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Current status of ductile tungsten alloy development by mechanical alloying

Y. Ishijima [a], H. Kurishita [a,*], K. Yubuta [a], H. Arakawa [a], M. Hasegawa [a], Y. Hiraoka [b], T. Takida [c], K. Takebe [c]

[a] *International Research Center for Nuclear Materials Science, Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan*
[b] *Okayama University of Science, 1-1 Ridai-cho, Okayama 700-0005, Japan*
[c] *ALMT Corp. (Japanese name: Kabushihigaisya Allied Material), Iwasekoshi-machi 2, Toyama 931-8543, Japan*

Abstract

There were considerable differences in ductility and recrystallization temperatures among fine-grained, carbide-dispersed tungsten alloys developed so far by mechanical alloying, followed by sintering and hot working. The differences are attributable mainly to three microstructural factors giving detrimental effects on the ductility and recrystallization temperature; (1) precipitation of the brittle W_2C phase, (2) heterogeneity in grain size and particle distributions and (3) loss of carbon which is a constituent of transition metal carbides. Therefore, a process to eliminate these factors is presented. The improved process was applied to fabricate tungsten alloys, and microstructural observation and three-point bending tests were performed on the alloys. It is demonstrated that the developed alloys have microstructures almost free from the three factors; the developed alloys exhibited no ductility before fracture in the as-HIPed state, but showed appreciable ductility in the as-forged state, indicating importance of plastic working to improve the ductility of the alloys.

1. Introduction

Tungsten has many favorable properties for use as high heat flux components and high-power density structural materials in radiation environments. However, it exhibits serious embrittlement in several regimes, i.e., low temperature embrittlement, recrystallization embrittlement and radiation embrittlement [1]. In order to overcome such embrittlement, the authors have been developing tungsten alloys with a microstructure of fine grains and finely dispersed particles of transition metal carbides. For the development, they applied mechanical alloying (MA) of the starting powders of W, TiC or Ti and C and sintering of the MA treated powder by vacuum hot pressing (VHP) and hot isostatic pressing (HIP), followed by hot forging and hot rolling. It was shown that the alloys developed exhibited improved ductility and high recrystallization temperature, but considerable difference was seen among the alloys [2–6]. Recent studies have shown that the difference is attributable mainly to three microstructural factors giving detrimental effects on the ductility and recrystallization temperature; (1) precipitation of the brittle W_2C phase, (2) heterogeneity in grain size and particle distributions and (3) significant loss of carbon necessary for the formation of finely dispersed particles of transition metal carbides. In this paper, a process to solve the three problems is presented. The results of microstructures and mechanical properties of the alloys prepared by the improved processes are discussed.

* Corresponding author. Tel.: +81-29 267 4314/4157; fax: +81-29 267 4947.
E-mail address: kurishi@imr.tohoku.ac.jp (H. Kurishita).

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2. Improved processes for solving the problems

W_2C was found to form during sintering by the reaction of W with WC impurity introduced from the containers and balls made of WC/Co used for MA [5]. The contamination of WC/Co was inevitable even by the optimization of MA conditions [5]. In addition, Co is a highly radioactive element after neutron irradiation and must be eliminated. Therefore, we decided to develop new containers and balls made of Mo and its alloy. Because Mo belongs to group VIa, which is the same as W, and its carbide, Mo_2C, may be less harmful and has a lower free energy for formation than W_2C under HIP conditions. We studied the effects of Mo additions on the microstructural evolution, relative density and Vickers microhardness for W–0.3 wt%TiC, which will be reported elsewhere [6]. Finally, we have chosen a Mo alloy, TZM, as the material for new containers and balls for MA.

Heterogeneity in grain size and particle distribution comes from MA processes with the use of a planetary ball mill. The milling often resulted in a mixture of powders having different degrees of MA, leading to sintered compacts with heterogeneity in grain size and particle distribution. To produce homogeneous MA treated powders, a 3 MPDA (three mutually perpendicular directions agitation) ball mill was newly developed. In the MA process using this equipment, the optimization was made so as to meet three requirements: (1) to reach the final stage of MA, (2) to collect a sufficient amount of mechanically alloyed powder, and (3) to suppress contamination with TZM coming from the milling containers and balls during MA. For the optimization of milling parameters, the weight ratio of balls to powder, vessel agitation speed and milling time were examined.

Significant loss of carbon was confirmed as the result of decarburization during VHP [5]. Since the MA treated powder included an appreciable amount of oxygen as an impurity, ~1000 wtppm, carbon reacted with the impurity oxygen during VHP above 1723 K for 3.6 ks and was removed as CO gas, which free energy for formation decreases significantly with increasing temperature. In order to suppress decarburization, HIP should be conducted with metal encapsulation of the MA powder. At first HIP with a mild steel capsule that allows sufficient outgassing from the MA treated powder is performed at 1623 K (0.44 T_m, where T_m is the melting point of W). Then, the sintered compact taken from the metal capsule and wrapped in Ta foil is subjected to further HIP processing at 2223 K (0.60 T_m) in an Ar atmosphere.

