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Structure and density of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ bulk glassy alloy

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Materials

ABSTRACT

Purpose: The work presents density measurements of bulk metallic glasses in as-cast state. Additionally casting method and structure characterization was displayed.
Design/methodology/approach: The studies were performed on $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ metallic glasses in form of rods with diameter 2 and 3 mm. Samples were fabricated using copper mould casting method. The master alloy characteristic temperatures (T_m – melting point and T_l – liquidus temperature) were determinate by differential thermal analysis (DTA). The structure was characterized by X-ray (XRD) method and scanning electron microscope (SEM). The densities of metallic glassy rods have been measured by using the Archimedes principle.
Findings: The XRD and SEM investigations revealed that the studied samples in form of rods were amorphous. Broad diffraction "halo" was observed for every testing piece. Fracture observation confirmed glassy state of samples. Archimedes principle allows calculating density of tested sample.
Practical implications: The FeCo-based bulk metallic glasses have attracted great interest for a variety application fields for example electric applications, precision machinery materials or structural materials. Metallic glasses exhibit higher density than their crystalline counterparts and could be apply as a satisfactory structural material.
Originality/value: The obtained results confirm the utility of applied investigation methods in the thermal and structure analysis of examined amorphous alloys. Density of metallic glasses is important properties which influence on specific application these materials. This materials offer attractive qualities, combining some of the desirable properties of conventional crystalline metals and the formability of conventional oxide glasses.
Keywords: Amorphous materials; Bulk metallic glasses; Copper mould casting; Density; Archimedes principle

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1. Introduction

The atomic structure of metallic glasses is still unknown entirely. It characterized not by long-range atomic order like crystalline materials but reveal short- and medium-range order at the atomic scale [1-2].

First metallic glasses were discovered in 1960 in $Au_{80}Si_{20}$ liquid metal. Since then, many of research centres working on new alloy systems with glass forming ability. In effect dimensions of glassy samples were rise progressively. And finally, in 1969, a first bulk metallic glass was reported. It was discovered from Pd based alloy system and had >1 mm diameter. From 1988 interest in the development of bulk metallic glasses (BMG) contribute to discover many of BMG formation in multicomponent alloys. Table 1 presents variety of alloy systems for bulk metallic glasses [3-7].

Table 1.
Summaries of some bulk metallic glasses [7]

System	Alloy	Critical size D_c, mm
Pd-based	$Pd_{40}Ni_{40}P_{20}$	10
	$Pd_{40}Cu_{30}Ni_{10}P_{20}$	72
Zr-based	$Zr_{85}Al_{7.5}Ni_{10}Cu_{17.5}$	16
	$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	25
Cu-based	$Cu_{46}Zr_{42}Al_7Y_5$	10
	$Cu_{49}Hf_{42}Al_9$	10
Mg-based	$Mg_{54}Cu_{26.5}Ag_{8.5}Gd_{11}$	25
	$Mg_{65}Cu_{7.5}Ni_{7.5}Zn_5Ag_5Y_5Gd_5$	14
Fe-based	$Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$	12
	$Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$	16
	$Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$	5
Co-based	$Co_{48}Cr_{15}Mo_{14}C_{15}B_6Er_2$	10
Ca-based	$Ca_{65}Mg_{15}Zn_{20}$	15
Pt-based	$Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$	20

In order to good glass forming ability there empirical rules should be realized as following [1-8]:

- multicomponent alloy should consist of at least three components,
- difference between atomic radius of alloying elements should equal 12% minimum,
- there is negative heat of mixing,
- chemical composition should reveal eutectic or near-eutectic mixture.

