A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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K. ZIEWIEC*, P. KURTYKA*, K. BRYŁA*, S. KĄC**

THERMAL STABILITY AND BEHAVIOUR DURING COMPRESSION OF THE $Cu_{68.5}Ni_{12}P_{19.5}$ ALLOY

STABILNOŚĆ CIEPLNA I PRZEBIEG PROCESU PRASOWANIA STOPU $Cu_{68,5}Ni_{12}P_{19,5}$

Copper-nickel-phosphorus $Cu_{68.5}Ni_{12}P_{19.5}$ alloy was cast using melt spinning with a linear rate of 23 m/s (approximate cooling rate 10^5 K/s). In order to study the thermal stability of the metallic glass the ribbon in the as-cast state was tested by DSC and X-ray diffraction at different temperatures. Then the as-cast melt-spun ribbon was preliminarily compacted using 60 MPa to form 5 g samples. After pre-pressing, the samples were compressed between plates at different temperatures and stresses required for a given deformation were assessed. In order to find the progress of consolidation the cross-sections were studied using SEM and EDS. It was found that at higher compression temperatures the samples were consolidated with the presence of the crystalline phases.

Stop miedź-nikiel-fosfor $Cu_{68,5}Ni_{12}P_{19,5}$ odlewano koło wirujące s liniową prędkością 23 m/s (szacunkowa szybkość chłodzenia 10^5 K/s). W celu zbadania stabilności termicznej taśmy z otrzymanego szkła metalicznego w stanie po odlewaniu zastosowano różnicową kalorymetrię skaningową (DSC), przeprowadzono rentgenowskie pomiary dyfraktometryczne przy różnych temperaturach. Następnie taśma w stanie po odlewaniu na wirujące koło była wstępnie prasowana przy użyciu 60 MPa w celu uzyskania 5 gramowych próbek. Po wstępnym prasowaniu, próbki były prasowane pomiędzy płytami maszyny wytrzymałościowej, przy różnych temperaturach oraz oszacowano naprężenia wymagane do odkształcenia próbki o ustaloną wartość. W celu zbadania przebiegu konsolidacji wykonano badania przekrojów poprzecznych prasowanych próbek przy użyciu skaningowego mikroskopu elektronowego (SEM) wyposażonego w EDS. Stwierdzono, że przy wyższych temperaturach prasowania próbki zostały skonsolidowane, a w ich strukturze stwierdzono występowanie faz krystalicznych.

1. Introduction

Amorphous or nanocrystalline metallic alloys have useful properties such as high strength, high elasticity and stiffness as well as good soft magnetic properties [1–3]. Substantial efforts have been made to produce bulk metallic glasses. The amorphization is relatively easy to for ribbons and powders because of the high cooling rates necessary to obtain an amorphous state. However, recent advances in the selection of glass forming compositions have made it possible to produce bulk metallic glasses in as-cast condition. Some of the alloys, mainly zirconium- and palladium-based can achieve vitrification with cooling rates at the level of 1 K/s [4, 5]. However, the size that can be obtained by casting is still considerably smaller that the one required for majority of applications. The solution for the limitation could be the use of consolidation. The potential of consolidation lies in the fact that the method does not require substantial thicknesses of amorphous alloys used for the manufacturing of the parts. On the other hand, relatively good glass forming ability and the supercooled liquid region presented by some of the Cu-Ni-P alloys [6, 7], allow to expect that they can be compacted to obtain amorphous or nanocrystalline bulk shapes. Therefore, the aim of the work was to study the behaviour of the $Cu_{68.5}Ni_{12}P_{19.5}$ alloy subjected to heat treatment and deformation at elevated temperatures and to assess the possibility of consolidation of the alloy.

2. Experimental

Copper-nickel-phosphorus $Cu_{68.5}Ni_{12}P_{19.5}$ alloy was cast using melt spinning with linear rate of 23 m/s (approximate cooling rate of 10^5 K/s). The ribbon in the as-cast state was tested by X-ray. Then it was investigated by means of differential scanning calorimetry

* FACULTY OF MATHEMATICS, PHYSICS AND TECHNICAL SCIENCES, PEDAGOGICAL UNIVERSITY, 30-084 KRAKÓW, PODCHORĄŻYCH 2 STR., POLAND
** FACULTY OF METALLURGY AND MATERIALS SCIENCE, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, 30-059 KRAKÓW, AL. MICKIEWICZA 30, POLAND

