Article

Microstructure and Mechanical Properties of CoWB Based Composites Produced by Crystallization of Ni-Co-Zr-Ta-W-B Bulk Metallic Glass

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Abstract: CoWB based composites were produced by annealing $\text{Ni}_{33.6}\text{Co}_{23.2}\text{Zr}_{0.5}\text{Ta}_4\text{W}_{23.7}\text{B}_{15}$ bulk metallic glass above the crystallization temperature. The effect of annealing on the microstructure of the composites was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Microhardness (Hv) and indentation fracture toughness (K_{IC}) of the composites were also measured. Microstructural examinations revealed that the first precipitated phase as a result of annealing is a nickel solid solution. As the annealing time is increased, CoWB and the nickel solid solution begins to precipitate. If the annealing time is increased further, the CoWB remains stable, while the nickel solid solution transforms into Ni_3Ta . The microhardness of the as-cast alloy was determined to be 1190 HV. As a result of annealing, composites with a microhardness of around 1400 HV were obtained due to the precipitation of CoWB. K_{IC} of the composite with the maximum hardness was determined to be $\sim 3 \text{ MPa}\cdot\text{m}^{1/2}$. The effect of microstructure on the mechanical properties of the composites is discussed.

Keywords: bulk metallic glass; crystallization; composite; mechanical properties; ternary borides; CoWB

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1. Introduction

Boride-based composites have attractive properties such as high hardness, high strength, high chemical stability, and excellent wear resistance. In addition, boride-based composites have higher high-temperature oxidation resistance compared to carbide-based composites [1–3]. Many boride based composites reinforced with TiB_2 [4–6], TiB [7], ZrB_2 [5], Mo_2NiB_2 [8–10], W_2NiB_2 [11,12], Mo_2FeB_2 [9,13–18], FeWB [19,20], CoWB [21,22], and Mo-CoB [23] have been developed. These composites are produced by sintering.

It has been shown that boride-based composites can also be produced by crystallization of bulk metallic glasses with high boron content [24–27]. The main advantage of producing boride based composites by crystallization of bulk metallic glasses is that composite material with the desired geometry can be obtained by casting and subsequent heat treatment. Reinforcing phases of these composites are Fe_3B , Fe_2B , $(\text{Co,Fe})_2\text{B}$, Fe_{23}B_6 , $(\text{Fe,Ni,Mo})_{23}\text{B}_6$, $(\text{Fe,Cr})_{23}(\text{C,B})_6$, $(\text{Co,Fe})_{21}\text{Ta}_2\text{B}_6$, MoB , and CoWB . The microhardness of these composites varies between 1400 and 1800 HV. Among these composites, only the composite developed by devitrification of the bulk metallic glass $\text{Ni}_{36.3}\text{Co}_{25}\text{W}_{23.7}\text{B}_{15}$ contains a ductile phase [27]. This composite consists of a nickel solid solution with a face centered cubic (FCC) structure and CoWB phase. Since the reinforcement phase of the composite, CoWB , is a phase with extremely high hardness, which is $\sim 4000 \text{ HV}$ [1,27], this alloy system has a very high potential to be used as a precursor in the production of composites with high hardness and high fracture toughness. However, the glass forming ability (GFA) of the alloy is quite low, and its critical casting thickness is only 0.5 mm, which limits its usage

potential. It has been recently shown that the GFA of Ni-Co-W-B bulk metallic glasses can be improved by tantalum additions [28]. Since tantalum-modified Ni-Co-W-B bulk metallic glasses have higher critical casting thickness, CoWB based composite materials to be produced by crystallization of these alloys will find a wider range of usage. Therefore, the potential of these alloys to be used as a precursor in the production of CoWB based composite materials should be revealed.

In this study, composites are produced by the devitrification of $\text{Ni}_{33.6}\text{Co}_{23.2}\text{Zr}_{0.5}\text{Ta}_4\text{W}_{23.7}\text{B}_{15}$ bulk metallic glass, whose critical casting thickness is 1.5 mm. The effects of annealing on the microstructure and mechanical properties of the composites are investigated.