Most important factor in fabrication bulk metallic glasses is critical cooling rate. For Fe-based BMGs critical cooling rate below 10^3K/s have been often found. For better understanding considerable of cooling rate TTT (Time-Temperature-Transition) diagram is very helpful (Fig. 1)[8-15]

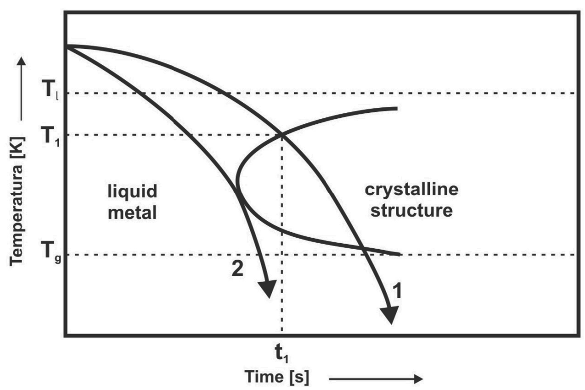

Fig. 1. TTT diagram of critical cooling rate for metallic glasses [11]

Because of specific properties, bulk metallic glasses have been attractive engineering materials for many applications. One of the most differences between amorphous and crystalline materials is its density. BMG`s exhibit highest density than its crystalline counterparts. This fact is bringing about by free volumes which occur in metallic glasses (Fig. 2). Free volume can be defined as nanometre space between atoms which appear in supercooled liquid [9].

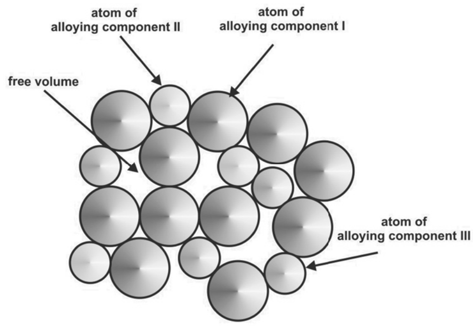

Fig. 2. Free volumes in metallic glasses structure [17]

For the sake of different cooling rates obtained in different fabrication techniques, it is probably that free volume will be different in samples produced by different methods. Since it is obvious that a free volume determines the density of metallic glasses it is possible that density of samples in different form (ribbon, rod, plate, ring) will be different [16].

Table 2.
Applications field of bulk metallic glasses [16]

Application	
structural	Sporting goods: • Golf clubs • Tennis rackets • Baseball and softball bats • Skis • Snowboards • Bicycle parts • Marine applications
	Precision gears
	Motors
	Automobile valve springs
	Diaphragms for pressure sensors
	Optical mirror devices
	Structural parts of aircrafts
magnetic	Magnetic yoke Magnetic cores Magnetic shielding sheets for computer
miscellaneous	Jewellery Biomedical applications (biocompatible implants) Medical devices
others	Mobile phone industry Military applications MEMS casings and components Missile components Aircraft fasteners