(DSC: DSC 2010 TA Instruments). Then X-ray high temperature studies of melt spun ribbons as a function of temperature were carried out using Siemens D5005 (Bruker-AXS) diffractometer equipped with Cu radiation. As-cast ribbons of 30 mm thickness were stuck to a glass plate. The measurements were made at 293, 453, 503, 553 and 603K in XRK-900 reaction chamber (Anton Paar). Diffraction patterns were registered in the range of 30–90° (2Θ) using Θ – Θ scan with 0.04°/1s speed. During heating of the samples with an average heating rate of 10°C/min selected diffraction peaks were monitored. Phase identification was made using JCPDS database [8]. Then the as-cast melt-spun ribbon was preliminarily compacted in a die to form 10mm diameter 5 g samples with use of 60 MPa. After pre-pressing (Fig. 1a) the samples were compressed between plates (Fig. 1b) at different temperatures in INSTRON TT-DM (100 kN) testing machine. The time used for stabilization of the temperature was 30 min. After this period, the stress – deformation characteristics were registered and stresses required for a given deformation (20%) of the samples compressed at different temperatures were evaluated. Afterwards the samples were cut and polished to obtain the cross-sections of the pellets after compression between plates. The cross-sections were observed with use of scanning electron microscope and EDS analysis was performed. X-ray analysis of the samples compressed at different temperatures was also made.

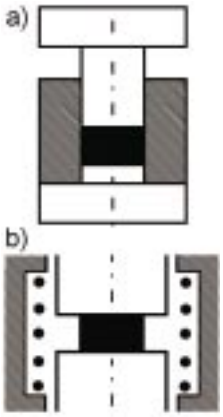

Fig. 1. The diagram showing: a) preliminary compaction of ribbons in a die; b) compressing the samples between plates in a furnace

3. Results and discussion

The results of X-ray study shown in Fig. 2 presents that in as-cast condition the $Cu_{68.5}Ni_{12}P_{19.5}$ alloy shows a broad peak around d = 2.05Å (39°–51°). The diffraction pattern of the alloy heated to 453K does not change significantly and seems to be amorphous. The crystalline peaks appear at 503K. The broad peak splits into the peaks that can be attributed to Cu-based solid solution and M_3P phosphide phase. Well-shaped peaks from crystalline phases mentioned above are observed at higher temperatures (553K, 603K). There is also one peak (41°) that could not be identified. Figure 3 presents DSC curve with glass transition at 452K and the crystallization onset at T_x = 459K. The crystallization sequence consist of three peaks with maximum at T_1 = 499K, T_2 = 543K and T_3 = 562K. The results of DSC at high temperature confirm lack of crystallization at the temperatures below T_x = 459K, and occurrence of the glass transition below the crystallization. Therefore, the viscous flow leading to easy deformation could be expected [9–12].

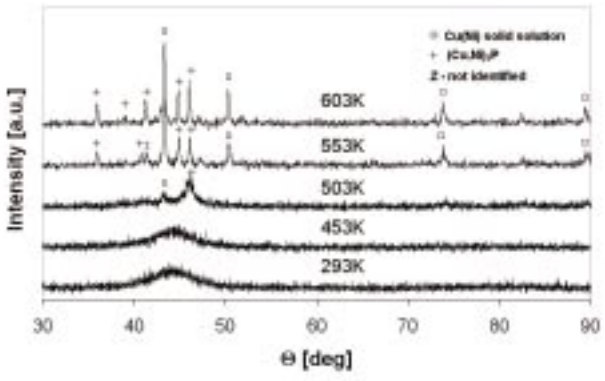

Fig. 2. X-ray patterns performed at different temperatures for $Cu_{68.5}Ni_{12}P_{19.5}$ melt spun ribbon

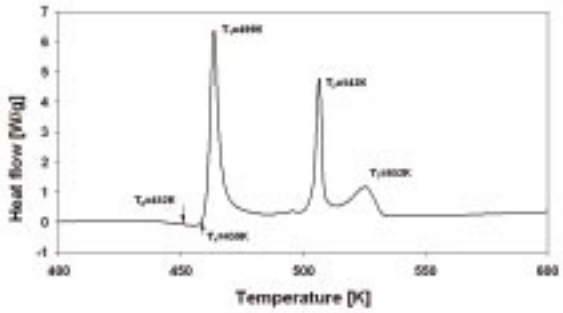

Fig. 3. DSC heating trace for $Cu_{68.5}Ni_{12}P_{19.5}$ ribbon produced by melt spinning showing crystallization sequence and arrows indicating glass transition temperature and crystallization onset