2. Materials and Methods

The master alloy $\text{Ni}_{33.6}\text{Co}_{23.2}\text{Zr}_{0.5}\text{Ta}_4\text{W}_{23.7}\text{B}_{15}$ (in at.%) was prepared by arc melting of the high purity metals Ni (99.9 wt.%), Co (99.8 wt.%), Zr (99.2 wt.%), Ta (99.9 wt.%), and W (99.9 wt.%), and pure crystalline B (98 wt.%) (Alfa Aesar, Ward Hill, MA, USA) in a Ti-Zr gettered ultra-high purity argon atmosphere. The alloy ingots were melted at least three times to ensure homogeneity. Alloy samples of 0.5 mm thickness were produced by the suction casting method in an arc furnace. The glass transition (T_g), crystallization (T_x), and liquidus (T_l) temperatures of the alloy were measured by differential scanning calorimetry (DSC) (NETZSCH Group, Selb, Germany). A heating rate of 20 K/min was used to measure T_g and T_x . After melting the sample completely by reaching a temperature of 1840 K, a cooling rate of 20 K/min was used to measure T_l . To produce composite samples, the fully amorphous samples were annealed at temperatures above the crystallization temperature. 1025 K was selected as the annealing temperature and the samples were heat treated for 10, 25, 50, 75, 100, 125, and 150 min. The structures of the as-cast and composite samples were examined by X-ray diffraction (Bruker AXS, Karlsruhe, Germany) with $\text{Cu-K}\alpha$ radiation. XRD data of the composite samples were refined with the Rietveld method using the Microstructural Analysis Using Diffraction (MAUD) software (Version 2.94, University of Trento, Trento, Italy). Microstructures of the composite samples were examined with SEM (FEI Company, Hillsboro, OR, USA). For this examination, the backscattered electron (BSE) imaging mode was used. The Vickers hardness test (Shimadzu Corporation, Kyoto, Japan) was used to determine the microhardness of the as-cast and annealed samples. For microhardness tests, a load of 2.94 N was applied for 15 s. For each sample, 10 microhardness measurements were taken randomly from different regions on the sample surface. The average of these measurements was taken as the microhardness value of that sample. To determine the Kc of the composite samples, loads up to 19.6 N were applied. In SEM, the secondary electron (SE) imaging mode was used to acquire images of the indents obtained from microhardness tests.

3. Results

3.1. Thermal Behaviour

A DSC scan of the amorphous alloy $\text{Ni}_{33.6}\text{Co}_{23.2}\text{Zr}_{0.5}\text{Ta}_4\text{W}_{23.7}\text{B}_{15}$ alloy used as the precursor to produce composites reveals that the T_g of the alloy is 901 K (Figure 1). Two crystallization peaks, T_{x1} and T_{x2} , are observed, and their values are measured as 981 and 1110 K, respectively. The presence of two crystallization peaks indicates that during devitrification, two crystallization events, involving the precipitation of multiple crystalline phases, occur. Also, the T_l of the alloy is measured during cooling and determined to be 1583 K.

3.2. XRD Results

Figure 2 shows the XRD patterns of the composites produced by annealing the fully amorphous samples at 1025 K for 10 to 150 min. After annealing the fully amorphous sample for 10 min, the nickel solid solution (Ni-phase), which has an FCC structure, precipitates. Since cobalt is completely soluble with nickel and the solubility of tungsten and tantalum in nickel are ~12.5 and ~11 at.%, respectively [29], the nickel solid solution

contains significant amounts of cobalt, tungsten, and tantalum. In addition, the composite sample contains a considerable amount of amorphous phase.

Figure 1. DSC scan of $\text{Ni}_{33.6}\text{Co}_{23.2}\text{Zr}_{0.5}\text{Ta}_4\text{W}_{23.7}\text{B}_{15}$ alloy. (a) Glass transition and crystallization behavior, (b) Melting behavior.

