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Article

A New Ni-Based Metallic Glass with High Thermal Stability and Hardness

Aytekin Hitit *, Hakan Şahin, Pelin Öztürk and Ahmet Malik Aşgın

Department of Materials Science and Engineering, Afyon Kocatepe University, Afyonkarahisar 03200, Turkey; E-Mails: hakansahin@aku.edu.tr (H.S.); pelinsuozturk@gmail.com (P.O.); amalikasgin@gmail.com (A.M.A.)

* Author to whom correspondence should be addressed; E-Mail: hitit@aku.edu.tr; Tel./Fax: +90-272-228-1441.

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Abstract: Glass forming ability (GFA), thermal stability and microhardness of $Ni_{51-x}Cu_xW_{31.6}B_{17.4}$ (x = 0, 5) metallic glasses have been investigated. For each alloy, thin sheets of samples having thickness of 20 µm and 100 µm were synthesized by piston and anvil method in a vacuum arc furnace. Also, 400 µm thick samples of the alloys were synthesized by suction casting method. The samples were investigated by X-ray diffractometry (XRD) and differential scanning calorimetry (DSC). Crystallization temperature of the base alloy, $Ni_{51}W_{31.6}B_{17.4}$, is found to be 996 K and 5 at.% copper substitution for nickel increases the crystallization temperature to 1063 K, which is the highest value reported for Ni-based metallic glasses up to the present. In addition, critical casting thickness of alloy $Ni_{51}W_{31.6}B_{17.4}$ is 100 µm and copper substitution does not have any effect on critical casting thickness of the alloys. Also, microhardness of the alloys are found to be around 1200 Hv, which is one of the highest microhardness values reported for a Ni-based metallic glass until now.

Keywords: metallic glass; refractory metal; glass forming ability; crystallization temperature; microhardness

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 [1]. The major factor which restricts the utilization 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, osmium, tantalum and niobium, have been studied in order to develop metallic glasses having high crystallization temperatures [2–10]. In these studies, metallic glasses which have crystallization temperatures higher than 1100–1200 K have been developed. In addition, microhardnesses of the refractory based metallic glasses determined to be between 1200–2000 Hv, which are much higher than almost all of the non-refractory metal based metallic glasses. 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 [2–10]. 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 are less than 30 µm [2–10]. Such 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 high liquidus temperatures that they can not be measured with thermal analysis equipment.

Therefore, in order to develop refractory metal based metallic glasses which have high critical casting 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. In a theoretical study on Ni-W-B system, it has been reported that one of the eutectic compositions is $Ni_{51}W_{31.6}B_{17.4}$ and its euctectic temperature is 1622 K [11]. This composition contains significantly high amount of tungsten and boron and has a quite low liquidus temperature with respect to other refractory metal based metallic glasses. Therefore, we believe that it deserves an investigation to determine its glass forming ability (GFA), thermal stability and microhardness.

In this study, GFA, thermal stability and microhardness of $Ni_{51-x}Cu_xW_{31.6}B_{17.4}$ (x = 0, 5) alloys are investigated. The base alloy, $Ni_{51}W_{31.6}B_{17.4}$, is modified with copper due to the fact that copper has such a low solubility with boron and tungsten that it is supposed not to form any phase with them. Therefore, copper substitution for nickel is expected to improve GFA of the alloy by hindering formation of precipitating phases during solidification.

2. Results

2.1. XRD Results

XRD patterns of 100 µm thick samples of the alloys are given in Figure 1a. In both of the XRD patterns, a broad diffraction peak, which is typical of amorphous structure, is observed. Also, no crystalline peak is visible in the patterns, which indicates that 100 µm thick samples of the alloys are fully amorphous. However, for the casting thickness of 400 µm, alloys almost completely crystallize during solidification (Figure 1b). Also, it should be noted that 400 µm thick sample of $Ni_{51}W_{31.6}B_{17.4}$ alloy contains some amount of amorphous phase. Examination of the XRD patterns revealed that for both of the alloys, Ni (space group Fm3m) and W_2B (space group I4/mcm) phases form in the samples having casting thickness of 400 µm. Lattice parameter of nickel is found to be 3.59 Å, which is higher than the lattice parameter of pure nickel, 3.5238 Å (JCPDS-PDF-4-850). This result clearly shows that this phase contains some amount of tungsten, so it is actually a Ni-W solid solution rather than pure nickel. In addition, lattice parameters of W_2B phase are also determined. They are found to be a = 5.58 Å and c = 4.73 Å. These values are very close to the tabulated cell parameters, which are a = 5.568 Å and c = 4.744 Å (JCPDS-PDF-25-990).