3. Experimental

Powders of pure tungsten (an average particle size 4.0 μm and purity 99.9%) and TiC (40 μm, 99.9%) were used as the starting materials. They were mixed to provide a nominal composition of W–0.3wt%TiC and then charged into two vessels with balls made of TZM. For comparison, containers and balls made of WC/Co were also used. MA treatments were conducted by a 3 MPDA ball mill under conditions that the weight ratio of balls to powder was 2, the agitation speed was between 300 and 450 rpm and the milling time was between 10 and 50 h. The pots containing the powder and balls were cooled by a fan so that the pot surface temperature was around 280 K. All of these procedures were conducted in a glove box in a purified Ar (purity 99.9999%) atmosphere.

The MA treated powder was placed in a Mo boat and heated at 1073 K for 3.6 ks in a vacuum to remove the introduced Ar during MA process. The vacuum-treated powder was charged into a mild steel capsule and then subjected to HIP in an Ar atmosphere at first at 1620 K and 200 MPa for 10.8 ks, and additional HIP at 2220 K and 200 MPa for 10.8 ks for the sintered compact taken from the metal capsule and wrapped in Ta foils. The HIPed compacts had the measured relative densities of 99% or more and were hot forged at around 1770 K to approximately 1.5 mm thick. In this case, to maintain the specimen temperature during hot working, the as-HIPed compacts were placed in a crucible made of pure Mo [5] and then hot worked.

Table 1
Specimen and chemical compositions of developed alloys together with those processed by the previous method

Designation	Pot and ball	Agitating speed (rpm)/ time (h)	Sintering method	wppm			wt%	
				C	N	O	Ti	Mo
W–0.3TiC–0.7Mo	TZM	350/25	2step-HIP	720	80	290	0.3	0.7
W–0.3TiC–1.4Mo		350/50		700	90	360	0.3	1.4
W–0.3TiC–1.7Mo		450/25		680	50	220	0.3	1.7
W–0.3TiC–1.4Mo	WC/Co	185/50	1step-VHP	120	30	650	0.3	1.4
W–0.3TiC–1.4Mo				50	10	160	0.3	1.4
W–0.3TiC–1.4Mo				90	10	340	0.3	1.4

Table 1 lists the specimens and chemical compositions of the developed alloys by the present method (the upper three alloys) together with those processed by the previous method, i.e., planetary ball milling with WC/Co containers and balls and sintering with VHP (the lower three alloys [6]) for comparison. The Mo contents in the upper three alloys came from vessels and ball of TZM during MA and varied significantly with the MA condition of agitating speed and time. This indicates that the contaminant Mo contents can be reduced by controlling the MA condition. It should be noted that the contents of carbon is between 680 and 720 wppm, indicating that almost all of the carbon content added as TiC was maintained. In addition, the content of oxygen remains almost constant at a low level, ~300 wppm, whereas it showed considerable variation between the alloys processed by the previous method.

From the as-HIPed and as-forged compacts, specimens for X-ray diffraction (XRD) analysis, microstructural observations, Vickers microhardness measurements and three-point bending tests were prepared. XRD with a voltage of 30 kV and current of 250 mA was used to identify the dispersed compound particles. Microstructural observations were made by transmission electron microscope (TEM) with JEM-2000 FX or JEM-4000 FX operating at 200 or 400 kV, respectively. Vickers microhardness measurements were conducted at room temperature with a load of 1.96 N for 20 s. Three-point bending tests were conducted for bend bar specimens with the dimensions of $1\times1\times20$ mm using a servo-hydraulic fatigue testing machine (Shimadzu Servopulser of 50-kN capacity equipped with a 5-kN shear-type load cell) with a span of 13.3 mm and a crosshead speed of 0.013 mm/s.

4. Results and discussion

4.1. Microstructure

As shown in Table 1, the content of carbon added as TiC, ~750 wppm, was almost retained in the as-HIPed compacts. In X-ray diffraction patterns from the as-HIPed specimens definite peaks of TiC and Mo_2C were observed, but no peaks of W_2C appeared, indicating that TiC and Mo_2C exist as the dispersed phases.

Fig. 1 shows the grain size distribution for the as-HIPed W–0.3TiC–1.7Mo, together with that for W–0.3TiC–1.4Mo processed by the previous method, i.e., planetary ball milling with WC/Co containers and balls and sintering with VHP at 2123 K. These grain sizes were measured from TEM micrographs. The grain size distribution in W–0.3TiC–1.7Mo is in a relatively narrow range from 0.5 to 1.3 μm with an average of 0.90 μm, whereas that of W–0.3TiC–1.2Mo is in a wide range from 0.5 to 2.5 μm with an average of 1.38 μm.

