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Glass forming ability of binary Ni_{60+x}Nb_{40-x} (x=0;1;2) alloys

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<u>ABSTRACT</u>

Purpose: This paper presents the investigations results of fabrication and structure tests binary Ni-Nb metallic glasses.

Design/methodology/approach: The studies were performed on $Ni_{60+x}Nb_{40-x}$ (x=0, 1, 2) alloys in form of ribbon and rods up to 2 mm. For the purpose of fabrication test pieces, melt spinning and pressure die casting methods were used. The main index for determine glass forming ability was thickness of specimens. To the tests of samples structure X-ray diffraction phase analysis (XRD) and scanning electron microscopy (SEM) were used. Owing to good mechanical properties of Ni-based metallic glasses, microhardness of cast rods were examined.

Findings: X-ray diffraction and SEM analysis have revealed that samples in form of ribbons were amorphous, while cast rods were crystalline.

Practical implications: The relationship between amorphous structure and good mechanical properties could be promising for many engineering application. The Ni-based bulk metallic glasses are newcomers engineering materials which may be applied to a new type pressure sensor exhibiting higher capability and higher sensitivity

Originality/value: Paper present quite new type of binary metallic glasses based on Ni. For the sake of alloy simplicity it is possible that this alloys will be used in many applications.

Keywords: Metallic glasses; Bulk metallic glasses; Mechanical properties; Glass forming ability; Die casting

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1. Introduction

First metallic glasses was found over forty years ago and they were used as magnetic cores or replacement other crystalline materials. However the field of application was limited because of small dimensions of this new materials. They were produce in few micrometer of its thickness. For the last decade scientists, mainly from Japanese and USA, work hard to improve the possibility of production metallic glasses in form of bulk. To make the best use of BMGs, several features of these materials, such as good glass forming ability (GFA), high thermal stability, wear resistance and corrosion resistance, excellent physical and mechanical properties, are required [1-6].

In many publications the three basic rules, which determine possibility of BMG formations was defined as the following: alloy should be multicomponent, from three or more alloying components; there is 12% or more difference between atomic radius of elements; between alloying component exist negative heat of mixing. However the binary alloys can be formed as a bulk metallic glasses. The very interesting example are binary alloys based on nickel, which are promising because of its unique mechanical properties and relatively simplicity of its preparation [7-10].

Bulk metallic glasses based on Ni exhibit high thermal stability, very good compressive strength, excellent corrosion resistance and good ductility. Combinations that excellent properties with relatively low material costs cause that this is promising engineering materials for many applications [11-15].

Amorphous alloys based on Ni can be divided into two classes: based on eutectic compositions, and with off-eutectic compositions. Ni forms the eutectics states with ETM elements (Ti, Zr, Nb, Hf and Ta). Approximate composition of this systems is $Ni_{60-70}ETM_{40-30}$. Table 1 show the physical and chemical properties of each components which create the binary eutectics with Ni [1, 11, 13]

Table 1.

Physical	and	chemical	properties	of	Ni	and	each	components
which cro	eate t	he binary	eutectics wi	th l	√i [1	1]		

Element	Atomic radius [nm]	Melting point [°C]	Ni-ETM eutectic	Eutectic melting point [°C]
Ni	0.1375	1455		
Та	0.1430	3017	Ni ₆₄ Ta ₃₆	1350
Nb	0.1429	2477	Ni ₆₀ Nb ₄₀	1175
Hf	0.1578	2233	Ni ₆₄ Hf ₃₆	1190
Zr	0.1603	1855	Ni ₆₄ Zr ₃₆	1070
Ti	0.1462	1668	Ni ₆₉ Ti ₃₁	1118

Possibility of fabrication binary bulk metallic glass based on Ni was presented in this paper. Theoretically binary alloys should be ideal models for examination of glass forming ability, thermal stability and properties of metallic glasses. However selection and preparation of chemical composition with good glass forming ability is difficult and demand a lot of trials.

Ni based metallic glasses can find application on new type pressure sensors exhibiting higher pressure capability and higher sensitivity. Thanks to much higher tensile strength, much lower Young's modulus and much better corrosion resistance this glassy alloys are able to successfully replace traditionally alloys which has been used in conventional pressure sensors [2, 7].

2. Material ve method

The aim of presented work is production testing Ni-based metallic glasses (also in bulk form) and microstructure characterization using basic fabrication methods of metallic glasses, moreover XRD and SEM methods to microstructure description was used. In order to verify the hardness of fabrication samples the microhardness test was realized.