In order to examine the behaviour of the amorphous ribbon, compression tests were performed at different temperatures. As it is shown on Fig. 4 the largest slope of the compression curve occurs at 423K. The stress level required to deform the samples to ε = 20% was also the largest in this case (Fig. 5). At higher temperatures and at ambient temperature the stress level was smaller (Fig. 5). As one can see the smallest stresses are required to deform the sample at 293K, however it is connected with the damaging of the pellets. At the higher temperatures we have not observed the breaking of the pellets and in spite of formation of brittle phos-

phides the samples compressed at higher temperatures were consolidated. The comparison of the cross sections

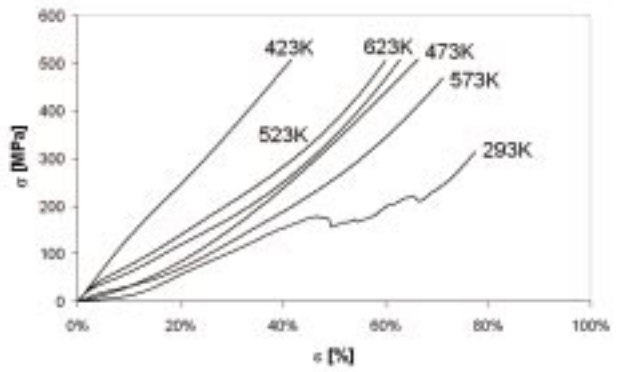

Fig. 4. The stress-strain characteristics for compression tests performed at different temperatures

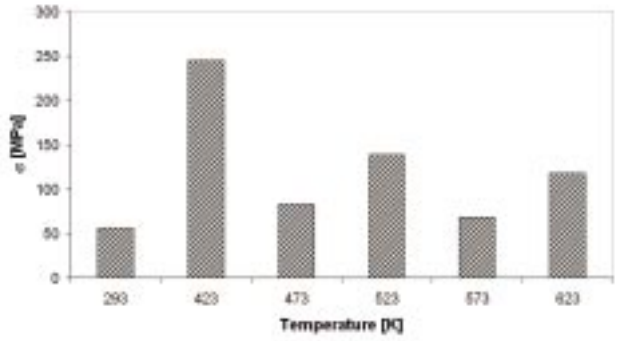

Fig. 5. The stress required for deformation of the samples to 20%. Various test temperatures

of the samples compressed at 523K, 573K and 623K (Fig. 6–Fig. 8) shows that at 523K the ribbons contact to each other, however no joints are observed, however at the 573K the boundaries between the ribbons disappear and only isolated voids are observed. At 623K the cross section is almost completely consolidated and no voids can be observed. For the 523K and 573K the EDS analysis shows the peaks at the voids (Fig. 6, 7) and there are no regular peaks present from the sample compressed at 623K (Fig. 8). One can also observe that the distances between peaks at 523K are higher than at 573K (Fig. 6b – Fig. 6d) and (Fig. 7b – Fig. 7d). This confirms the distinct plastic deformation of the ribbons during the compression. Fig. 9. presents the X-ray diffractions of the samples compressed at higher temperatures and the X-ray diffraction of the ribbon in as-cast state. The comparison of the diffractograms shows that the samples compressed at 473K, 573K and 623K temperatures are crystallized during the tests. The X-ray diffraction of the sample compressed at 473K presents peaks from Cu(Ni,P) solid solution and $(Cu,Ni)_3P$ phosphide. The increase of the compression temperature gives better shaped diffraction peaks (573K and 623K).

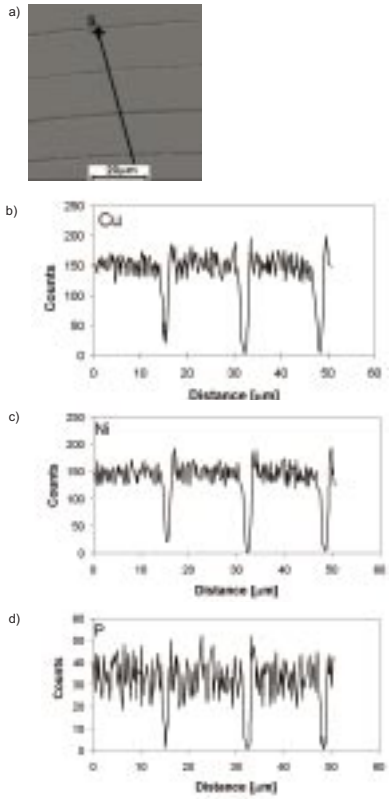

Fig. 6. Cross-sections of the pellet after compression between plates at 523K; a) SEM micrograph; b) Cu – profile, c) Ni – profile, d) P – profile