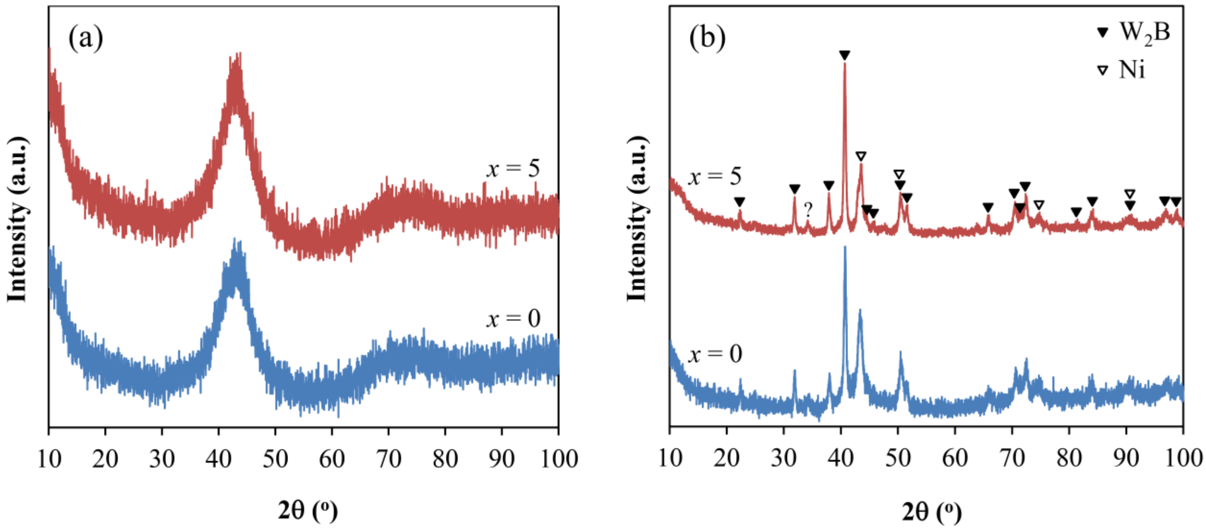

Figure 1. X-ray diffractometry (XRD) patterns of $Ni_{51-x}Cu_xW_{31.6}B_{17.4}$ alloys (**a**) 100 µm thick samples; (**b**) 400 µm thick samples.

2.2. Thermal Stability

DSC scans of the alloys are shown in Figure 2. Each DSC scan exhibits exothermic reactions corresponding to crystallization of the undercooled liquid. However, glass transition temperatures of the alloys cannot be well defined. Only tentatively determined T_g values of the alloys are shown in Figure 2a. Glass transition temperatures of $Ni_{51}W_{31.6}B_{17.4}$ and $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloys are determined as 929 and 971 K, respectively. Also, crystallization temperatures of $Ni_{51}W_{31.6}B_{17.4}$ and $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloys are found to be 996 and 1063 K, respectively. In addition, solidus temperatures of $Ni_{51}W_{31.6}B_{17.4}$, and $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloys are measured as 1610 and 1620 K, respectively. Moreover, liquidus temperatures of $Ni_{51}W_{31.6}B_{17.4}$ and $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloys are found to be 1784 and 1780 K, respectively. Thermal properties of the alloys are summarized in Table 1. In addition, XRD patterns of the samples of $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloy which were annealed at 950 and 1025 K are given in Figure 3. XRD patterns show that after annealing at 950 K small amount of nickel precipitates. Annealing at 1025 K results in significant increase in the amount of nickel which forms in the structure. These results show that T_g values of the alloys are lower than those determined tentatively.

