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# Effect of tungsten content on glass forming ability and microhardness of Ni-Cr-B-W metallic glasses

## A. Hitit\*, P. Öztürk, H. Şahin, A.M. Aşgın

Department of Materials Science & Engineering, Afyon Kocatepe University, ANS Kampusu 03200 Afyonkarahisar, Turkey \* Corresponding e-mail address: hitit@aku.edu.tr

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#### ABSTRACT

**Purpose:** The thermal and mechanical properties of Ni-Cr-B-W alloys as a function of tungsten content were studied.

**Design/methodology/approach:** : The studies were performed on  $(Ni_{49.7}Cr_{14.7}B_{35.6})_{100-x}W_x$  (x:15-40) metallic glass in the form of foils, which have thickness of 20 and 100 µm. Structures of samples were examined by X-ray diffraction (XRD). Thermal stabilities of the amorphous samples were measured using differential scanning calorimetry (DSC). Microhardness of the amorphous samples were determined by Vicker's hardness tester.

**Findings:** The XRD investigations revealed that samples of the alloys which have the thickness of 20  $\mu$ m were amorphous. However, 100  $\mu$ m samples of the alloys were not amorphous, but contained crystalline phases. Increasing the tungsten addition improved the glass transition and crystallization temperatures of the alloys. Also, microhardness of the alloys improved with tungsten addition.

**Practical implications:** Thermal and mechanical properties of the alloys investigated depend on their tungsten content.

**Originality/value:** This is the first study on Ni-Cr-B-W metallic glass system. Also, because of the production method used, all of the alloys were obtained as amorphous regardless of their composition, so their thermal and mechanical properties could be determined.

**Keywords:** : Amorphous materials; Ni-based alloy; Hardness

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#### MATERIALS

## **1. Introduction**

For the last two decades, multicomponent bulk metallic glasses (BMGs) have attracted great attention because of their unusual physical, chemical and mechanical properties.

As a result, a large number of metallic glass alloys have been succesfully developed in Zr [1-3], La [4,5], Pd [6-8], Mg [6-9], Ni [10,13,14], Cu [13,14], Fe [15-18] and Co [18-20] based systems. The major factor which limits the usage of the bulk metallic glasses at high temperatures is

their crystallization temperatures, above which they crystallize and lose their excellent properties. In general, if a metallic glass alloy contains elements having high melting point, it is expected to have high crystallization temperature. For this reason, number of metallic glass alloys containing high amount of refractory metals, such as tungsten, ruthenium, rhenium, iridium, tantalum and niobium, have been studied in order to develop metallic glasses having high crystallization temperatures [21-29]. As a result, metallic glasses which have crystallization temperatures higher than 1100-1200 K have been developed. In fact, for a Ta-based metallic glass, crystallization temperature of 1456 K has been achieved [21]. In addition, microhardnesses of the refractory based metallic glasses determined to be between 1200-2000 HV, which are much higher than most of the non-refractory metal based metallic glasses. In addition, examinations of the compositions of the refractory metal based metallic glasses show that most of these alloys contain high amount of boron in addition to refractory metals. This indicates that these alloys owe their attractive mechanical and thermal properties to strong bonds form between refractory metals and boron.

Although refractory metal based metallic glasses are superior to other metallic glasses in terms of mechanical properties and thermal stability, their critical casting thicknesses are quite low, which is less than 50 µm. Such a low critical casting thickness values prevent them from being used in industrial applications. The reason of these low critical casting values is that their liquidus temperatures are quite high because of high refractory metal contents. As known, increasing the liquidus temperature of an alloy for a constant glass transition temperature increases the cooling rate required for glass formation without crystallization. As a result, critical casting thickness decreases. In fact, most of the refractory metal based metallic glasses have such a high liquidus temperatures that they can not be measured with thermal analysis equipment.

For this reason, in order to develop refractory metal based metallic glasses which have high critical thickness, alloy compositions having sufficiently low liquidus temperatures must be found. Unfortunately, there is very limited information about RM-B-X (X: other elements) systems in the literature. Ni-Cr-B system is one of the alloy systems whose liquidus projections are known [30]. One of the eutectic compositions of this system is  $Ni_{49.7}Cr_{14.7}B_{35.6}$  whose eutectic temperature is 1369 K. This composition is modified with tungsten and  $(Ni_{49.7}Cr_{14.7}B_{35.6})_{100-x}W_x$  (x:15-40) alloys were synthesized. Effect of tungsten content on glass forming ability and microhardness of the alloys were investigated.

