Effect of reinforcement phase on the mechanical property of tungsten nanocomposite synthesized by spark plasma sintering

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Abstract

Nanostructured tungsten composites were fabricated by spark plasma sintering of nanostructured composite powders. The composite powders, which were synthesized by mechanical milling of tungsten and Ni-based alloy powders, are comprised of alternating layers of tungsten and metallic glass several hundred nanometers in size. The mechanical behavior of the nanostructured W composite is similar to pure tungsten, however, in contrast to monolithic pure tungsten, some macroscopic compressive plasticity accompanies the enhanced maximum strength up to 2.4 GPa by introducing reinforcement. We have found that the mechanical properties of the composites strongly depend on the uniformity of the nano-grained tungsten matrix and reinforcement phase distribution.

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Introduction

Tungsten (W) alloy or pure tungsten metal contacts, electrodes, and wires are used in electrical, electronic, heating, lighting, and welding applications due to their exceptional properties such as high density, hardness, very high melting temperature, relatively high radiation opacity and good thermal conductivity combined with very low thermal expansion.¹ Tungsten is also used to make heavy metal alloys for armaments, heat sinks, radiation shielding, weights and counterweights; superalloys for turbine blades; tool steels; and wear-resistant alloy parts and coatings.¹ The leading use is as tungsten carbide in cemented carbides, which are sintered powder metallurgical parts that are used as cutting tools and wear-resistant components by the construction, metalworking, mining, and oil drilling industries.²

Tungsten tool materials as carbides are the largest consumption volume of tungsten in end-use sector, which account for about 60% of the tungsten consumption.² The higher the volume fraction of carbide particles there are within the material, the harder it is, but the less tough it behaves during loading; and, vice versa, significant increases in toughness can be achieved by a higher amount of metallic binder (i.e., Co, Ni) at the expense of hardness. The cobalt and/or nickel metal powder is used as a binder to hold together the tungsten carbide particles. The use of coarse W or WC particles/grains, which are preferred for the manufacturing process, promotes the increasing product efficiency but decreasing mechanical property (especially toughness) of the tool materials by coarse W particles.³⁻⁵ Due to limitations in decreasing the particle size as well as

processing complications, however, most WC tools materials have not achieved uniform nanometer-size scale homogeneity, which is essential to increase toughness.

One noteworthy exception to this are uniformly-layered nanometer-scale tungsten composites, which are obtained by a controlled milling process to yield composite powders that are consolidated by spark plasma sintering (SPS) into fully dense bulk shapes.^{6,7} The composites show more preferred shear banding in a nanometer-scale reinforcing metallic glass (MG) phase homogeneously-distributed in a metallic tungsten matrix. Spark plasma sintering (SPS), where the material is bonded by viscous melt flow at the particle surface, can be a suitable compaction technique to maintain the nanostructured metallic glass-tungsten composite that is created by high-energy ball milling since it utilizes low sintering temperatures and short sintering times.^{8,9}

Typically the processing temperature and time for synthesizing MG composite are determined by the thermal characteristics of the MG, i.e., supercooled liquid region, because crystallization of the MG critically significantly deteriorates the mechanical properties.¹⁰ However, improvement of plasticity in Zr-based MG after dispersion of crystalline nanoparticles by annealing has been reported.¹¹ There are no reports in the literature, however, on the relation between mechanical property and crystallization of amorphous phase in MG reinforced tungsten nano-composite before and after consolidation.

In the current study, we investigated the effect of crystallization of the reinforcing metallic glass phase on the mechanical behavior of tungsten nano-composites, which

have uniformly dispersed reinforcements in the ultra-fine grained tungsten matrix exhibiting a novel nano-mixture structure by utilizing SPS.

Experiment

A master alloy was prepared by induction melting high-purity elemental constituents (electron beam melted Ni 99.999%, crystal bar Zr 99.99%, Ti sponge 99.99%, Si 99.9%, and Sn 99.9%) in a yttria-stabilized zirconia crucible under an Ar gas atmosphere. The homogenized molten alloy was bottom pour cast into a 5-cm diameter water-cooled Cu mold. The master alloy was re-melted in the atomization furnace. Spherical $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_2\text{Sn}_3$ (at%) metallic glass alloy powders, which prepared by high pressure gas atomization at a dynamic pressure of 2.8 MPa and at a molten temperature of 1350 °C using a close-coupled annulus with a melt delivery nozzle 3.2 mm in diameter at the Ames Laboratory (USDOE), and W powders (>99.9% purity, Perkin Elmer/Metco, SPI12430) both with have -45 μm sizes were used as starting materials. Because from the previous study, the atomized Ni-based MG powders were sieved according by conventional sieve analysis and were divided into the following 12 different size ranges: under 10, 10-20, 20-38, 38-45, 45-53, 53-63, 63-75, 75-90, 90-106, 106-125, 125-150 and over 150 μm . The oxygen content of the powder analyzed by an elemental inorganic analysis method decreases as the increase powder size up to 40 μm . The oxygen content is nearly constant (about 450 ppm) for powder sizes larger than 40 μm . For this study, the W contents were selected 50 vol.% (=65 wt.%) to reveal possible effect of reinforcement to the deformation behavior as a fraction of microstructural change and 50 vol.% of Ni-