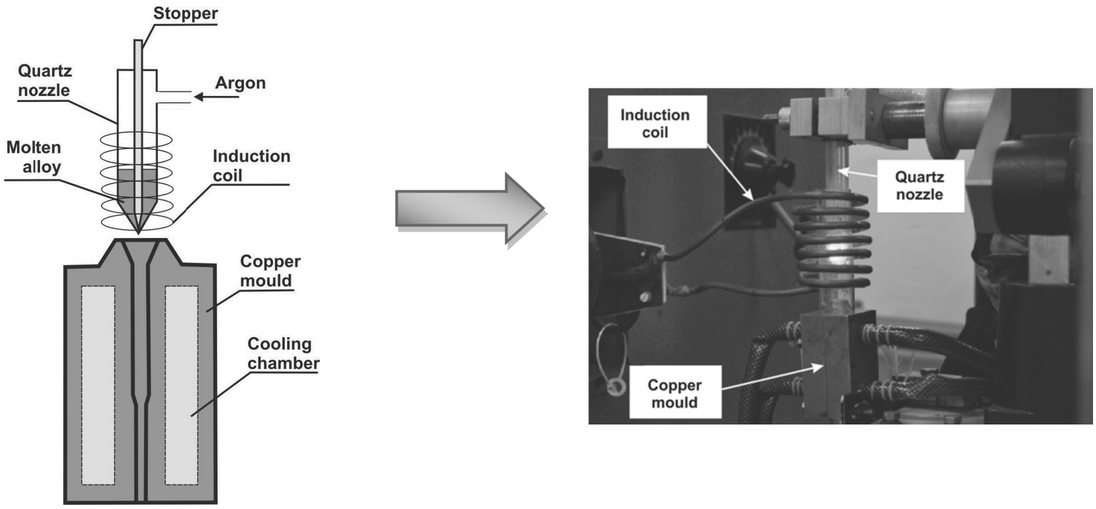

Fig. 3. Scheme of copper mould casting method [3]

Metallic glasses, especially BMG, have very interesting potential and existing applications. Because of its unique mechanical, physical, magnetic and corrosion properties, can be used in many fields of activity. Table 2 present some existing applications of bulk metallic glasses.

2. Materials and research methodology

The aim of the present work is the structure characterization and density analysis of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ bulk amorphous alloy using of XRD, SEM, LM methods and Archimedes principle.

Master alloy was prepared from high purity elements Fe (purity 99.75%) Co (purity 99.89%), B (purity 99.9%), Si (purity 99.9%), Nb (purity 99.85%). Induction melting of alloying components allows obtaining ingot of nominal content $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$. Melting process was carried out under argon atmosphere.

Bulk amorphous samples in form of rod with diameter ø=2 mm (P1, P2) and ø=3 mm (P3, P4) were prepared by copper mould casting (Fig. 3).

Thermal properties (liquidus – T_l and eutectic – T_e temperatures) of the master alloy upon heating and cooling were analysed by a NETZSCH model DSC 404 C under the purified argon atmosphere, at the heating and cooling rate of 10 K/min. Structure analysis of studied materials were carried out using X-ray diffraction (XRD). Seifert-FPM XRD 7 diffractometer with CoKα radiation and PANalytical X'Pert diffractometer with CoKα radiation were used for samples examination.

The fracture morphology of studied glassy material in form of rods with diameter of 2 and 3 mm was analysed using the scanning electron microscopy (SEM) ZEISS - SUPRA 25. Structure of the fabricated glassy rod samples was studied also by scanning electron microscopy method at different magnifications

Density of selected samples was measured by using Archimedes principle. The density ρ is the quotient of the mass *m* and the volume *V*.

$$\rho = \frac{m}{V} \left[\frac{g}{cm^3} \right] \tag{1}$$

Figure 4 present the density kit components which are used in examination.

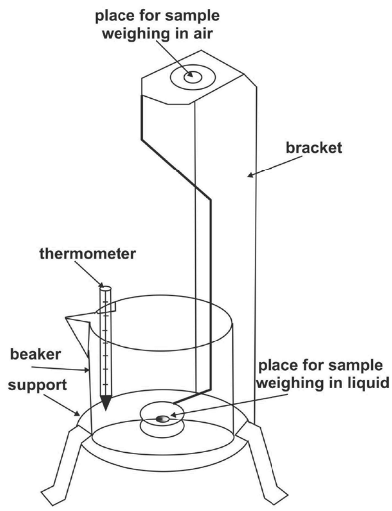

Fig. 4. Density kit components

The Archimedes principle states that every solid body immersed in a fluid loses weight by an amount equal to that of the fluid it displaces. The density of a solid is determined with the aid of a liquid whose density ρ_0 is known (in this testing it was distilled water ρ=1 g/cm^3). The solid is weighed in the air (A) and then in the auxiliary liquid (B). The density ρ of solid samples was calculated from the equation 2 as follow:

$$\rho = \frac{A}{A-B} \cdot \rho_0 \tag{2}$$

where:
ρ – density of the sample, g/cm^3,
A – weight of the sample in air, g,
B – weight of the sample in the auxiliary liquid, g,
ρ_0 – density of the auxiliary liquid, g/cm^3.