## 2. Material and research methodology

Ni-Cr-B-W alloy ingots with compositions of  $(Ni_{49.7}Cr_{14.7}B_{35.6})_{100-x}W_x$  (x:15-40) were prepared by arc melting the mixtures of Ni (99.9 mass%), Cr (99.8 mass%) and W (99.9 mass %) metals and crystalline B (98 mass%) in a high purity argon atmosphere. In order to ensure homogeneity, samples were melted three times. Compositions of the alloys represent nominal atomic percentages. Thin foils of the alloys were produced by piston and anvil method in an arc furnace. In order to produce the thin foils, a molten sample of each alloy was squeezed between two copper plates pushed by pneumatic pistons. Velocity of each piston was about 400 mm/sec. Thicknesses of the foils were determined by optical microscopy and are found to be about 20 µm. In addition, 100 µm thick samples of the alloys were produced by piston and anvil method with the piston velocity of 50 mm/sec. Also, samples having thickness of 0.4 mm were produced by suction casting method. The as-cast structures of the samples were examined by X-ray diffraction (XRD) (Bruker D8 Advance) with Cu-K<sub>a</sub> radiation The glass transition temperatures  $(T_g)$ , crystallization temperatures  $(T_x)$ , melting temperatures  $(T_m)$ and liquidus temperatures (T<sub>1</sub>) of the alloys were measured by differential scanning calorimetry (DSC) (Netzsch STA 449 F3) at a heating rate of 0.33 K/s. Vickers hardness of the samples were measured with a Vickers hardness tester (Shimadzu HMV 2L) under a load of 1.96 N.

## **3. Results and discussion**

XRD patterns of the samples which have the thickness of 20  $\mu$ m are shown in Fig. 1. It is seen that all of the sample have amorphous structure.

However, 100  $\mu$ m thick samples of the alloys contain crystalline phases, which are W<sub>2</sub>B, Cr<sub>2</sub>B, Ni<sub>2</sub>B, W<sub>2</sub>B<sub>5</sub>, Ni, Cr<sub>5</sub>B<sub>3</sub> and Cr<sub>2</sub>B<sub>3</sub> (Fig. 2).

It is also determined that glass transition temperatures of  $Ni_{42.2}Cr_{12.5}B_{30.3}W_{15}$  and  $Ni_{30}Cr_9B_{21}W_{40}$  alloys are 1007 and 1060 K, respectively (Fig. 3). In addition, crystallization temperatures of  $Ni_{42.2}Cr_{12.5}B_{30.3}W_{15}$  and  $Ni_{30}Cr_9B_{21}W_{40}$  alloys are determined to be 1065 and 1112 K, respectively. Liquidus temperatures of the alloys could not be measured because they are higher than the measurement limit of the instrument used.



Fig. 1. XRD patterns of the 20  $\mu$ m thick samples of (Ni<sub>49.7</sub>Cr<sub>14.7</sub>B<sub>35.6</sub>)<sub>100-x</sub>W<sub>x</sub> alloys



Fig. 2. XRD patterns of the 100  $\mu$ m thick samples of (Ni<sub>49.7</sub>Cr<sub>14.7</sub>B<sub>35.6</sub>)<sub>100-x</sub>W<sub>x</sub> alloys

Thermal properties of the alloys are given in Table 1. Besides, microhardnesses of  $Ni_{42.2}Cr_{12.5}B_{30.3}W_{15}$  and  $Ni_{30}Cr_9B_{21}W_{40}$  alloys are measured as 1235 and 1400 HV, respectively.

 $20 \ \mu m$  sample of the alloys obtained as amorphous because of the production technique which provides extremely high cooling rate. However,  $100 \ \mu m$  samples of none of the alloys contain crystalline phases, which indicate that glass forming ability (GFA) of the alloys are

less than 100  $\mu$ m. The reason of this low GFA is that they have very high liquidus temperature. Therefore, in order to improve GFA of the alloys, liquidus temperatures must be reduced by suitable alloying additions.



Fig. 3. DSC curves of the 20  $\mu m$  thick samples of  $(Ni_{49.7}Cr_{14.7}B_{35.6})_{100\text{-}x}W_x$  alloys

Table 1.

Thermal properties and microhardnesses of alloys  $Ni_{42.2}Cr_{12.5}B_{30.3}W_{15}$  and  $Ni_{30}Cr_9B_{21}W_{40}$ 

Alloys	T <sub>g</sub> , K	T <sub>x</sub> , K	T <sub>m</sub> , K	T <sub>l</sub> , K	$\mathrm{H}_{v(0.1)}$
Ni <sub>42.2</sub> Cr <sub>12.5</sub> B <sub>30.3</sub> W <sub>15</sub>	1007	1065	1325	-	1235
$Ni_{30}Cr_9B_{21}W_{40}$	1060	1112	1582	-	1400

Tungsten addition improves glass transition and crystallization temperatures significantly. This improvement results from increased number of W-B and W-W bonds. As the number of W-B and W-W bonds increase, total cohesive energy of the glass structure increases, which causes improvement in thermal stability. Because of this increase in thermal stability, this alloys can be used at higher temperatures.

Tungsten addition also improved the microhardness values of the alloys. Increasing the tungsten content from 15 at.% to 40 at.% increases the microhardness from 1235 HV to 1400 HV. It is most likely that this improvement also caused by increased number of W-W and W-B bonds.

Although alloys have very low GFA, there are still potential applications where high thermal stability and hardness are required. For example, they can be coated on various substrates by thermal spraying techniques. Also, powders of the alloys can be sintered by spark plasma sintering in order to produce pieces having larger dimensions for desired applications.

## 4. Conclusions

Tungsten addition improved thermal stability and microhardness of Ni-Cr-B-W metallic glasses. Especially,  $Ni_{30}Cr_9B_{21}W_{40}$  have quite high crystallization temperature and hardness. The alloys have very low GFA because of their extremely high liquidus temperatures. In order to improve GFA of the alloys, liquidus temperatures of the alloys must be lowered by suitable alloying additions.

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