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The study of structure and glass forming ability of Zr-based amorphous alloy

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ABSTRACT

Purpose: This paper tends to present the structure and thermal analysis of selected Zr-based amorphous alloy for welding processes.

Design/methodology/approach: The studies were performed on Zr-Cu-Ni-Al system alloy in form of plate. The structure analysis of the studied materials in as-cast state was carried out using XRD method. The thermal properties of the as-cast alloy were examined by DSC and DTA methods. The parameters of GFA included Trg, ΔTx, α, β, γ, δ and S were calculated.

Findings: The Zr-based amorphous alloy in form of plate with good GFA was produced by die pressure casting method. The investigation methods revealed that the studied as-cast alloy was amorphous. Although, there is probability of crystallites existence which could not be detected by XRD method. The literature study and calculated GFA parameters indicated that the $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy exhibits good GFA and thermal stability. It is confirmed that these parameters could be used to determine GFA of tested amorphous alloy for welding processes. This Zr-based BMG could be used as tested material for laser welding process.

Research limitations/implications: It is very difficult to obtain a Zr-based BMG with large sizes. Usually, the difficulties of the production of zirconium amorphous alloy are connected with the fact that the constituent elements of the analyzed materials have a high chemical affinity for oxygen, and have different melting points. For this reason, the process of producing BMG in zirconium matrix require the using of additional technology to provide specific conditions for the melting and casting.

Practical implications: These obtained values of GFA parameters can suggest that studied alloys are suitable materials for further practical application at welding process.

Originality/value: The success formation and investigation of the casted Zr-based BMG. The chemical composition of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy was tested first time in our laboratory.

Keywords: Amorphous materials, Bulk metallic glasses, Glass-forming ability, Welding

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MATERIALS

1. Introduction

Due to the special structure of amorphous materials, bulk metallic glasses have different properties from conventional crystalline alloys. They exhibit high strength, high hardness, high fracture toughness, superplasticity in a supercooled liquid region. Besides, they also have other, favorable properties such as corrosion resistance, wear and radialization resistance [1, 2].

From the analysis of literature data it can be concluded that Zr-based bulk amorphous alloys exhibit simultaneously various characteristic such as high glass forming ability, good cast ability into bulk form, good and precise deformability, high strength and good ductility, high corrosion resistance, low coefficient of thermal expansion and high elasticity [3,4].

In the last years, the Zr-based BMG (bulk metallic glasses) have attracted attention because of their excellent glass forming ability and outstanding mechanical properties [5]. Table 1 presents the Zr-based bulk amorphous alloy system and the bulk amorphous alloy system with Zr addition, together with the years when each alloy system was reported [6,7].

Table 1.
Zr-based bulk amorphous alloy systems and the bulk amorphous alloy systems with Zr addition, years when first papers and patents were presented [6,7]

Bulk glassy alloy system	Year
Zr-Al-TM	1990
Zr-Ln-Al-TM	1992
Ti-Zr-TM	1993
Zr-Ti-TM-Be	1993
Zr-(Ti, Nb, Pd)-Al-TM	1995
Cu-Zr, Cu-Hf	2001
Cu-(Zr, Hf)-Ti	2001
Cu-(Zr, Hf)-Al	2003
Cu-(Zr, Hf)-Al-(Ag, Pd)	2004
Ti-Cu-(Zr, Hf)-(Co, Ni)	2004
Cu-(Zr, Hf)-Ag	2005
Zr-Cu-Al-Ag-Pd	2007
Ti-Zr-Cu-Pd	2007
Ti-Zr-Cu-Pd-Sn	2007
Fe-(Zr, Hf, Nb)-B	1996
Co-(Zr, Hf, Nb)-B	1996
Ni-Zr-Ti-Sn-Si	2001
Ni-(Nb, Ta)-Zr-Ti	2002
Ni-(Nb, Ta)-Ti-Zr-Pd	2006

Based on the experimental results, the features of alloy elements for stabilization of supercooled liquid and glass forming ability were proposed. These features consist of the following three factors [7]:

- Multicomponent alloy, which consists of three elements or more;
- Significant atomic size mismatch > 12% among the three main constituent elements;
- Negative heats of mixing among the three main elements.