3. Results

The base master alloy DTA curve under the heating shows two endothermic peaks (Fig. 5). The first peak begins near melting (eutectic) point T_m (T_e) – 1226 K. The maximum signal of the second peak is associated with liquidus temperature. This peak is separate and occurs at temperature 1372 and 1398 K.

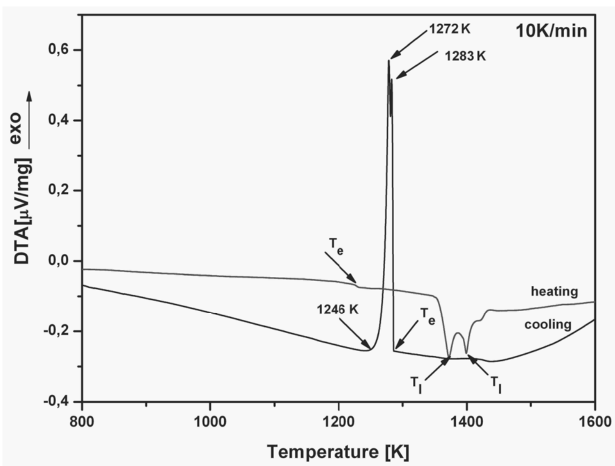

Fig. 5. Differential thermal analysis (DTA) curves of the base master alloy under the heating/cooling rate of 10 K/min

In DTA curves under the cooling one major peak is observed. Signal is also separate and occurs in 1272 and 1283 K. This peak indicates eutectic (or rather near eutectic) chemical composition of the investigated alloy.

It was found from the obtained results of microstructure testing performing by X-ray diffraction that the diffraction pattern of rods with diameter 2 and 3 mm of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ alloy consists of broad-angle peak (Figs. 6-7). These peaks correspond with the Bragg line originating from amorphous phase of alloy on the basis of Fe-Co.

Figures 8-9 show fracture of glassy rod with diameter of 2 and 3 mm. The fracture surface reveals some kind of zones, which probably inform about different amorphous structure of the studied samples.

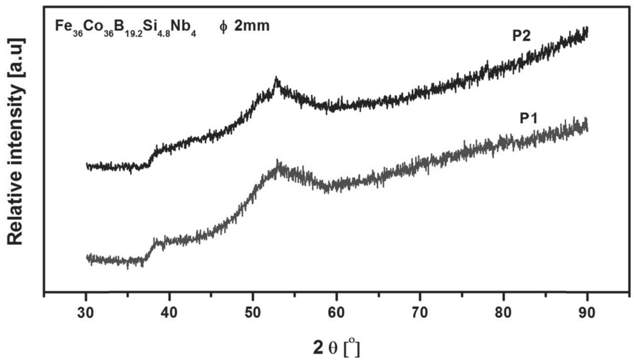

Fig. 6. X-ray diffraction pattern of the $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ rods with 2 mm in diameter

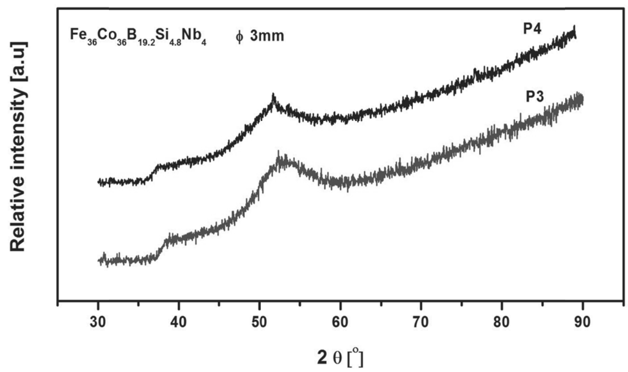

Fig. 7. X-ray diffraction pattern of the $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ rods with 3 mm in diameter

The presented fractures could be named "mixed" fractures. It can be specify two areas which are identify as "vein" (Zone I) and "smooth" (Zone II) patterns.