For examination samples in form of thin ribbons (with thickness 0.05 and 0.07 mm) and in form of rods (with dimension 1.5 and 2 mm) was used.

Amorphous and crystalline structures were examined by X-ray diffraction (XRD) using a Seifert – FPM XRD 7 diffractometer with Co K α radiation at 35 kV. The data of diffraction lines were recorded by means of the stepwise method within the angular range of 20° to 90°. The counting time in the measuring point was 2s. The morphology of fracture surfaces glassy ribbons and crystalline rods was observed in scanning microscope ZEISS SUPRA 25. In order to define hardness the Vickers microharness tester FM-700 Future-Tech was used. The load was 50 G and load time was 15s. The test was measured on the rods, which were prepared in form of metallographic specimens. The measure pattern was proceed from edge to edge (along dimension). Distance between stamps was equal 100 μ m.

2.1. Master alloy preparation

Three Ni-based binary master alloy ingots witch chemical composition $Ni_{60}Nb_{40}$, $Ni_{61}Nb_{39}$, $Ni_{62}Nb_{38}$ (Table 2) were prepared by induction melting of pure Ni elements and Nb powders (Fig. 1) in argon atmosphere (Fig. 2). In order to obtain homogeneity each of ingots was melted several times. The alloy compositions represent nominal atomic percentages.



Fig. 1. Pure Nb powder and Ni elements

Table 2.

Chemical	composition	of Ni-based	binary alloys	
				,

Number of	Ni		Nb		
alloy	at. [%]	mass [g]	at. [%]	mass [g]	
Ι	60	48.655	40	51.344	
II	61	49.701	39	50.298	
III	62	50.757	38	49.242	

2.2. Samples casting

The investigation materials were cast in form of ribbons with thickness 0.05, 0.07 and 0.1 mm and width 2.2 mm and rods with dimension 1.5 and 2 mm.

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Fig. 2. Schematic and real process of master alloy preparation



Fig. 3. Schematic and real devices of fabrication glassy ribbons by melt-spinning method



Fig. 4. Schematic and real process of fabrication glassy rods by die-casting method

The ribbons were prepared by the single copper roller melt spinning method (Fig. 3). The master alloy was induction melted in a quartz crucible and next pushed on a copper wheel by argon pressure. The speed of copper wheel amount to 20 m/s and ejection over-pressure of molten alloy equal 200 mBar.

Samples in form of rods were prepared by die-casting method. The ingots (master alloy) was melted in quartz crucible using an induction coil and pushed into a water-cooled copper mould under a pressure (Fig. 4).

3. Results and discussion

3.1. X-ray phase analysis

Results of XRD-diffraction reveal that all rods are crystalline, while thin ribbons exhibit amorphous structure. Thin ribbons were tested on the surface which had not direct contact with copper

In crystalline rods the intermetallic compounds NbNi

and NbNi3 were detected. A little Nb and Ni oxides in samples

barrel (and cooling rate was lower) and that is cause to suppose that amorphous structure enclose all samples.

Figures 5-7 shows result of XRD phase analysis.

1800 g = 70 μm ribbon 1600 Relative intensity (a.u) 1400 1200 1000 800 600 400 200 30 40 50 60 70 80 90 2 θ (°) 300 NbO₂
 NbNi φ = 1,5 mm rod ^ Nbl * NiO NbNi 250 Relative intensity (a.u) 200 150 100 50 30 40 50 60 70 2 θ (°) NbO₂
NbNi
NbNi 800 φ = 2mm rod ^ * 700 NiO Relative intensity (a.u) 600 500 400 300 200 100 30 40 50 60 70 80



Fig. 5. X-ray diffraction patterns of $Ni_{60}Nb_{40}$ glassy ribbon with thickness 70 μm and crystalline rods with dimension 1.5 mm and 2 mm

2 0 (°)

Fig. 6. X-ray diffraction patterns of $Ni_{61}Nb_{39}$ glassy ribbon with thickness 50 μm and crystalline rods with dimension 1.5 mm and 2 mm



Fig. 7. X-ray diffraction patterns of $Ni_{62}Nb_{38}$ glassy ribbon with thickness 70 μm and crystalline rods with dimension 1.5 mm and 2 mm

3.2. Microhardness analyses

Microhardness testing (H_V) was realized for samples in rod forms with dimension 1.5 and 2 mm of every alloy. It was observed that results of microhardness for every testing samples was diversified. However, for Ni₆₀Nb₄₀ samples the microhardness is the highest on the margin. Additionally, on hole surface of samples difference of results were make note too.