In author's opinion the alloys with the three empirical rules [7,8] can have a new glassy and liquid structures with the following features:

- A high degree of dense packed atomic configuration;
- New local atomic configurations which are different from those for corresponding crystalline phases;
- Long-range homogeneity with attractive interaction.

Bulk metallic alloys including Zr metal as a main constituent element have been recognize as engineering materials. It is known that six types of Zr-based BMGs in Zr-Al-(Ni, Cu) (1990), Zr-Al-Ni (1990), Zr-Al-Cu (1991), Zr-Be-Ti-Ni-Cu (1993), Zr-Al-Co (1995) and Zr-Cu-Al-Ag (2007) systems were developed as basis and typical Zr-based alloy system [7]. The maximum diameter for Zr-Al-Ni-Cu system is 32mm, for Zr-Al-Ni is 15 mm, for Zr-Al-Cu system is 22 mm, for Zr-Be-Ti-Ni-Cu system is more than 30 mm, for Zr-Al-Co system is 18 mm and 30 mm for Zr-Cu-Al-Ag base system.

One of the most important and well recognized amorphous alloys is Zr-Cu-Ni-Al system, because of high glass-forming ability in a wide composition range of 50-70% Zr, high corrosion resistance, good mechanical properties and the absence of special toxic elements. It was reported that the eutectic $Zr_{55}Al_{10}Cu_{30}Ni_5$ alloy rods kept a glassy structure in the diameter range up to 30 mm in the case of copper mold suction casting and 32 mm using copper mold cap casting [7].

In order to realize the wide application of Zr-based BMGs in industry, it is essential to develop new, more efficient technologies, new techniques to production BMGs of larger size. By reason of this M. M. Zhen and co-workers [1] have conducted research in the fluidity and filling ability of glass-forming Zr-based alloy melt in copper mould. They determined major factors which affected the flowing behavior of the metallic melt in the mold. These factors provide the foundation for overcoming the contradiction between the filling and formation of amorphous alloy during the rapid cooling process of the metallic melts. A Zr-Ti-Cu-Ni-Be ring with the inner diameter of 42 mm and outer diameter of 63 mm was prepared in their experiments [1]. The flow distance of the metallic melts in the runner was measured at three casting temperatures: 1000, 1100 and 1200 K, and at the casting velocity of 90 mm/s. As a result of the tests it was observed that the flow distance of the metallic melts increases with the increase of the casting temperature [1].

In presented work, Zr-Cu-Ni-Al system has been studied and tested.

The scientists H. Somekowa, A. Inoue and K. Higashi [9] conducted research in the Zr-Cu-Ni-Al system as well. They have investigated the superplastic and diffusion bonding behavior on Zr-Cu-Ni-Al metallic glass in supercooled liquid region. On the basis of the investigations it was observed that the metallic glass exhibited superplasticity in this region. The results indicate that the excellent elongation, 55%, was obtained at a temperature of 673 K in a strain rate $1\times10^{-2}s^{-1}$. The tests reveal that the maximum compression lap shear strength was 155 MPa at a bonding pressure of 200 MPa with bonding time of 0.9 ks. Ultimately, it can be noted that this experimental diffusion bonding condition was satisfied with the value calculated by the theoretical model including only the plasticity controlled process [9].

Moreover, L. Liu et al. [5] have studied the effect of high temperature plastic deformation on the thermal stability and microstructure of $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glasses. In this experiment, the plastic deformation of mentioned above alloy was conducted in the supercooled liquid region under uniaxial tension with various strain rates ranging from 8.31×10^{-4} to $2\times10^{-2}s^{-1}$. As a result of the tests it was noted that the deformation behavior of the Zr-based BMG is strongly dependent on strain rate. As it was expected, thermal and structural investigations revealed that the plastic deformation reduced the thermal stability of tested material. Furthermore, plastic deformation promoted crystallization or reordering of amorphous structure. To clarify the correlation between strain and structure of the studied Zr-based BMGs, the sample that was deformed at a high strain rate and exhibited significant necking was selected for a detailed investigation of its structure in different parts by HRTEM. From the analysis of obtained data it was found that a band crystalline structure with a strongly crystallographic orientation was formed at the tip part, while inhomogeneous nanocrystallization occurred in the middle parts, and the amorphous structure remained almost unchanged in the end part [5]. L. Liu et al. [5] maintain that the different structures observed in different parts of the deformed sample are attributed to the inhomogeneous deformation of the BMG at high strain rates.