Figure 2. XRD patterns of the samples annealed at 1025 K.

After increasing the annealing time to 50 min, a small amount of CoWB precipitates besides the Ni-phase. It should be noted that there is still some amount of amorphous phase in the composite. With 100 min of annealing, the CoWB has a higher volume fraction. Also, there is some amount of Ni-phase in the composite sample. In addition to these two phases, another phase, Ni_3Ta , precipitates in the microstructure. The volume fraction of CoWB increases slightly after annealing for 150 min. However, there is a considerable

increase in the volume fraction Ni_3Ta while the volume fraction of the Ni-phase decreases. The decrease in the intensity of (200) the peak of Ni-phase, which is located at $2\theta = 50.18^\circ$, indicates that the volume fraction of the Ni-phase is quite small. This result reveals that the Ni-phase transforms into Ni_3Ta . Since the Ni-phase is a solid solution containing Ni, Co, W, and Ta, Ni_3Ta should also contain Co and W in addition to Ni and Ta. Therefore, Ni_3Ta forms as $(\text{Ni},\text{Co})_3(\text{Ta},\text{W})$. The lattice constants of the phases precipitating in the composites were determined by Rietveld analysis (Table 1).

Table 1. The lattice constants of the observed phases.

Phase	a (nm)	b (nm)	c (nm)
Ni (Fm3m)	0.3623 ± 0.0001	-	-
CoWB (Pnma)	0.5745 ± 0.0001	0.3244 ± 0.0001	0.6663 ± 0.0001
Ni_3Ta (Pmmn)	0.5073 ± 0.0004	0.4183 ± 0.0004	0.4507 ± 0.0004

Also, the Rietveld refinement of the XRD data of the composites produced by annealing the amorphous samples at 1025 K for 100 and 150 min was carried out to determine the volume fractions of the phases (Figure 3).

Figure 3. The Rietveld refinement of the XRD data of the composites produced by annealing the amorphous alloy at 1025 K for (a) 100 min, (b) 150 min. Observed data is indicated by black color. Calculated and difference data are represented by red and blue colors, respectively.

The results revealed that the volume fraction CoWB is ~ 0.4 in the composites obtained after annealing the amorphous alloy for 100 and 150 min (Table 2). After annealing for 100 min, the volume fractions of Ni-phase and Ni_3Ta are determined to be ~ 0.2 and 0.4 , respectively. As the annealing temperature is increased to 150 min, the volume fraction of Ni-phase decreases and becomes 0.1 , whereas the volume fraction of Ni_3Ta increases to ~ 0.5 .

Table 2. The volume fractions of the phases precipitated in the composites.

Annealing Time (min)	Ni-Phase	CoWB	Ni_3Ta
100	0.18	0.42	0.40
150	0.12	0.38	0.50

Since the Ni-phase transforms into $(\text{Ni},\text{Co})_3(\text{Ta},\text{W})$, both phases must have the same composition. It is possible to estimate the Ni, Co, W, and Ta contents of the Ni-phase.

Because boron is not soluble in Ni [29] and there exists only one phase containing boron, all of the boron atoms are expected to be in CoWB after completion of the crystallization. Therefore, CoWB contains 45 at.% of the atoms, which are 15 at.% B, 15 at.% Co, and 15 at.% W. The remaining 55 at.% atoms, 33.6 at.% Ni, 8.2 at.% Co, 0.5 at.% Zr, 8.7 at.% W, and 4 at.% Ta, must be in the Ni-phase. As a result, the mole fractions of the components, X_{Ni} , X_{Co} , X_{Zr} , X_W , and X_{Ta} , are determined to be, 0.61, 0.15, 0.01, 0.16, and 0.07, respectively. These results show that total nickel and cobalt content and total tungsten and tantalum content of the Ni-phase are 76 at.% and 24 at.%, respectively, which perfectly satisfies the stoichiometry of $(Ni,Co)_3(Ta,W)$. It should be noted that zirconium is assumed to be in the tantalum and/or tungsten positions.