based MG in the composites. Milling of the Ni-based MG powder blended with W powder was performed with a Retsch Pulverisette 5 planetary ball mill using a rotational velocity of 100 rpm for 144 ks using hardened steel milling tools and a ball to powder ratio of 10:1. Milling conditions with relatively low velocity were chosen to prevent crystallization of metallic glass or excess phase transformation during milling process. All milling and powder handling steps were done in a glove box in purified Ar atmosphere (less than 3 ppm O₂ and H₂O). The consolidation of the milled powders using SPS to form bulk samples with 20 mm diameter and 10 mm thickness was performed with a SPS Syntex Inc. Model Dr. Sinter SPS-515S with tungsten carbide punches and die. SPS was done under vacuum with an external compaction pressure of 300 MPa and a heating rate of 40 K/min. The temperature for sintering and processing time window were determined based on the T-T-T curve for the onset of crystallization.⁶ Considering the heating rate, an SPS temperature of 577 °C was selected, crystallization of Ni-based metallic glass can be retarded up to about 300 s at this temperature. The sintering temperature and time were varied to optimize the sintering parameters leading to dense (93.3 %) sintered parts. The samples were cut and the surface was micro-polished to obtain 2 mm x 2 mm x 4 mm rectangular bars for compression testing. Structural characterization was performed using a Philips APD 3520 X-ray diffractometer with monochromatic Cu-K_α radiation and a LEO 1530 scanning electron microscope (SEM). The thermal properties of the samples were measured with a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) using continuous heating at a rate of 40 K/min. Uniaxial compression tests were conducted on an Instron Model 8563 at room

temperature at a constant cross head speed and an initial strain rate of $3 \times 10^{-3} \text{ s}^{-1}$. The density of the samples was determined by the Archimedes method in water using a Mettler Toledo-AT261 Delta-Range density measurement system.

Results and discussion

The SEM images in Fig. 1 of the transverse cross-section of the sintered samples show two types of nanostructured W composites fabricated by SPS. Both structures show a uniform size and distribution of the Ni-based reinforcement particles (dark contrast area) dispersed within the W matrices (bright contrast area). The dark phase, however, in sample A, corresponds to a Ni-based crystalline phase and in sample B, it corresponds to a Ni-based amorphous phase. Fig. 1a displays a polished transverse section (i.e., the consolidation direction is normal to the plane of the image) of the spark plasma sintered 144 ks milled 50 vol.% Ni-based crystalline (devitrified MG during SPS) reinforced W composite (sample A). Fig. 1b shows the fine layered structure developed in the composite powders during milling is composed of homogeneously dispersed dark layers of the Ni-based MG separated by adjacent lighter W phases.

The observed size range of the layers is relatively broad and varies from ~20-500 nm, which is similar to the previously reported result in a Cu-based MG and Hf-based MG nanocomposites.^{7,12} Due to longer milling time (144 ks), the thicknesses of the layers for the finely mixed structure between W and MG are more smaller than previously reported for a 72 ks milled 50 vol.% W composite which has a layer size range from 100 nm to 2 μm thickness.⁶ For the W-composite reinforced with the crystallized MG phase

(sample A; Fig. 1a), the crystallized MG and the W matrix are intimately mixed in multiple layers similar to the Sample B composite. The microstructures of the nano-grained tungsten matrix are mostly uniformly throughout for samples A and B, while the reinforcing phase is different for the two samples. This is not unexpected since both composite samples utilized the same starting composites powder, but were subject to different sintering times in the SPS consolidation. Sample A (420 s at 577 °C), which has the devitrified MG phase, was heated longer than Sample B (240 s at 577 °C), which maintained the amorphous structure of the MG second-phase.

