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In-situ synthesis of tungsten nanoparticle attached spherical tungsten micro-powder by inductively coupled thermal plasma process

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ABSTRACT

Tungsten spherical micro-powder, tungsten nanoparticle, and tungsten nanoparticle attached spherical micro-powder were synthesized by manipulating feedstock and plasma gas composition in the present study. Powder preparation strategy is simple and phase evolution pathway of each component was tailored by exploiting thermos-physical properties of feedstock and thermal plasma reactivity. Irregular W aggregates underwent melting–solidification pathway and accordingly, spherical micro-powders were obtained. On the other hand, low boiling point WO_3 micro-powders were vaporized and reduced in Ar–H_2 thermal plasma. After that, vapor species condensed to nanoparticles which were composed of α-W and β-W. These results demonstrated that phase evolution pathway and resulting powder properties were determined by feedstock powders. In this context, W and WO_3 blended powders were prepared by a simple blending and they were fed into Ar–H_2 thermal plasma. Owing to individual interactions of in-flight particles with thermal plasma and co-flight of spherical W micro-powders and W nanoparticles, nanoparticle dispersed spheroidized micro-powder was in-situ synthesized. 3 dimension architecture of the synthesized nanoparticle dispersed micro-powder was revealed by ultrasonic detachment.

1. Introduction

Tungsten (W) is a representative refractory element. W is hard to sinter though W engineering components are usually manufactured by powder metallurgy. In general, high sintering temperature above 2273 K is required to fully densify pure W powders. In order to reduce sintering temperature, low melting point binder phases are intentionally added and it is known as liquid phase sintering: transition metal elements such as nickel and iron or immiscible binder elements such as copper. The secondary elements are regarded as heterogeneous sinter-activators and they are impurities [1,2]. On the other hand, enlarged surface-to-volume ratio makes fine particles unstable and sintering is remarkably enhanced owing to the substantial sinter stress and diffusivity by size effects [3,4]. In this context, W nanoparticle can be a homogeneous sinter-activator for W micro-powder. As a matter of fact, it is proven that enhanced sintering is achieved by the addition of W nanoparticle to W micro-powder in our previous study [5,6]. However, W nanoparticles were ex-situ blended with micro-powders by wet milling process. Though it enhanced sintering at the low sintering temperature, it is a time consuming process and moreover, dispersion uniformity of nanoparticle in nano-micro bimodal powder is still challenging. To solve the problems, in-situ synthesis route for nano-micro-bimodal W powder is designed and feasibility is assessed in the present study. The thermal plasma process shows versatility in powder preparation because it has high energy density and thermal plasma reactivity can be tailored by selecting process gas composition. In the case of inductively coupled thermal plasma process, longer interaction time between in-flight particle and thermal plasma as well as electrode-less plasmatron is more advantageous over other thermal plasma processes [7–9]. With respect to feedstock selection, powder feedstock was chosen from the viewpoint of material selectivity and economics. Additionally, phase evolution pathway is largely dependent on thermos-physical properties of feedstock. Once feedstock powders are fed into thermal plasma, they individually fly and react with thermal plasma and they undergo heating–cooling thermal cycle. According to heat balance between in-flight powder and hot gas dynamics, physical phase transformation pathway of the powder is determined within the time span of several milliseconds: melting–solidification pathway and vaporization–condensation pathway [10–12]. After proving the dominant reaction pathway of each feedstock, melting–solidification pathway and vaporization–condensation pathway were intentionally coupled by preparing blended feedstock in order to in situ synthesize nanoparticle dispersed spherical micro-powder.

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2. Material and methods

A commercial W micro-powder [TaeguTec Ltd. — P-4527]) and WO_3 (tungsten trioxide) micro-powder [LTS (Chemical) Inc. — PWO33250004N] were used for feedstock: W micro-powder for spherical W micro-powder and WO_3 as precursor for W nanoparticle. They were characterized by scanning electron microscopy, image analysis, and X-ray diffractometry. Three different kinds of feedstock were prepared according to the weight fraction of W and WO_3 components: pure W micro-powder feedstock, pure WO_3 micro-powder feedstock, and blended feedstock of W and WO_3 micro-powders at weight fraction of 50% respectively. In the case of blended feedstock, W and WO_3 powders were mixed at the weight fraction of 50% in a turbulent mixer for 2 h. Each feedstock powder was fed into thermal plasma under the same experimental condition which is summarized in Table 1. Mass flow hydrogen gas is higher than the stoichiometric one that is required for full reduction of WO_3 component at the mass feed-rate. On the other hand, N_2 gas is used for quenching hot gas dynamics in order to accelerate nucleation kinetics of gaseous tungsten species. Additionally, rapid quenching will increase collision probability between nanoparticle and spherical powders during the process. Morphology and phase composition of the synthesized particles were investigated after the thermal plasma process. In order to clarify structural features of the nanoparticle attached micro-powder, surface nanoparticles were ultrasonically detached from underlying micro-powder. To do this, the synthesized powders were immersed in ethyl alcohol and ultrasonic treatment was conducted for 10 min. Just after ultrasonic treatment, coarse micro-powders sink to the bottom of the vessel faster than fine particles. Nanoparticle dispersed liquid was separated from sediment micro-powder. After that, filtered fine particles and micro-powders were dried in a vacuum oven at 423 K for 12 h. In the case of nanoparticles, samples for transmission electron microscopy were prepared by dropping of nanoparticle dispersed ethyl alcohol solution which was mounted on the holey carbon coated copper grid, and dried for 10 min at 60 °C in the oven.