The "vein" fracture could be observed on margin of the samples. It is possibly cause by high cooling rate during casting process

Density of studied amorphous rods was examined by Archimedes principle. Measurement were realized by analytical balance Adventurer™ Pro with special density determination kit. Density was measured for four samples, two of each diameter. In order to limit measure error, measurements were repeated five times. Measurements were performed in distilled water which density equal 1 g/cm^3.

Additionally Student`s t-test was calculated. For number of measurements less than 30 this valuation of measuring errors method is suitable.

The essence of the Student`s test boil to calculation of the standard deviation and multiplication it by Student`s coefficient. Because Student`s coefficient depend on number of measurement "n" and the confidence level "α", the value of above named must be select from chart.

A confidence level for standard error equal α=0.68≈0.7. Table 3 present Student`s coefficient depending of the number of measurement (n) and confidence level (α).

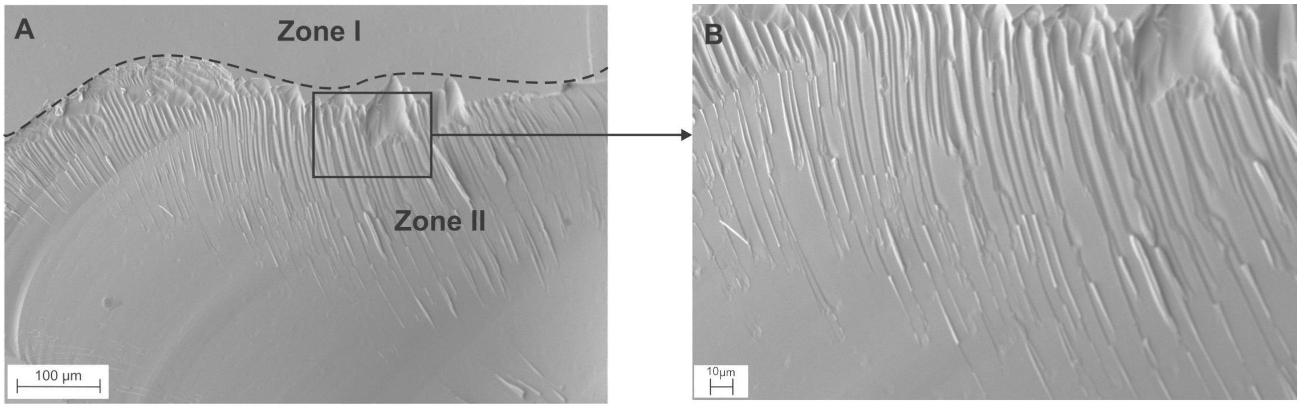

Fig. 8. SEM micrographs of the fracture morphology of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ amorphous rod with diameter of 2 mm in as-cast state: A – magn. 1000x, B – magn. 6000x