X-ray diffraction (XRD) patterns taken from the starting composite powders and two different composite samples (Fig. 2) show clear differences between crystalline composite Sample A and MG composite Sample B. Furthermore, the XRD for the starting MG and W composite powder (i.e., after milling) do not show any evidence of crystallization of the metallic glass phase. The starting MG-W composite powder displays only the W bcc peaks without any obvious amorphous broad halo. This can be attributed to the large difference in scattered intensity between the MG reinforcement and the strongly scattering W, as shown in Fig. 2a. Similarly, for Sample B there are no visible diffraction peaks except from those of the W matrix indicating that the MG phase in the composites Sample B has not undergone any significant devitrification during sintering. In contrast to Sample B, distinct Bragg peaks not corresponding to the W-matrix can be seen in the XRD pattern. These peaks correspond to scattering from the crystalline NiZr and Ni₁₀(Zr, Ti)₇ phases that have formed in the devitrified MG second-phase.¹³

The inset in Fig. 2a shows the measured change of the 2θ values for the (110) plane of W-matrix phase after the milling and sintering processes. A shift of the W peaks to lower diffraction angles is observed in the milled composite samples. This peak shift to the lower angle side corresponds to an increase of the lattice parameter of W due to dissolution of metallic glass elements into the W lattice, which is similar to the previously observed result by Eckert *et al.* as the milling time increases.¹⁴ Interestingly, the magnitude of the peak shifting to a lower angle is smaller for Sample A (devitrified second-phase) compared to Sample B (amorphous second-phase). Moreover, the peak position of (110) plane of W obtained from as-milled composite powders shifts to higher angle side corresponding to an decrease of lattice parameter of W. It has been reported that the lattice parameter increases in the disordered state, if the disordering occurs by anti-site disorder, whereas the lattice parameter decreases if disordering occurs by the triple defect, as the formation of vacancies due to relaxation around vacancies, disorder.^{15,16} Moreover, in case of triple defect type disorder, the materials is not transformed to solid solution or amorphous state even after long time milling. Only in the case of anti-site disorder of components, can a compound transform to solid solution or the amorphous state.¹⁶ Therefore, it can be considered that there is existence of vacancy type defects by cyclic compressive strain during milling in the starting as-milled composite powder between W and MG rather than substitutional defects which are likely present in the consolidated bulk W/MG composite (sample B) by solutioning during SPS. These substitutional defects transform to vacancy type by the diffusion of elements

during crystallization of the MG, which is characterized by the abnormal diffraction peak shifting of composite Sample A.

Fig. 2b shows the dependence of the lattice parameter of tungsten on phase of reinforcements. Tungsten powder milled with Ni-based metallic glass powder for 144 ks has already a slightly different smaller lattice parameter (3.152 Å) than the pure W starting material (3.155 Å), which can likely be attributed to residual compressive straining during the milling process.¹⁷ Following thermoplastic consolidation of the powders by SPS, the lattice parameter increases to 3.172 Å, which should promote solute incorporation. The lattice parameter of the W-phase decreases again, however, to 3.165 Å following the crystallization of MG phase. This change in the lattice parameter is believed to be due to the diffusion of solute atoms from the lattice to form crystalline phases. The lattice parameter variation with changing mechanical milling time coincides with previously reported results.⁷ The amount of lattice distortion initiated from the change of lattice parameter during processing is significant in the MG reinforcement rather than crystalline reinforcement due to the deformation behavior of MG. Amorphous metallic alloys exhibit large elastic limit (~2%), no long-range order, the thus there are no well-defined atomic planes, dislocations or slip systems to absorb external strain, which shown in the typical crystalline metals.⁶ Accordingly, at temperatures below the glass transition temperature (T_g) under appropriately high stress levels, level of comparative strain induced mismatch of elastic limit between MG reinforcement and W matrix during deformation is much higher than those level of strain in crystalline reinforcement.

The thermal analysis results obtained for the MG reinforced W composite and crystallized W composites are given in Fig. 3a, respectively. The DSC trace of the as-sintered MG reinforced W composite (Sample B) exhibits a crystallization onset temperature, T_x , of 600 °C and an integrated heat of crystallization, ΔH_x , of -5.8 J/g. In contrast, no exothermic reaction corresponded to transformation from amorphous to crystalline is observed in the DSC data for Sample A due to the full crystallization of the MG phase during the sintering process. Compared to the monolithic MG alloy (not shown), the crystallization temperature of the composite shifts to a slightly lower temperature with a broadening of the primary crystallization peak. One possible explanation for this difference is partial alloying or dissolution of the Ni-based MG with W during milling, leading to a slight compositional change in the glass.¹⁴ Another possibility may be related to the chemical inhomogeneity at the MG interfaces due to the relative diffusion of some elements during SPS.^{8,9} Considering the self-diffusivity of constituents and atomic radii, it can be supposed to Si and Ni diffused out from amorphous phase, which has relative high diffusivity (Si: 2.4 cm²/s and Ni: 4.4 cm²/s, respectively) and small atomic radius (Si: 1.10 Å and Ni: 1.35 Å, respectively) rather than those of the other elements.¹⁸ The heat of crystallization in the composites is quite close to the monolithic metallic glass after the endothermic signals are normalized to their specific metallic glass mass fractions.