Fig. 2 shows a bright field image showing dispersed particles for the as–HIPed W–0.3TiC–0.7Mo. The size distributions of the dispersed particles in the W–0.3TiC–0.7Mo and W–0.3TiC–1.7Mo are shown in Fig. 3. In both cases, there is no appreciable difference in the size distributions with sharp peaks between 10 and 15 nm, although a small amount of dispersed particles with diameters above 30 nm were formed in W–0.3TiC–0.7Mo. The average diameter of the particles was 21 nm for W–0.3TiC–0.7Mo and 17 nm for W–0.3TiC–1.7Mo. On the other hand, for the compact

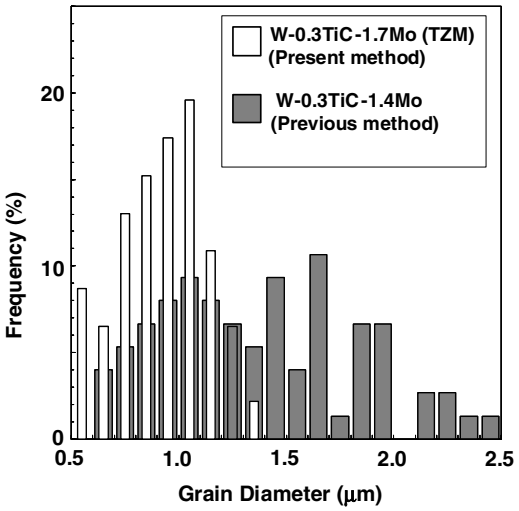

Fig. 1. Grain size distribution for W–0.3TiC–1.7Mo (TZM) developed by the present method together with that for W–0.3TiC–1.4Mo processed by the previous method.

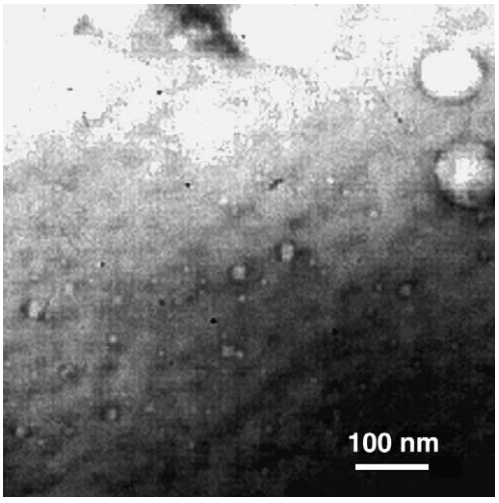

Fig. 2. TEM micrograph showing dispersed particles in W–0.3TiC–0.7Mo (TZM) in the as-HIPed state.

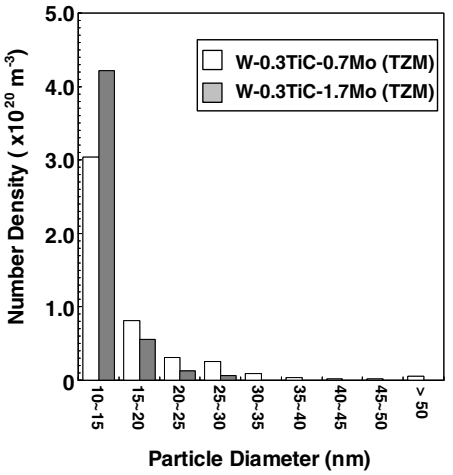

Fig. 3. Size distribution of dispersed particles in W–0.3TiC–0.7Mo (TZM) and W–0.3TiC–1.7Mo (TZM) in the as-HIPed state.

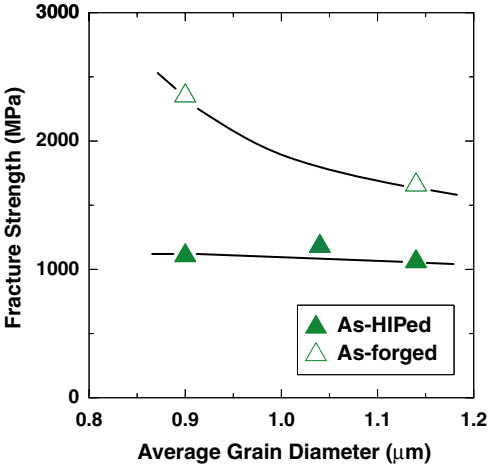

Fig. 4. Fracture strength against average grain diameter for W–0.3TiC–0.7Mo (TZM), W–0.3TiC–1.4Mo (TZM) and W–0.3TiC–1.7Mo (TZM) in the as-HIPed and as-forged states.