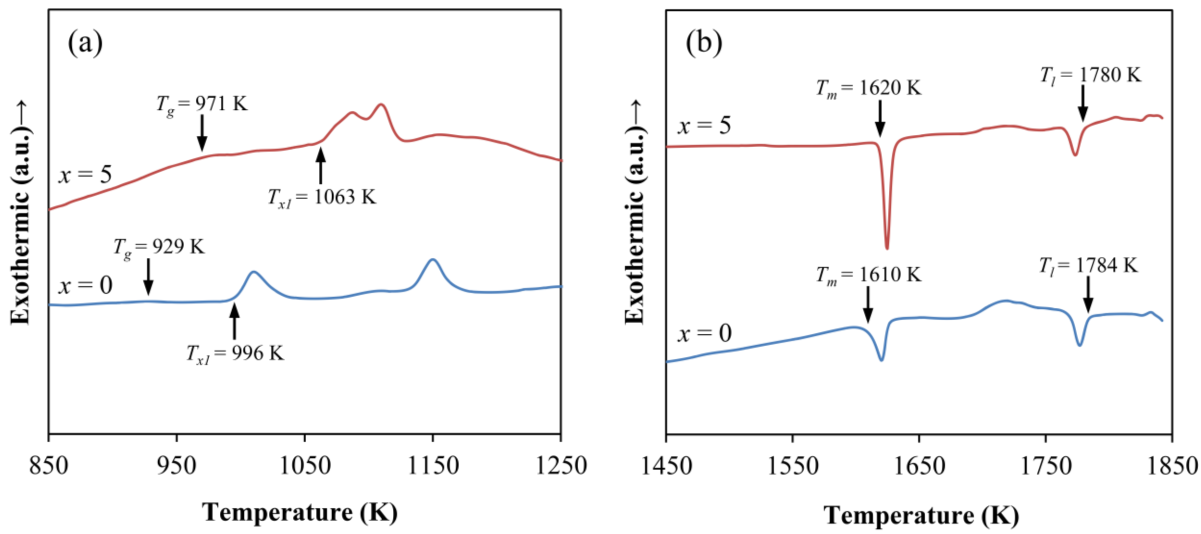

Figure 2. Differential scanning calorimetry (DSC) curves of $Ni_{51-x}Cu_xW_{31.6}B_{17.4}$ alloys (**a**) low temperature measurements; (**b**) high temperature measurements.

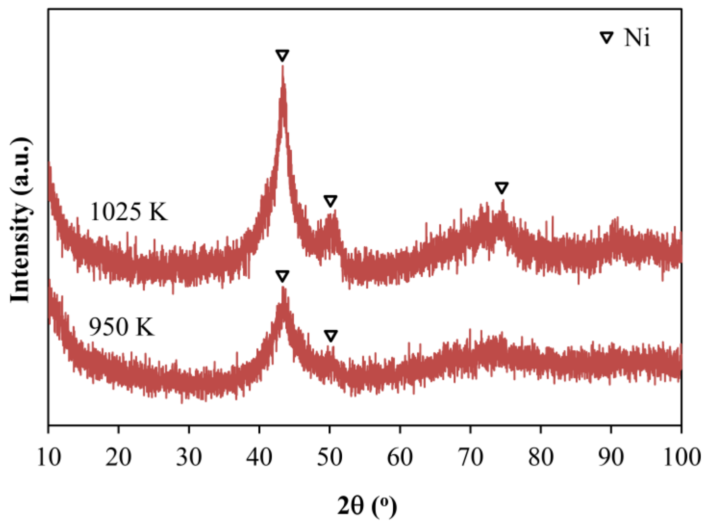

Figure 3. XRD patterns of annealed samples of $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloy.

2.3. Microhardness

Vickers hardness values of $Ni_{51}W_{31.6}B_{17.4}$ and $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloys are found to be 1265 and 1213 Hv, respectively. Also, standart deviations of hardness measurements for $Ni_{51}W_{31.6}B_{17.4}$ and $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloys are 49 and 31 Hv, respectively. SEM image of an indent obtained from 100 µm thick sample of $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloy is shown in Figure 4.