The influence of niobium addition on the structure and properties of Zr-Cu-Ni-Al alloy system was investigated in [10,11]. C. Fan and A. Inoue have observed that the crystallization process of the first step is quite different with different Nb content in the Zr-Cu-Ni-Al-Nb metallic glasses and the metallic glass precipitate nanosized quasicrystals in the first transformation step upon annealing. Besides, it has been shown a better glass-forming ability with increasing Nb content. To sum up, it can be concluded that Nb has a distinct effect on the precipitation of quasicrystals in Zr-Cu-Ni-Al-Nb metallic glasses, what is more Nb is a decisive element favoring the glass forming ability.

Furthermore, $(Zr_{65}Al_{10}Ni_{10}Cu_{15})_{100-x}Nb_x$ glass forming alloys with Nb contents from 0 to 15 at.% were prepared and tested by Y. F. Sun et al. group [11]. The alloys with different Nb contents exhibited different microstructures and mechanical properties. In alloy with 5 at.% Nb except fully amorphous structure some dendrites with very small size were founded. As a result of the tests it was observed that quasicrystalline phase with the size of less than 200 nm was the dominant elements in alloy with 10 at.% Nb and some bcc phase was formed too. In alloy with 15 at.% Nb the bcc phase with the size of about 15μm and some quasicrystalline phases were formed. On the basis of the investigation, the authors [11] concluded that the $(Zr_{65}Al_{10}Ni_{10}Cu_{15})_{95}Nb_5$ exhibited plastic deformation with about 3.05 % of plastic strain prior to fracture. Because of branching of the shear bands the plasticity was improved. The other alloys failed in brittle fracture manner under compression test. The study show that glass transition temperature slightly increased and the supercooled liquid region decreased with increased Nb content. In this experiment for $(Zr_{65}Al_{10}Ni_{10}Cu_{15})_{90}Nb_{10}$ and $(Zr_{65}Al_{10}Ni_{10}Cu_{15})_{85}Nb_{15}$ alloys, the DSC curves exhibit more than one exothermic peak due to the precipitation of quasicrystalline phase.

The scientists Y. J. Sun et al. [12] also have conducted research in the Zr-Cu-Ni-Al bulk metallic glasses with super-high glass forming ability. They have made attempt to production this system alloy by an efficient method of proportional mixing of binary eutectics. In author's opinion, the drastic improvement in GFA is attributed to balancing the chemical affinities of the Zr, Cu, Ni and Al components in the melt prior to solidification which makes the precipitation of competing crystalline phases more difficult. As the glass forming ability increases, the concentration of Cu in the alloys exhibits a same trend. It was notice that the substitution of additional small Cu atoms for large Zr atoms in the investigated alloys stabilizes the efficient cluster packing structure of the amorphous alloys, leading to the pronounced increase in their glass forming ability. Consequently, $Zr_{51.9}Cu_{23.25}Ni_{13.5}Al_{12.25}$ glass forming alloy with a critical size of 10 mm and $Zr_{50.7}Cu_{28}Ni_9Al_{12.3}$ glass forming alloy with a critical size of 14 mm were achieved [12].

Glass forming ability and thermal stability of a new bulk metallic glasses in the quaternary Zr-Cu-Ni-Al system were studied by J. Shen et al., too [13]. The new Zr-based bulk metallic glass $Zr_{51}Al_{20.7}Ni_{12}Cu_{16.3}$ was developed by using newly proposed approach which based on the concept that the formation of glassy metals requires suppression of nucleation and growth of the crystalline phases. In order to evaluate the $Zr_{51}Al_{20.7}Ni_{12}Cu_{16.3}$ alloy, the well-know $Zr_{65}Al_{17.5}Ni_{10}Cu_{7.5}$ was obtained for comparison. In this study the thermal analyses show a distinct glass transition and a significant supercooled liquid region, what illustrating characteristics of alloys with high GFA and high thermal stability against crystallization. The authors [13] suppose that the reason of the better glass forming alloy probably is primarily due to the fact that the chemical interaction between the base element (Zr) and the glass forming elements (Al, Ni, Cu) has been balanced in the melt prior to solidification, and consequently providing an extent more favorable for glass formation.

