIPing. However, PM compacts undergo particles rearrangement instead of lamellae movement in early stage of HIPing owing to initial granular structure.

Second, PM compacts (initial density of 60–65%) shrank approximately 30–40 vol% during vacuum sintering or HIPing.31–33) This is true especially for thin-walled and large-scale parts with complex shape such as nozzle, crucible and the like. These parts tend to undergo extensive distortion during HIPing and cause stress related problems such as cracking and collapsing etc. Differing from PM compacts, shrinkage of PSF parts during HIPing is much less (about 10%) with relative density high up to 85–90%. Less distortion and stress associated problems are then expected to occur in PSF parts and this trend has been observed in our study. From the abovementioned analysis, we can conclude that densification mechanism of HIPing of PSF parts must be differed from that of PM products owing to differences in microstructure changes and volume shrinkage. According to our experimental work and experiences, we believe that PSF will find wide applications in making thin-walled or large-scale parts with complex shapes for ceramics, intermetallics and refractory metallic alloys etc. in the oncoming future.

4. Conclusions

Based on experimental investigations and detailed discussions out of this work, we can make following conclusions:

(1) PSF can be used to make thin-walled and large-scaled refractory metallic parts.

(2) A lamellar structure consisting of vertical columnar grains, micron-sized pores, partially melted particles and rough interlamellar contacts with gaps of sub-micron sizes between lamellae were found in PSF Mo deposits. Relative density, micro-hardness and UTS of the deposits were about 89%, 150HV0.025 and 44 MPa, respectively.

(3) After low-pressure HIPing, relative density, micro-hardness and UTS of the deposits changed up to about 92%, 250–400HV0.025 (interior ~ exterior layers) and 93 MPa, respectively. Those of two-step HIPed deposits were further increased up to about 97%, 325HV0.025 and 170 MPa, respectively. And lamellar structure of PSF parts has been transformed into granular structure with larger grain sizes.

(4) In order to explain our experimental results, we proposed a four-stage mechanism of HIPing for PSF parts which including heating up, recrystallization, lamella movement, plastic yielding and creep with detailed discussions.

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