Table 1. Thermal properties (T_g,T_x,T_m,T_l) and microhardnesses of $Ni_{51-x}Cu_xW_{31.6}B_{17.4}$ alloys.

Alloy	T_g (K)	T_x (K)	T_m (K)	T_l (K)	H_v
$Ni_{51}W_{31.6}B_{17.4}$	929	996	1610	1784	1265
$Ni_{46}Cu_5W_{31.6}B_{17.4}$	971	1063	1620	1780	1213

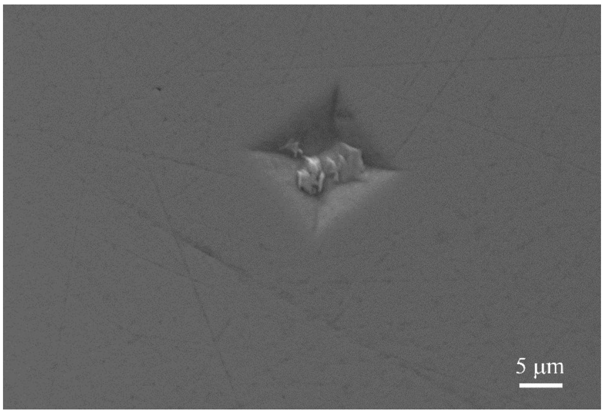

Figure 4. Scanning electron microscopy (SEM) image of an indent obtained from 100 μm thick sample of $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloy.

3. Discussion

XRD results clearly show that critical casting thicknesses of the alloys are at least 100 μm but less than 400 μm. This critical casting thickness value is higher than critical casting thicknesses of most of the refractory metal based metallic glasses [2–10]. This is due to the fact that liquidus temperatures of the alloys investigated in this study are much lower than those of other refractory metal based metallic glasses. Because of lower liquidus temperatures, $Ni_{51}W_{31.6}B_{17.4}$ and $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloys have lower reduced glass transition temperatures, T_g/T_l; as a result, they have higher GFA values.

Glass transition and crystallization temperatures of the alloys are increasing with copper addition. Copper is not soluble with tungsten in even liquid state [12], but completely soluble with nickel. Also, nickel and tungsten are completely soluble in liquid state and tungsten is partially soluble in nickel in solid state. Therefore, copper substitution for nickel must be lowering solubility of tungsten in nickel in liquid state. For this reason, in $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloy, the number of Ni-W neighbors is decreasing and the number of W-W and W-B neighbors is increasing. Because of the reduction in the number of Ni-W pairs, formation of the first phase, nickel-tungsten solid solution, becomes more difficult during heating. In other words, crystallization of nickel takes places at a higher temperature (Figure 5). On the other hand, due to the increase in number of W-B neighbors, formation of the second phase, W_2B, becomes easier. In fact, the second crystallization temperature of $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloy is lower than that of $Ni_{51}W_{31.6}B_{17.4}$ alloy. Crystallization temperature of $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloy, 1063 K, is higher than those of many of the refractory metal based metallic glasses [2–10] and the highest value reported for a Ni-based metallic glass until now (Table 2).

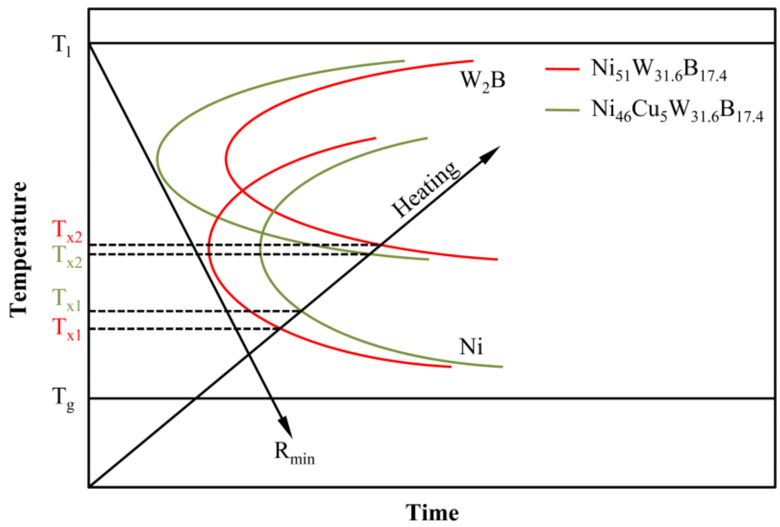

Figure 5. Schematic time-temperature-transformations (TTT) diagram of $Ni_{51}W_{31.6}B_{17.4}$ and $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloys.