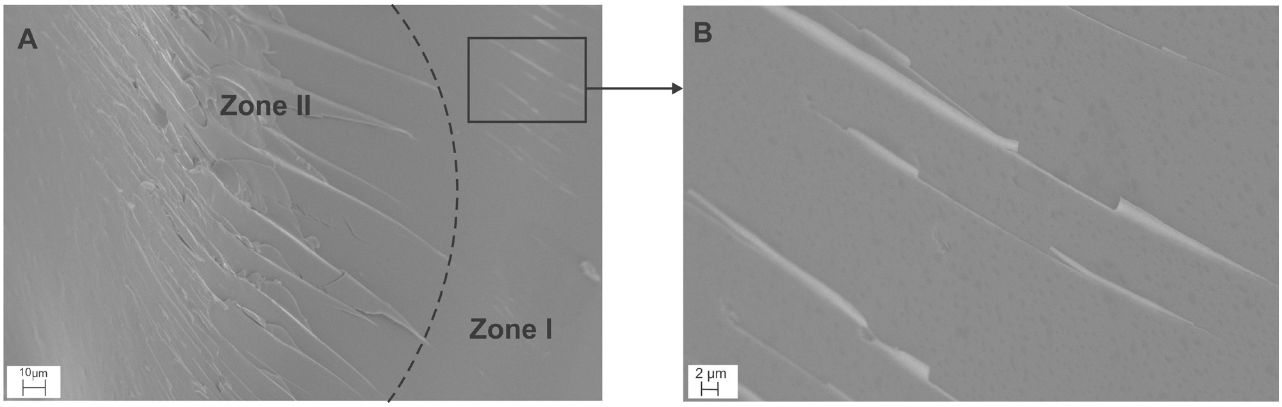

Fig. 9. SEM micrographs of the fracture morphology of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ amorphous rod with diameter of 3 mm in as-cast state: A – magn. 500x, B – magn. 6000x

Table 3.
Student`s coefficients with number of measurement -n and confidence level -α

n	α			
	0.5	0.7	0.95	0.997
2	1.00	1.96	12.71	636.6
3	0.82	1.34	4.30	31.6
4	0.77	1.25	3.18	12.9
5	0.74	1.19	2.78	8.6
6	0.73	1.16	2.57	6.9
7	0.72	1.13	2.45	6.0
8	0.71	1,12	2.36	5.4

Density measurements show that $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ bulk glassy alloy reveal density about 7.7 g/cm^3. For samples with diameter 2 mm density average ρ=(7.652±0.054) g/cm^3 for first sample (P1) and ρ=(7.721±0.083) g/cm^3 for second sample (P2) Tables 4-5 and 7-8 present results of density measurements for glassy rods with diameter 2 mm. Tables 6 and 9 show measurement errors calculations including Student`s test.

Table 4.
Sample P1 mass measurement in air and in liquid

2 mm – P1		
No	m1 (in air)	m2 (in liquid)
1	0.254	0.220
2	0.254	0.221
3	0.254	0.221
4	0.254	0.221
5	0.254	0.221

Table 5.
Density results for P1 with diameter 2 mm

No	Density m1/(m1-m2)*liquid density
1	7.471
2	7.697
3	7.697
4	7.697
5	7.697

Table 6.
Student`s test calculation for P1 with diameter 2 mm

Student`s test						
No	Density	Squares	Average	Standard deviation	Student`s coefficient	Modified standard deviation
1	7.471	55.816	7.652	0.045	1.19	0.054
2	7.697	59.244				
3	7.697	59.244				
4	7.697	59.244				
5	7.697	59.244				
Sum	38.259	292.791				

Table 7.
Sample P2 mass measurement in air and in liquid

2 mm – P2		
No	m1 (in air)	m2 (in liquid)
1	0.548	0.479
2	0.548	0.478
3	0.548	0.476
4	0.548	0.476
5	0.548	0.476

Table 8.
Density results for P2 with diameter 2 mm

No	Density
	m1/(m1-m2)*liquid density
1	7.942
2	7.829
3	7.611
4	7.611
5	7.611

Table 9.
Student`s test calculation for P2 with diameter 2 mm

Student`s test						
No	Density	Square	Average	Standard deviation	Student`s coefficient	Modified standard deviation
1	7.942	63.075	7.721	0.070	1.19	0.083
2	7.829	61.293				
3	7.611	57.927				
4	7.611	57.927				
5	7.611	57.927				
Sum	38.604	298.151				

Table 10.
Sample P3 mass measurement in air and in liquid

3 mm – P3		
No	m1 (in air)	m2 (in liquid)
1	0.386	0.336
2	0.386	0.336
3	0.386	0.336
4	0.386	0.336
5	0.386	0.337