of W–0.3TiC–1.2Mo sintered by VHP at 2123 K the average particle size was 58 nm [6]. The significant difference in the particle size distribution between W–0.3TiC–0.7Mo or W–0.3TiC–1.7Mo and W–0.3TiC–1.2Mo is attributed to the temperature history during sintering, because VHP with two-step heating at 1523 and 2123 K for 3.6 ks leads to a significant decrease in the particle size; from 58 nm for one-step heating at 2123 K to 21 nm for the two-step heating [6]. This is most likely due to enhanced nucleation but relatively slow growth of the precipitates at 1523 K compared with the nucleation and growth of the particles in the one-step heating at 2123 K for 3.6 ks. Therefore, it can be stated that sintering with two-step heating at ~0.4 and ~0.6 T_m is very effective to obtain dispersion of nano-size particles of the transition metal carbides.

4.2. Mechanical properties

The three developed alloys processed by the present method (Table 1) showed a slight variation in grain size between 0.9 and 1.15 μm, which is mainly attributable to the difference in Mo content; the grain size decreased with increasing Mo content, because solute atoms of transition metals in matrix are known to retard grain growth. Therefore, the effects of grain size and hot forging on bending fracture strength were examined for the developed alloys. Fig. 4 shows bending fracture strength at room temperature against average grain size for the developed alloys in the as-HIPed and as-forged states. Fracture strength was estimated to be the maximum fiber stress given by

$$\sigma = 3PL/2Bt^2.$$

Here, σ is the stress, P is the applied load, L is the span (13.3 mm), B and t are the specimen width and thickness, respectively. The fracture strength significantly increases by hot forging. In particular, the fracture strength of the as-forged W–0.3TiC–1.7Mo exceeded its yield stress indicated by the arrow, as shown in Fig. 5. This occurrence of appreciable ductility before fracture in the as-forged W–0.3TiC–1.7Mo should be noted because all of sheet specimens of W and its alloys exhibited appreciable ductility only after severe plastic working as hot rolling [2,5]. The effects of severe plastic working for fine-grained and particle-dispersed tungsten developed by MA–HIP are not fully understood yet. A possible explanation for the effects is that the residual pores can be eliminated from the matrix by interaction with a high

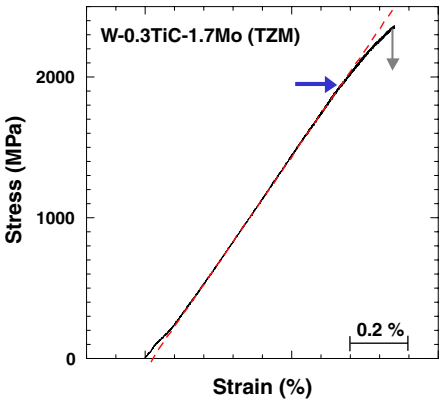

Fig. 5. Stress–strain curve by three-point bending at room temperature for as-forged W–0.3TiC–1.7Mo (TZM), showing an appreciable ductility before fracture. The arrow indicates the onset of plastic deformation.

density of dislocations introduced during plastic working. If this is the case, more improvement in ductility in tungsten should be made by eliminating such residual pores. This suggests that fabrication of densified compacts having the theoretical density by complete outgassing from the MA treated powder prior to HIP is very important. Such efforts of fabrication together with mechanical tests for specimens in the hot rolled states will be presented elsewhere [7].

5. Conclusions

To eliminate the detrimental effects of three microstructural factors on the ductility and recrystallization temperature, such as (1) precipitation of the brittle W_2C phase, (2) heterogeneity in grain size and particle distribution and (3) significant loss of carbon which is a constituent of finely dispersed particles of transition metal carbides, an improved process was proposed and applied to fabricate W–0.3wt%TiC–(0.7–1.7)wt%Mo alloys. The alloys were subjected to microstructural observations, XRD analysis and three-point bending tests at room temperature. The main results are as follows.

(1) The developed alloys had grain sizes ranging from 0.5 to 1.15 μm and particle sizes with a sharp peak around 10–15 nm, indicating homogeneous distributions in grain size and particle size.
(2) XRD analysis showed peaks of TiC and Mo_2C, suggesting dispersed particles of TiC and Mo_2C.
(3) The developed alloys had almost the same carbon content as that added as TiC. The oxygen contents in the alloys were low and almost constant, ~300 wppm.
(4) The developed alloys exhibited no ductility before fracture in the as-HIPed state. However, the alloys after hot forging showed appreciable ductility, indicating the importance of plastic working to improve the ductility of the alloys.

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