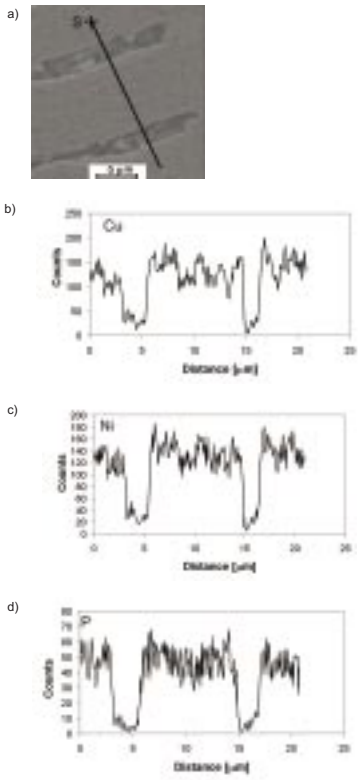

Fig. 7. Cross-sections of the pellet after compression between plates at 573K; a) SEM micrograph; b) Cu – profile, c) Ni – profile, d) P – profile

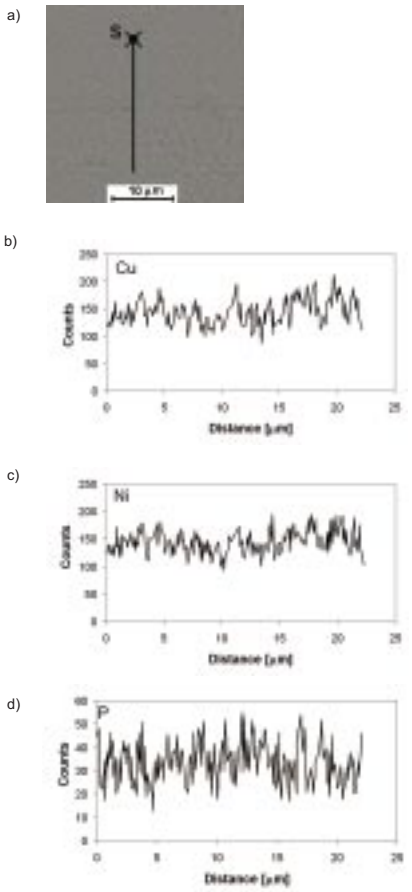

Fig. 8. Cross-sections of the pellet after compression between plates at 523K; a) SEM micrograph; b) Cu – profile, c) Ni – profile, d) P – profile

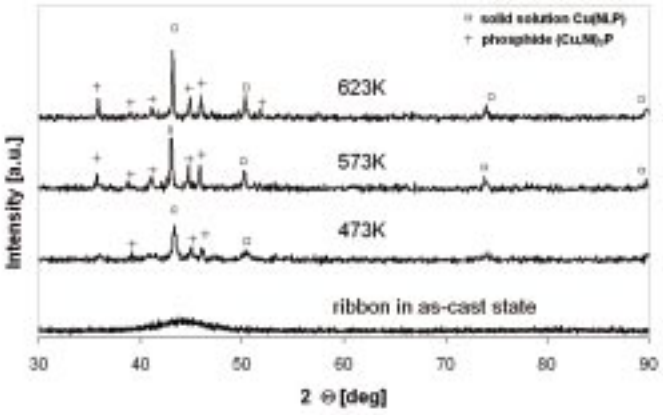

Fig. 9. X-ray diffractions of the pellet after compression between plates at 623K

The results obtained in the present study suggest that above 423K the deformation of the alloy is easier which is confirmed by a decrease of the stress required to deform the sample about 100 MPa to 250 MPa at higher temperatures. At the sufficiently high temperature, samples consolidate however with the presence of crystalline phases.

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4. Conclusions

1. The $Cu_{68.5}Ni_{12}P_{19.5}$ melt spun amorphous alloy has the glass transition temperature T_g = 452K, crystallization onset temperature T_x = 459K, and supercooled liquid region ΔT_x = 7K. Crystallization sequence consists of three peaks T_1 = 499K, T_2 = 543K and T_3 = 562K. The crystalline phases were observed by X-ray diffraction at 503K. It was possible to identify copper based fcc solid solution and $(Cu, Ni)_3P$ phosphide phase.
2. Temperature influences the compression σ-ε characteristic of the $Cu_{68.5}Ni_{12}P_{19.5}$ amorphous alloy. The largest stress is required to deform the sample at 423K. For the higher test temperatures i.e.: 473K, 523K, 573K and 623K the deformation of the alloy is easier which is confirmed by decrease of the stress required to deform the sample.
3. At 623K we obtained the complete consolidation of the samples with a distinct plastic deformation of the ribbons during the compression.

Acknowledgements

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