Table 11.
Density results for P3 with diameter 3 mm

No	Density m1/(m1-m2)*liquid density
1	7.720
2	7.720
3	7.720
4	7.720
5	7.878

Table 12.
Student`s test calculation for P3 with diameter 3 mm

Student`s test						
No	Density	Square	Average	Standard deviation	Student`s coefficient	Modified standard deviation
1	7.720	59.598	7.752	0.032	1.19	0.038
2	7.720	59.598				
3	7.720	59.598				
4	7.720	59.598				
5	7.878	62.063				
Sum	38.758	300.456				

Table 13.
Sample P4 mass measurement in air and in liquid

3 mm – P4		
No	m1 (in air)	m2 (in liquid)
1	0.486	0.424
2	0.486	0.422
3	0.485	0.424
4	0.485	0.422
5	0.486	0.423

Table 14.
Density results for P4 with diameter 3 mm

No	Density m1/(m1-m2)*liquid density
1	7.839
2	7.594
3	7.951
4	7.698
5	7.714

Table 15.
Student`s test calculation for P4 with diameter 3 mm

Student`s test						
No	Density	Square	Average	Standard deviation	Student`s coefficient	Modified standard deviation
1	7.839	61.450	7.759	0.062	1.19	0.073
2	7.594	57.669				
3	7.951	63.218				
4	7.698	59.259				
5	7.714	59.506				
Sum	38.796	301.102				

For samples with diameter 3 mm density average $\rho=(7.752\pm0.038)$ g/cm^3 for first sample (P3) and $\rho=(7.759\pm0.073)$ g/cm^3 for second sample (P4). Tables 10-11 and 13-14 present results of density measurements for glassy rods with diameter 3 mm. Table 12 and 15 show measurement errors calculations including Student`s test.

On the basis of obtained measurement it was found that density of glassy rods of $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ alloy average 7.7 g/cm^3. There is no meaningful difference between densities of samples with different dimension. Figure 10 present density results for bulk glassy rods with diameter 2 and 3 mm.

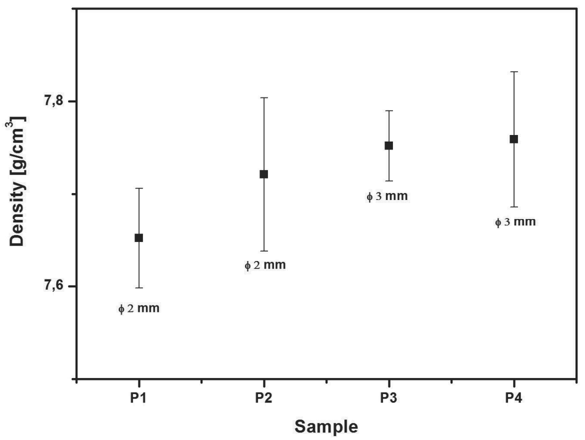

Fig. 10. Density results with error measurements for bulk metallic glasses with diameter 2 and 3 mm

4. Conclusions

The results obtained are summarized as follows:

- the bulk samples in form of rods with diameter of ø=2.0 and ø=3.0 mm were performed at $Fe_{36}Co_{36}B_{19.2}Si_{4.8}Nb_4$ alloy by pressure die casting method. It was found that this method allow fabricate bulk metallic glasses in different diameter,
- the DTA results indicate, that the chemical composition of investigated alloy is eutectic (or near eutectic). Thermal analysis allow identification liquidus and solidus temperatures of master alloy,
- the X-ray diffraction investigation revealed that the rods with diameter of ø=2.0 and ø=3.0 mm has amorphous structure,
- the SEM images showed that studied fractures could be classified as mixed fractures with indicated two zones contained "vein" and "smooth" areas,
- the density of sample with diameter 2 mm average $\rho=(7.652\pm0.054)$ g/cm^3 for first sample P1 and $\rho=(7.721\pm0.083)$ g/cm^3 for second sample P2,
- the density of samples with diameter 3 mm average $\rho=(7.752\pm0.038)$ g/cm^3 for first sample P3 and $\rho=(7.759\pm0.073)$ g/cm^3 for second sample P4,
- there is no meaningful difference between densities of samples with different dimension.

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