3. Results and discussions

Characteristics of W and WO_3 feedstock micro-powders are shown in Fig. 1. W micro-powder was prepared by hydrogen reduction of tungsten oxide powder. It shows typical morphology that facet primary particles make open structured aggregates by sinter-neck formation between them as shown in Fig. 1(a). On the other hand, WO_3 micro-powders are facet and bulky as shown in Fig. 1(b). Particle size distributions were measured by image analysis and they are plotted in Fig. 1(c) and (d). It is noted that particle size distribution of W is not aggregate size but primary particle size. Mean particle size of W primary particles is about 3.9 mm and that of WO_3 particle is 24.6 mm.

Phase compositions of both feedstocks are identified by X-ray diffraction patterns in Fig. 2. W micro-powder is composed of bcc α-W (JCPDS No. 04-0806) while monoclinic γ-WO_3 (JCPDS No. 84-2404) is for tungsten trioxide powder.

Morphologies of the synthesized powders are shown in Fig. 3. According to feedstock materials, synthesized powders show different morphologies. It is apparent that irregular W aggregates (Fig. 1(a)) are fully spheroidized by thermal plasma treatment as shown in Fig. 3(a). In addition to spherical morphology, dust like fine particles cover the surface of spherical micro-powders and they are agglomerated nanoparticles. A part of them forms build-ups on the surface of spherical powder marked as [I] and a part of them forms agglomerated granules of nanoparticles marked as [II]. On the other hand, WO_3 feedstock shows quite different results from W feedstock. As shown in Fig. 3(b), nanoparticles are obtained when WO_3 micro-powders are fed into Ar–H_2 thermal plasma. It is worthwhile to note that all the WO_3 micro-powders were converted to nanoparticles within the scope of this study. As-synthesized nanoparticles consist of spherical particles and cubic particles and also part of them forms open structured aggregates which is typical in vapor phase condensation synthesis of nanoparticles. In the case of blended feedstock of W and WO_3 micro-powders, apparent morphology becomes more irregular than spheroidized W micro-powder (Fig. 3(a)). Rough surface is composed of nanoparticles and is identical to spherical W micro-powder. However, nanoparticle content is much higher than spherical W micro-powder.

From the results of morphological changes, it is concluded that W and WO_3 feedstock micro-powders undergo different phase evolution pathways during the thermal plasma process. Melting–solidification pathway is dominant for W micro-powder while vaporization–condensation phase evolution is preferential for WO_3 micro-powder. At the given thermal plasma condition, differentiated phase evolution routes are caused by different thermos-physical properties of W and WO_3 feedstock micro-powders. WO_3 has much lower boiling point (1973 K) as compared to tungsten (5828 K). Moreover, it is well-known that tungsten trioxide substantially sublimates above 1173 K. As a result, vaporization degree of WO_3 is much higher than W even though WO_3 particle size is much larger than W feedstock particle. Though WO_3 micro-powder was absent in pure W feedstock micro-powder, nanoparticles are present in spheroidized W micro-powder. It is related to particle size of W feedstock micro-powder. Closer look of commercial W feedstock is shown in Fig. 3(d). Primary particle size is relatively similar but aggregate size is quite different. During flight, the aggregate behaves as a unit particle system which individually interacts with thermal plasma. It means that aggregate is heated to form spherical molten droplet in order to reduce surface energy. After that, molten droplet is solidified to form spherical solid powder. Mean particle size of the as-spheroidized powder was about 8 mm. It is the reason why spheroidized micro-powder is larger than primary particle size of W feedstock micro-powder. During the process, part of W feedstock powder is vaporized by heat transfer from hot gas dynamics even though W has high boiling point. Because of surface-to-mass effect, it is known that vaporization degree is enhanced as particle size decreases. Accordingly, small aggregate may be primary source for the nanoparticle in spheroidized W micro-powder.

In addition to morphological change, phase evolution of each feedstock is reported in Fig. 4. Oxide phases are not identified for the synthesized powders. It implies that H2 in thermal plasma reduces WO_3 effectively. During the thermal plasma process, hydrogen molecule is dissociated to hydrogen atoms and further ionized to hydrogen protons which are much more active reducing agents. Spheroidized W micro-powder consists of mainly α-W (JCPDS No. 04-0806) and however, β-W (JCPDS No. 47-1319) is notable as shown in Fig. 4(a). β-W is more

Table 1
Inductively coupled thermal plasma process parameters[a].

Feedstock		Plasma power	Plasma gas					
Weight fraction	Feed-rate		Pressure	Central gas	Carrier gas	Sheath gas	Sheath gas	Quench gas
1 (100% W) 0.5 (50% W) 0 (0% W)	5 g·min^{-1}	28 kW	14.7 psia	Ar 15 slpm	Ar 5 slpm	Ar 60 slpm	H_2 10 slpm	N_2 100 slpm

[a] Inductively coupled thermal plasma system (Tekna-30 kW system, Canada).