A single endothermic peak upon melting and a single exothermic peak upon cooling from the melt imply a concurrent melting and formation of the equilibrium compounds in the heating and cooling cycle, respectively. This is why the composition of selected alloy is close to the eutectic [13].

Two or three distinctly separated endothermic and exothermic peaks appear in the heating and cooling DSC curves, indicating a melting and solidification behavior of an off-eutectic alloy. Ultimately, it can be noted that glass formation favors for the alloys with or near eutectic composition [13, 14].

Table 2 summarizes the characteristic thermal parameters, deduced from DTA and DSC data, namely, the glass transition temperature T_g, the onset crystallization temperature T_x, the melting point T_m, the peak crystallization temperature T_p, the liquidus temperature T_l, the supercooled liquid region ΔT_x and the reduced glass transition temperature T_{rg}.

In the last years, Zr-based bulk metallic glasses in Zr-Cu-Ni-Al system were commercialized as sporting goods in golf clubs, watch parts, electro-magnetic device casting, connecting parts for optical fibers, optical mirrors. Furthermore, Zr-Al-Ni-Cu glassy alloy has been applied to pressure sensors for automobiles and ordinary industries. The sensors of Zr-based amorphous alloy have higher sensitivity, smaller size and higher pressure endurance than sensors produced from conventional materials. The Zr-Al-Ni-Cu alloy has been applied to micro-geared motor parts production, too. The micro-geared motor part has a high torque than that for conventional vibration motors. In addition, Zr-based alloys can be used to production of various types of connection adapters of curved sections and circular piping [4,7].

Developed and fabricated micro-geared motors in conjunction with connection adapters have been tested for commercialization in micro-machines, precision optics, micro-pumps, endoscopes and the others parts in advanced medical equipment [4, 7].

The low temperature properties of Zr-based BMG have become a new research field in glassy alloys. It is expected that fields of applications of Zr based bulk metallic glasses will be significantly extended in the near future on the basis of the useful and unique engineering properties. It resulting from the simultaneous achievements of novel atomic configuration, various bulk form, multi-component alloy composition, slow solidification process, Newtonian flow deformability and net-shape casting formability [7].

Table 2.
Thermal stability of the selected bulk glassy Zr-based alloys [7,12, 15-21]