Table 2. Thermal properties (T_g,T_x) and microhardnesses of various Ni-based metallic glasses.

Alloy	D (mm)	T_g (K)	T_x (K)	Ref.
$Ni_{40}Ta_{42}Co_{18}$	2	993	1032	[13]
$Ni_{62}Ta_{36}Sn_2$	1	977	1035	[14]
$Ni_{64}(Nb_{0.85}Zr_{0.15})_{36}$	2	899	935	[15]
$Ni_{60}Nb_{40}$	1	891	924	[16]
$Ni_{60}Zr_{20}Ta_{10}Nb_5Al_5$	3	870	938	[17]
$Ni_{45}Ti_{20}Zr_{23}Al_{12}$	<0.5	783	832	[18]

For a constant T_l, increasing T_g and T_x is expected to result in improved critical casting thickness. However, as mentioned, since formation of W_2B phase becomes easier because of copper addition, minimum cooling rate, R_{min}, required for the formation of glass phase is still high (Figure 5). As a result no change in critical casting thickness is observed. In order to improve GFA of Ni-W-B metallic glasses, R_{min} must be reduced, which can be accomplished by decreasing the liquidus temperature of the alloy and hindering the formation of precipitating phases, W_2B and nickel. These can be achieved by decreasing the tungsten and boron contents of the alloy. However, it should be considered that decreasing tungsten and boron contents of the alloy also decreases T_g and T_x, which causes deterioration of thermal stability. Therefore, reduction of tungsten and boron contents of the alloy should be carried out systematically to obtain optimum critical casting thickness-thermal stability combination. In addition, if element(s) which will be substituted for tungsten and boron have low solubility with nickel in solid state, formation of nickel solid solution is hindered. As a result, R_{min} decreases further, which causes more improvement in GFA.

Microhardness values of the alloys are found to be around 1200 Hv (11.7 GPa), which is one of the highest values reported for a Ni-based metallic glass (Table 3). Also, tensile yield strengths of the alloys can be estimated by using the equation $\sigma_y = Hv/3$ [19]. Based on the microhardness values, the tensile yield strengths of the alloys are determined to be about 3.9 GPa, which is higher than yield strengths of other Ni-based metallic glasses [1]. In addition to mechanical properties, one of the advantages of

Ni-W-B metallic glasses over those reported in Table 3 is that Ni-W-B metallic glasses have higher thermal stability. In fact, crystallization temperature of $Ni_{59.35}Nb_{34.45}Sn_{6.2}$ alloy is 930 K, which is about 130 K less than that of $Ni_{46}Cu_5W_{31.6}B_{17.4}$ alloy. The other advantage of Ni-W-B metallic glasses is their lower cost with respect to costs of those containing high amount of Nb, Ta and Hf.

Table 3. Microhardnesses of various Ni-based metallic glasses.

Alloy	H_v	Ref.
$Ni_{59.35}Nb_{34.45}Sn_{6.2}$	1280	[20]
$Ni_{60}(Nb_{60}Ta_{40})_{34}Sn_6$	1192	[21]
$Ni_{59.5}Nb_{40.5}$	1173	[22]
$Ni_{58}Ta_{36}Sn_6$	1066	[15]
$Ni_{50}Nb_{28}Zr_{22}$	1020	[23]
$Ni_{62}Ta_{36}Sn_2$	1002	[14]
$Ni_{40}Ta_{42}Co_{18}$	993	[13]
$Ni_{59}Ta_{41}$	969	[24]
$Ni_{62}Nb_{33}Zr_5$	965	[25]
$Ni_{40}Cu_5Ti_{17}Zr_{28}Al_{10}$	862	[18]
$Ni_{60}Nb_{20}Hf_{15}Ti_5$	847	[26]
$Ni_{53}Nb_{20}Ti_{10}Zr_8Co_6Cu_3$	759	[27]
$Ni_{60}Zr_{17}Al_6Hf_7Nb_{10}$	713	[28]
$Ni_{58.5}Nb_{20.25}Y_{21.25}$	663	[22]