The validity of this estimation can be checked by calculating the lattice parameter of the Ni-phase by using the mole fractions and average radii of the components and comparing it to the experimentally measured value. It is known that for an FCC unit cell, the relationship between the lattice constant, a , and the atomic radius, r , is:

$$a = \frac{4r}{\sqrt{2}} \quad (1)$$

The average atomic radius of the elements in Ni-phase is:

$$\bar{r} = \sum X_i r_i \quad (2)$$

where atomic radii of the elements, r_{Ni} , r_{Co} , r_{Zr} , r_W and r_{Ta} , are 0.1246, 0.1251, 0.1603, 0.1367, and 0.143 nm, respectively [30]. The average radius is determined to be 0.1283 nm. By using this value, the lattice constant of the Ni-phase is calculated as 0.3628 nm, which is very close to the measured value of 0.3623 nm. These results clearly show that mole fractions of the elements forming the Ni-phase were estimated correctly.

3.3. SEM Analyses

SEM images acquired from the composite samples are shown in Figure 4. The 50 min annealed sample contains the Ni-phase and the CoWB.

Figure 4. SEM images of the samples annealed at 1025 K for (a) 50 min, (b) 100 min.

It was found that the volume fraction of CoWB is 0.12. It was also determined that the average particle size of CoWB precipitates is 74 nm. The 100 min annealed sample contains the Ni-phase, CoWB, and Ni_3Ta . The compositions of the Ni-phase and Ni_3Ta are the same, so they have the same average atomic number per unit volume (Table 3). For this reason, it is not possible to distinguish these two phases in the SEM image obtained with the BSE mode. Only the CoWB phase, which has the highest average atomic number per unit volume, can be distinguished from the others. The volume fraction of CoWB was determined to be 0.35, which is consistent with the result obtained from the Rietveld refinement. In addition, it was determined that the average grain size of the CoWB was 86 nm.

Table 3. Average atomic number per unit volume of the phases precipitate in the composites.

Phase	Average Atomic Number ($Z/\text{\AA}^3$)
Ni	2.901
Ni ₃ Ta	2.893
CoWB	3.415

3.4. Microhardness

The as-cast sample has a microhardness of 1190 HV. The microhardness values of the composites are given in Figure 5. After 10 min. of annealing, the microhardness of the composite is measured as 1352 HV. As the annealing time increased, the microhardness value increased and the highest hardness value of 1410 HV is obtained as a result of 75 min. of heat treatment. A hardness value of 1403 HV is obtained after 100 min of annealing. Microhardness of the composite decreases as a result of a further increase in annealing time.

Figure 5. Microhardness of the samples annealed at 1025 K.

3.5. Indentation Fracture Toughness

The K_C of the composite sample with the highest microhardness, which is obtained by annealing the amorphous alloy at 1025 K for 100 min, was determined. An example of an indent used for the calculation is given in Figure 6. The calculations showed that K_C of the composite ranges between 2.9 and 3.7 MPa.m^{1/2} (Table 4). The K_C values given in Table 4 are the arithmetic mean of the calculations made using the measurements obtained from three different indents.

Table 4. Indentation fracture toughness of the composite with the highest microhardness.

Equation	K_C (MPa.m ^{1/2})	Ref.
$K_C = 0.079 \left(\frac{P}{a^{1.5}} \right) \log \left(\frac{4.5a}{c} \right)$	3.7	Evans & Wilshaw [31]
$K_C = 0.45 \left(\frac{H_v a^{0.5}}{\Phi} \right) \left(\frac{c}{a} \right)^{-1.5}$	2.9	Evans & Charles [32]

H_v = Vickers Hardness (GPa), P = Indentation load (MN), a = Half diagonal length (m), l = Crack length (m), $c = a + l$, Φ = Constraint factor (~ 3).