On the basis of this results we suppose that structure may be partially amorphous and microhardness is different for different phases (crystalline or amorphous). The highest microhardness exhibit sample with dimension 1.5 mm for $Ni_{60}Nb_{40}$ alloy and it oscillates between 1180 and 1463 HV. The lowest microhardness reveal sample of $Ni_{62}Nb_{38}$ alloy with the dimension 2 mm and it's value range from 988 to 1284 HV.

Figures 8-9 show distribution of microhardness results for $Ni_{60}Nb_{40}$ rod with dimension 1.5 mm and for $Ni_{62}Nb_{38}$ rod with dimension 2 mm



Fig. 8. Microhardness results distribution for rods of $\rm Ni_{60}Nb_{40}$ with dimension 1.5 mm



Fig. 9. Microhardness results distribution for rods of $\rm Ni_{62}Nb_{38}$ with dimension 2 mm

3.3. Fracture analyses

Figures 10-15 presents SEM micrographs of as-cast glassy ribbon and crystalline rods from every alloy with different maginification. The fracture testing was realized on all surface of ribbons and only on the edge of crystalline rods. It was found that morphology of glassy ribbon (Figs. 10-11) is mixed with smooth, fluvial and vein areas. The fluvial fracture is characteristic for glassy alloy.

For crystalline rods on the edge of samples (where surface had contact with cooper mould) singly veins were observed, but in farther areas the micrographs of the fracture surface changes on shell and intercrystalline (Figs. 12-15).





Fig. 10. SEM micrograph of the fracture morphology of as-cast thin ribbon with thickness70 μ m of Ni₆₀Nb₄₀ alloy (with magnification 7000x - a), 20000x - b)





Fig. 11. SEM micrograph of the fracture morphology of as-cast thin ribbon with thickness70 μ m of Ni₆₂Nb₃₈ alloy (with magnification 10000x - a), 30000x - b)



Fig. 12. SEM micrograph of the fracture morphology of crystalline rod with dimension 1.5 mm of $Ni_{60}Nb_{40}$ alloy (with magnification 115x and 1500x)



Fig. 13. SEM micrograph of the fracture morphology of crystalline rod with dimension 2 mm of $Ni_{60}Nb_{40}$ alloy (with magnification 86x and 1500x)



Fig. 14. SEM micrograph of the fracture morphology of crystalline rod with dimension 2 mm of $Ni_{61}Nb_{39}$ alloy (with magnification 83x and 1500x)



Fig. 15. SEM micrograph of the fracture morphology of crystalline rod with dimension 1.5 mm of $Ni_{62}Nb_{38}$ alloy (with magnification 100x and 5000x)

On the basis this analysis can suppose that as-cast rods have partially (mainly on the edge) amorphous structure.

4. Conclusions

The investigations allows to formulate conclusions as the following:

- thin ribbons with thickness 0.05; 0.07; 0.1 mm and rods with dimension 1.5 and 2 mm were formed at Ni₆₀Nb₄₀, Ni₆₁Nb₃₉ and Ni₆₂Nb₃₈ alloys by single copper roller melt spinning and die-casting methods;
- X-ray diffraction confirm that respectively thin ribbons exhibit amorphous structure and rods are crystalline. Probably, the Ni-based alloy composition is not exactly in eutectic point and that is why they does not exhibit good glass forming ability. However the fracture morphology show that on the edge of rods characteristic for amorphous structure areas are existed. Sum up chemical composition of investigated alloys allow to obtain metallic glasses in form of ribbons;
- results of microhardnes tests are diversified, but in some case there is clearly increase of microhardness in the edge of rod samples. In hole of samples, depending on phase, microhardness was change;
- the microscopic observation reveal mixed fracture for glassy thin ribbons with smooth, fluvial and veins morphology;

• samples in form of rods exhibit singly veins morphology on the edge (where surface had contact with cooper mould), but in farther areas the micrographs of the fracture surface changes on shell and intercrystalline.

Additional information

Selected issues related to this paper are planned to be presented at the 16th International Scientific Conference on Contemporary Achievements in Mechanics, Manufacturing and Materials Science CAM3S'2010 celebrating 65 years of the tradition of Materials Engineering in Silesia, Poland and the 13th International Symposium Materials IMSP'2010, Denizli, Turkey.

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