Although the alloys synthesized in this study have low critical casting thicknesses, 100 μm, there are still some potential applications where they can be utilized because of their high thermal stabilities and microhardnesses. Also, since the alloys contain significantly high amount of nickel, they are expected to have high corrosion resistance. For example, alloys can be coated on substrates by thermal spraying techniques to obtain hard, wear resistant and corrosion resistant coatings [29,30]. Besides, powders of the alloys having diameter less than 100 μm can be produced by gas atomization, and then they can be sintered by spark plasma sintering to manufacture components with desired shape and dimensions [31]. In addition, considering the fact that nickel and W_2B phases precipitates, the alloys can be used as precursors to develop Ni-W_2B metal matrix composite coatings having high hardness and high toughness.

4. Experimental Section

Ni-Cu-W-B alloy ingots with compositions of $Ni_{51-x}Cu_xW_{31.6}B_{17.4}$ (x = 0, 5) were prepared by arc melting the mixtures of Ni (99.9 mass%), W (99.9 mass%) and Cu (99.9 mass%) metals and crystalline B (98 mass%) in a Ti-gettered high purity argon atmosphere. In order to obtain homogeneous master alloys, samples were melted three times. Compositions of the alloys represent nominal atomic percentages. 20 μm and 100 μm thick thin foils of the alloys were produced by piston and anvil method in an arc furnace. For the production of 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/s and 50 mm/s for 20 μm and 100 μm thick samples, respectively. Thicknesses of the foils were determined by optical microscopy. Also, samples having thickness of 400 μm were produced by suction casting method. In addition, samples of copper containing alloy, $Ni_{46}Cu_5W_{31.6}B_{17.4}$, were annealed at 950 and 1025 K for

5 min. under high purity argon atmosphere to determine the thermal stability of the alloy. The structures of the samples were examined by X-ray diffraction (XRD) (Bruker Karlsruhe, Germany, D8 Advance equipped with Vantec-1 detector) with Cu-K_{α} radiation. The glass transition temperature (T_g), crystallization temperature (T_x), solidus temperature (T_m) and liquidus temperatures (T_l) of the alloys were measured by differential scanning calorimetry (DSC) (Netzsch Selb, Germany, STA 449 F3) at a heating rate of 0.33 K/s. Vickers hardnesses of the samples were measured with a Vickers hardness tester (Shimadzu Kyoto, Japan, HMV 2L) under a load of 1.96 N. Images of the indents obtained after microhardness measurements were acquired with scanning electron microscopy (SEM) (Leo Cambridge, UK, 1430 VP) under secondary electron (SE) imaging mode.

5. Conclusions

GFA, thermal stabilities and microhardnesses of $Ni_{51-x}Cu_xW_{31.6}B_{17.4}$ (x = 0, 5) metallic glass alloys are investigated. It is found that copper substitutions for nickel improves the glass transition and crystallization temperatures, which are comparable to those of other refractory metal based metallic glasses and higher than those of other Ni-based metallic glasses. However, copper substitutions for nickel do not have any effect on critical casting thicknesses of the alloys studied. Critical casting thicknesses of the alloys are found to be 100 µm. Although this value is quite low, it is still higher than critical casting thicknesses of most of the refractory metal based metallic glasses. Also, microhardness of the alloys are found to be around 1200 Hv and this value is higher than microhardness of other Ni-based metallic glasses. Furthermore, alloys can be used as a precursor to manufacture Ni-W_2B metal matrix composites.

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Author Contributions

Aytekin Hitit wrote and edited the paper, and contributed in all activities. Pelin Öztürk and Ahmet Malik Aşgın synthesized the alloys and cast the samples. Hakan Şahin performed XRD and DSC experiments and analyzed the results.

Conflicts of Interest

The authors declare no conflict of interest.

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