L.p.	Alloy	Dimension Ø [mm]	Thermal stability				
			T_g [K]	ΔT_x[K]	T_g/T_l	T_x	T_l[K]
1	$Zr_{53}Cu_{18.7}Ni_{12}Al_{16.3}$	6	709	106	0.621	815	1141
2	$Zr_{51.9}Cu_{23.3}Ni_{10.5}Al_{14.3}$	10	710	94	0.629	804	1129
3	$Zr_{50.7}Cu_{28}Ni_9Al_{12.3}$	14	719	80	0.630	799	1142
4	$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$	<6	657	79	0.563	736	1168
5	$Zr_{55}Cu_{30}Ni_5Al_{10}$	<10	682	63	0.618	745	1104
6	$Zr_{57.5}Cu_{27.3}Ni_{6.5}Al_{8.7}$	<14	651	104	0.596	755	1124
7	$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$	10	627	124		751	
8	$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$	16	625	125		750	
9	$Zr_{64.5}Ni_{15.5}Al_{11.5}Cu_{8.5}$	3	640.3	94.9	0.568	735.2	1127
10	$Zr_{64.5}Ni_{15.5}Al_{11.5}Cu_{8.5}$	-	650	100	0.564	750	1153
11	$Zr_{64.5}Ni_{15.5}Al_{11.5}Cu_{8.5}$	-	671	87	0.582	758	1153
12	$Zr_{65.5}Cu_{22.4}Ni_{6.5}Al_{5.6}$	3	636	97	0.525	733	1211
13	$Zr_{65.3}Cu_{20}Ni_{8.2}Al_{6.5}$	3	640	105	0.539	745	1188
14	$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$	3	650	100	0.564	750	1153
15	$Zr_{64.8}Cu_{15.5}Ni_{11.4}Al_{8.3}$	3	653	99	0.572	752	1143
16	$Zr_{64.5}Cu_{13.1}Ni_{13.2}Al_{9.2}$	3	658	99	0.578	757	1138
17	$Zr_{63.8}Cu_{7.6}Ni_{17.2}Al_{11.4}$	3	671	87	0.582	758	1153
18	$Zr_{70}Ni_{7.5}Cu_{13.5}Al_9$	2	631	74		705	
19	$Zr_{52}Cu_{32}Ni_6Al_{10}$	8	694	90	0.619	784	1122
20	$Zr_{54}Cu_{28}Ni_6Al_{10}$	8	692	83	0.627	775	1103
21	$Zr_{61}Al_{12.2}Ni_5Cu_{21.8}$	3	665	85	0.574	750	1159
22	$Zr_{60.6}Al_{13.6}Ni_{7.5}Cu_{18.3}$	3	693	80	0.569	773	1218
23	$Zr_{60}Al_{15}Ni_{10}Cu_{15}$	3	683	83	0.566	766	1207
24	$Zr_{50}Cu_{40}Al_{10}$	22	706	86	0.647	792	1092
25	$Zr_{55}Cu_{30}Al_{10}Ni_5$	30	683	84	0.587	767	1163
26	$Zr_{60}Cu_{20}Al_{10}Ni_{10}$	20	662	92	0.569	754	1164

2. Materials for research and work methodology

The aim of this work is the presentation of the structure and thermal analysis of selected Zr-based alloy for welding processes.

Zr-based master alloy ingot with compositions (Table 3.) of $Zr_{55}Cu_{30}Ni_5Al_{10}$ was prepared by induction melting of pure Zr, Cu, Ni, Al elements (Table 4.) in argon atmosphere. Applied ingot was melted one at a time. The alloy composition represent nominal atomic percentages.

The studies were carried out on bulk metallic materials as plate. The investigated material was cast in form of plate with thickness of 0.5mm. From the master alloy, plate samples were prepared by the pressure die casting method in an argon atmosphere. The master alloy was melted in a quartz crucible using an induction coil and pushed in a copper mould by applying an ejection pressure.

The microstructure characterization and thermal analysis of the Zr-Cu-Ni-Al bulk metallic alloy using XRD, DTA and DSC methods were carried out.

Table 3.
Chemical composition of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy

No	Elements	mass. [%]	at. [%]
1	Zr	67.0141	55
2	Cu	25.4627	30
3	Ni	3.9195	5
4	Al	3.6037	10

Glassy structures were examined by X-ray diffraction using a Seifert - FPM XRD 7 diffractometer with Co Kα radiation at

35kV. The data of diffraction lines were recorded by means of the stepwise method within the angular range of 30° to 80°.

Table 4.
Purity and shape of used elements

No	Elements	Purity [%]	Shape
1	Zr	99.9	lump
2	Cu	99.99	globule
3	Ni	99.9	pieces
4	Al	99.99	lump

The thermal properties: glass transition temperature (T_g), onset crystallization temperature (T_x) and peak crystallization temperature (T_p) of the as-cast alloy were examined by differential scanning calorimetry method using DSC822 Mettler Toledo at a constant heating rate of 40K/min.

The melting temperature (T_m), liquidus temperature (T_l) were determined by differential thermal analysis method using STA 449 F3 Jupiter by NETZSCH factory thermal analyzer.