Stress-strain curves from quasi-static room temperature uniaxial compression testing of the composites are shown in Fig. 3b. The maximum compressive strength of the composites reaches almost the same level (~2 GPa) for both samples and the yield

strength of Sample B is 2.4 GPa, which is slightly higher than the yield strength of Sample A (2.2 GPa), but slightly lower than the yield strength of the monolithic bulk metallic glass (2.6 GPa). It is reported a representative yield strength for monolithic bulk nanostructured W is 0.75 GPa.¹⁹ The total strain of 2.6%, including the plastic strain, for Sample B is slightly higher than the value of Sample A (2.1% total strain) and much higher than that exhibited by the monolithic BMG (1.7% total strain), as summarized in Table 1. The Elastic modulus is a measure of the resistance offered by an elastic body to deformation and appears slope of stress-strain curve. The slope of stress-strain curve in elastic region, known as elastic modulus or stiffness, is one of the most structure-insensitive parameters being only affected by: (1) alloying additions, (2) heat treatment and (3) cold work.²⁰ However, the stiffness is property of structure rather than property of material (elastic modulus).²⁰ In the current study, the compositions and microstructures of the two composites are very similar with the major difference being the reinforcing phase in crystalline in Sample A and amorphous in Sample B. As shown Fig. 3b stress strain curves, the shape of stress strain curve between MG reinforced Sample B and crystalline reinforced Sample A are similar each other. It means that the fracture toughnesses of samples are almost same, resulting in the stiffness of Sample B and Sample A are also similar, even though the MG reinforcement has large elastic limit.

It is well known that crystallized MG can exhibit poor mechanical properties due to the extreme brittleness of the intermetallic phases that often form. However, the results in current study show the crystallization of reinforcing-MG phase does not significantly degrading effect on the mechanical property of composites. This can be attributed to the

layered structure between the reinforcement and submicron scale W matrix controlling the mechanical behavior of the composites. Both nanostructured composites containing 50 vol.% W exhibit similar fracture behavior as a monolithic MG due to the development of a primary shear band propagating through the whole specimen.⁵ This result is consistent with previous work showing that, plastic flow is more likely to localize in narrow regions when the layered structure of the composites approaches the nanometer scale.⁶ Since ultra-fine grained W shows a low resistance to shear softening, especially at very high strain rates, but the maximum strength of the composites increases at strain rates higher than the one used in the current study by strain rate hardening.¹⁹

Conclusions

Nanostructured W composites reinforced by MG and crystalline phases were fabricated using mechanical milling and consolidation by SPS to obtain bulk nanostructured composite materials with high strength and enhanced compressive plasticity. The mechanical behavior of the nanostructured W composites is similar to that of typical monolithic tungsten. However, the deformation behavior of W composites mainly depends on the layered structure between the nano-grained tungsten matrix and reinforcement rather than the phase(s) of the reinforcing constituent.

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Table 1 Summary of mechanical properties for metallic glass reinforced nanostructured W composites.

Sample	Measured Density (g/cm ³)	Calculated Density (g/cm ³)	Young's modulus (GPa)	Maximum strength (MPa)	Total strain (%)	Plastic strain (%)
Monolithic polycrystalline W	19.3	-	400	980	-	-
Single-phase MG	7.6	7.4	123	2657	1.7	-
Sample A (Cr _x +50 vol.% W)	12.6	13.5	166	2262	2.1	-
Sample B (Am+50 vol.% W)	12.6	13.5	173	2409	2.6	-

Figure captions

Fig. 1

SEM backscattered electron images obtained from the polished cross section of the spark plasma sintered nanostructured W composites containing 50 vol.% Ni-based alloy reinforcement.

(a) Sample A: crystalline phase Ni-based alloy reinforcement particles within the W matrix

(b) Sample B: amorphous Ni-based alloy reinforcement within the W matrix

Fig. 2

(a) XRD patterns taken from the nanostructured W composites containing 50 vol.% Ni-based crystalline alloy (Sample A) and metallic glass (Sample B), respectively. Inset: Change of XRD diffraction peak position for the (110) plane for W matrix after milling and sintering.

(b) Shifting of the lattice parameter of (110) plane of W phase related with lattice distortion by strain.

Fig. 3

(a) DSC traces obtained during constant-rate heating at 40 K/min for the nanostructured W composites containing 50 vol.% Ni-based crystalline alloy (Sample A) and metallic glass (Sample B), respectively.

(b) Compressive stress-strain curves with 3×10^{-4} strain rate for the monolithic $\text{Ni}_{59}\text{Zr}_{20}\text{Ti}_{16}\text{Si}_2\text{Sn}_3$ metallic glass and 50 vol.% Ni-based crystalline alloy (Sample A) and metallic glass (Sample B) reinforced W composites, respectively.

Fig. 1

Fig. 2

Fig. 3