Figure 6. SEM image of an indent obtained from the composite with the highest microhardness by applying a load of 19.6 N.

4. Discussion

During the heat treatment, the first precipitating phase is the Ni-phase, a nickel solid solution containing nickel, cobalt, tungsten, and tantalum. Although the solubility limits of tungsten and tantalum in nickel are ~12.5 and ~11 at.%, respectively, the total tungsten and tantalum content of the Ni-phase is about 24 at.%. Such a high solubility of tungsten in nickel has also been observed in Ni-W alloys prepared by mechanical alloying [33] and electrodeposition [34,35].

The microhardness of Ni-25 at.% W solid solution with a grain size of 12 nm is about 1450 HV [34]. Because it is the majority phase in the composites obtained as a result of annealing for less than 50 min, the microhardness of the composites is about 1350 HV. When the annealing time is increased to 50 min, the precipitation of CoWB begins, so the microhardness of the composite increases slightly. The volume fraction of CoWB continues to increase with the increasing annealing time. Therefore, the microhardness of the composite also increases and reaches its maximum value, 1410 HV. The volume fraction of CoWB becomes ~0.4 after annealing the amorphous alloy for 100 min. However, the microhardness of the composite does not improve but remains constant because the Ni-phase has substantially transformed into the Ni_3Ta phase, which has much lower microhardness values of ~500 HV [36]. With further annealing, the volume fraction of CoWB remains constant, but the Ni-phase continues to transform into Ni_3Ta . Also, the particle size of CoWB and Ni_3Ta increases with annealing time. As a result, the microhardness of the composite becomes even lower.

The composite with the highest microhardness has a very low indentation fracture toughness value. Such a low fracture toughness results from the fact that the composite contains only a small amount of ductile phase, Ni-phase. To improve the indentation fracture toughness of the composite, the formation of Ni_3Ta must be prevented. For this reason, the refractory metal content of the alloy should be lower. It is also possible to prevent the formation of the Ni_3Ta by lowering the solubility of the refractory metals in the Ni-phase. When the Cu-Ni, Cu-W, and Cu-Ta binary phase diagrams are examined, it is seen that while copper is completely soluble with nickel, it is completely immiscible with tungsten and tantalum in a solid state [29]. Therefore, if copper is partially substituted for nickel, the tungsten and tantalum content of the Ni-phase forming during annealing is expected to be lower. As a result, there will be no transformation of the Ni-phase into the Ni_3Ta . In addition, increasing the boron content of the alloy might be another way of increasing the fracture toughness. Increasing the boron content will cause the precipitation of a high amount of CoWB, so more refractory metal will take part in the formation of CoWB. As a result, the formation of the Ni_3Ta will be prevented due to the decrease in the refractory metal content of the Ni-phase. However, while reducing the refractory metal

content of the alloy, making a copper substitution for nickel, and increasing the boron content of the alloy, care should be taken not to adversely affect the GFA of the alloy.

5. Conclusions

In conclusion, CoWB based composites are produced by annealing $\text{Ni}_{33.6}\text{Co}_{23.2}\text{Zr}_{0.5}\text{Ta}_4\text{W}_{23.7}\text{B}_{15}$ bulk metallic glass above the crystallization temperature. Composites having a microhardness of 1400 HV are obtained as a result of precipitation of CoWB. Increasing the annealing time results in a decrease in microhardness due to the increase in the average particle size of CoWB and transformation of the Ni-phase into Ni_3Ta , whose hardness is much lower than that of the Ni-phase. The K_C of the composite with the highest microhardness is quite low since it contains a small amount of ductile phase, Ni-phase. To improve both the hardness and toughness of the composite, the formation of Ni_3Ta must be prevented by either decreasing the total refractory metal content or increasing the boron content of the alloy.

6. Patents

The patent with the PCT application number PCT/TR2019/050997 has emerged as a result of the studies, some of which are presented in this article.

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