The parameters of glass forming ability included reduced glass transition temperature (T_{rg}), supercooled liquid region (ΔT_x), α, β, γ, δ and stability (S) were calculated in the following way [8]:

$$T_{rg} = \frac{T_g}{T_l} \quad (1)$$

$$\Delta T_x = T_x - T_g \quad (2)$$

$$\alpha = \frac{T_x}{T_l} \quad (3)$$

$$\beta = \left(\frac{T_x}{T_g} + \frac{T_g}{T_l}\right) \quad (4)$$

$$\gamma = \left(\frac{T_x}{T_{g+T_l}}\right) \quad (5)$$

$$\delta = \left(\frac{T_x}{T_l - T_g}\right) \quad (6)$$

$$S = \frac{(T_p - T_x)(T_x - T_g)}{T_g} \quad (7)$$

3. Results of researches

3.1. X-ray analysis

The bulk metallic glasses samples in plate form were produced and investigated. The structure of as-cast Zr-Cu-Ni-Al system alloy in form of plate with thickness of 0.5mm was examined by X-ray diffraction method.

The Zr-based sample of determined chemical composition consist of a glassy phase as was evidenced from a main halo peak without crystalline peaks. One of the obtained halo peak of tested alloy is presented in Fig. 1.

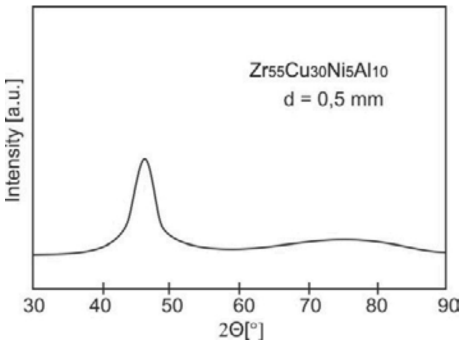

Fig. 1. X-ray diffraction pattern of as-cast amorphous alloy

The X-ray analysis exhibits that the studied Zr-based bulk metallic alloy is amorphous, but further and more precisely analysis by HRTEM is required.

3.2. Thermal analysis

Fig. 2 shows a double melting process. The first peak is sharp whereas the second one is smaller and more gentle than first peak. Fig. 2 shows a two-step melting process which indicates that the alloy is no completely eutectic.

It is often acceptance that the deepest eutectic composition is characterized by one sharp endothermic peak. Then, eutectic composition has the best glass forming ability (GFA). Considerations on the subject dependence of eutectic composition and thermal properties were carried on in article [8, 22, 23].

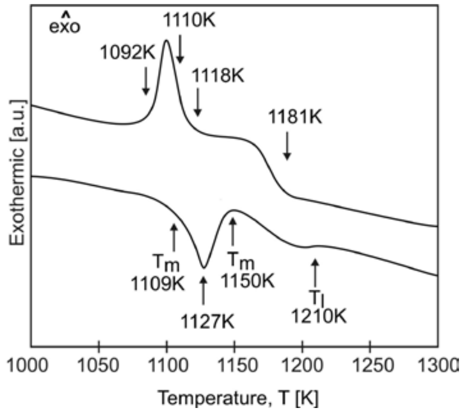

Fig. 2. DTA curve of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy as master-alloy

Table 5.
Thermal properties of $Zr_{55}Cu_{30}Ni_5Al_{10}$ glassy alloy in form of plate

amorphous alloy	thickness [mm]	T_g [K]	T_x [K]	T_p [K]	T_l [K]
$Zr_{55}Cu_{30}Ni_5Al_{10}$	plate, 0.5	711	790	802	1210

Table 6.
Glass-forming ability parameters of $Zr_{55}Cu_{30}Ni_5Al_{10}$ bulk metallic glass in form of plate

amorphous alloy	Dimension [mm]	T_{rg} [K]	ΔT_x [K]	α	β	γ	δ	S
$Zr_{55}Cu_{30}Ni_5Al_{10}$	plate, thickness 0.5	0.5876	79	0.6528	1.6987	0.4112	1.5831	1.3333

For estimating thermal stability, the melting point, liquidus temperature and reduced glass transition temperature of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy were measured by differential thermal analysis. The melting point and liquidus temperature are the onset and the end temperature of the melting curve on the DTA diagram. Fig. 2 shows DTA curve of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy as master-alloy. Liquidus temperature of melting Zr-based alloy equals T_l=1210K.

In addition DTA analysis of master alloy is presented in Table 5.

The DSC curve measured at 40K/min. on amorphous plate of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy with thickness of 0.5 mm in as-cast state is shown in Fig. 3.

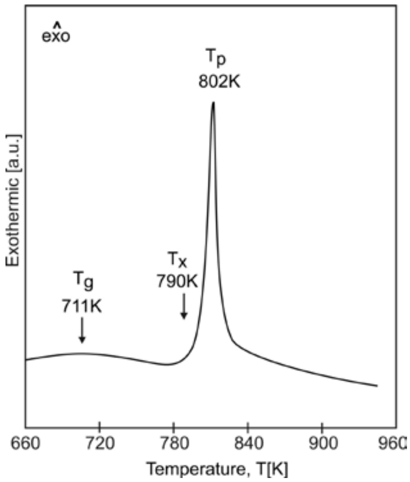

Fig. 3. DSC curve of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy in as-cast state in form of plate with thickness of 0.5 mm

The distinct exothermic peak describing crystallization process of studied glassy alloy is observed. The crystallization effect has onset crystallization temperature T_x=790K and peak crystallization temperature T_p=802K. The glass transition temperature equals 711K.

In scientist's opinion, the width of supercooled liquid region is a very good GFA measure. In this study, supercooled liquid region is presented as $\Delta T_x=(T_x-T_g)$ and has a value of 79K. From the analysis of literature and obtained data it can be concluded that when range of temperature ΔT_x is larger, GFA is higher. ΔT_x criterion is acknowledged through researchers in this field of science.

Next indicator, the reduce glass transition temperature value is calculated according to the pattern: $T_{rg}=T_g/T_l$. In this test, the value of T_{rg} equals 0.5876. This indicator is going to achieve a value of 0.6 what means excellent GFA of analyzed alloy.

Afterwards, γ parameter was defined with the help of formulae: $\gamma=T_x/T_g+T_l$. This indicator is most often applied because it can be easily determined with the help of calorimetric test. The γ parameter reached a value equals 0.3931. This calculated value is sufficient for obtained alloy.

The thermal stability temperatures: glass transition temperature, onset crystallization temperature, crystallization peak temperature and calculated glass-forming ability T_{rg}, ΔT_x, α, β, γ, δ and S parameters of studied glassy alloy in form of plate are listed in Table 6.

The calculated GFA parameters indicated that the $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy exhibits good glass-forming ability and thermal stability.

The dependence between thermal parameters, thermal stability and microstructure of bulk metallic glasses were discussed earlier [8].

4. Conclusions

Recently, the thickness of bulk metallic glasses is too small for structural applications. Therefore, the development of joining processes for these materials is desirable. Welding and other engineering processes require the materials of high glass forming ability and high phase stability.

It is very important to know all thermal parameters of joined materials. The thermal parameters determination is necessary to determine and select welding parameters.

It is necessary mention that the higher value of T_g and T_x may extend the application temperature region of the bulk metallic glasses as engineering materials. Additionally, ΔT_x corresponds to the good stability of the supercooled liquid.

In this research, the Zr-based glassy alloy in form of plate with good glass forming ability was produced by die pressure casting method. Moreover, the structure and thermal parameters of Zr-based alloy were studied. Afterwards, it is planned the laser welding of obtained amorphous materials.

The investigation performed on the plate with thickness of 0.5mm of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy allowed to formulate the following statements:

- The X-ray analysis exhibits that the studied Zr-based glassy alloy is amorphous.
- This sample shows a considerable glass transition process. The crystallization of the tested alloy exhibits one step process. The exothermic effect includes onset crystallization temperature at value of T_x=790K and peak crystallization temperature at T_p=802K. The width of ΔT_x is 79K, indicating that the alloy possesses a sufficient stability of the supercooled liquid.
- The glass-forming parameters included T_{rg}, ΔT_x, α, β, γ, δ and S were calculated. It is evident that the above enumerated indicators could be used to determine glass-forming ability of studied joining process-oriented materials.
- These obtained values of GFA parameters can suggest that studied alloy is suitable material for further practical application at welding process.

The success of Zr-based bulk metallic glasses production in form of plate is important for future progress in joining research of this group of materials.

This studied Zr-based alloy will be appropriate to first tests of BMG joining process in Poland.

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