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The microstructure and mechanical properties of $Ni_{78}Ag_2P_{20}$ alloy

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ABSTRACT

Purpose: The aim of the work was to investigate the influence of silver as a modifying constituent on structure formation in Ni-P based glass forming matrix and to characterize mechanical properties of the alloys.

Design/methodology/approach: Nickel-silver-phosphorus $Ni_{78}Ag_2P_{20}$ alloy was produced using arc melting in argon protective atmosphere from commercial powders. The alloy was melt spun. The microstructure of the arc melted droplet is investigated in scanning electron microscope with EDS and micro-hardness tester and the melt spun ribbon is investigated using light microscope and transmission electron microscope. Then the mechanical properties are evaluated with use of micro-hardness measurements.

Findings: A strong tendency for demixing of Ni-P-rich and Ag-rich liquids is observed leading to formation of the primary structure consisting of slightly hypo-eutectic Ni-P-rich regions and Ag rich regions. The melt spinning process produced the amorphous Ni-P and Ag-rich crystalline structure. The alloys hardness and elasticity modulus were characterized. The melt spun ribbons are slightly softer than the crystalline Ni-P regions. In case of the melt spun ribbons, a softening influence of silver was observed giving the lower hardness for $Ni_{78}Ag_2P_{20}$ than $Ni_{80}P_{20}$. The alloy constituents in a bulk crystalline state present the higher values of elasticity modulus when compared to the melt spun ribbons.

Research limitations/implications: It has been shown that the criterion of a high positive values of mixing enthalpies can be applied to design the materials that should separate before the solidification to form a hard glassy matrix / soft crystalline composite. The amorphization of the crystalline Ni-P-based alloys can lead to formation of more flexible materials with a lower elasticity modulus and lower hardness.

Practical implications: The main limits for application of the glassy alloys are the high prices of the materials used for alloying and the low plasticity of the amorphous metals. Therefore, the work provides the alloy produced from a low-cost commercial purity precursors that are able to form a glassy matrix composite with a crystalline soft particles included. The future works on the development of the idea can lead to a successful manufacturing of a hard and ductile metallic composite parts.

Originality/value: The work delivers a new information on possibility of amorphous/crystalline composite formation starting from Ni Ag P system. This includes the original microstructural and mechanical characteristics of the arc melt and melt spun alloy. The information could be used by researchers for future works on development of Ni-P based composites complementary to the electroless coatings.

Keywords: Mechanical properties; Amorphous materials; Immiscibility; Arc melting; Melt spinning

PROPERTIES

1. Introduction

The amorphous alloys as a new group of prospective materials due to their superior properties very often better than those found in the traditional materials. Amorphous metallic alloys with excellent properties have been designed and produced in Ni-, Ti-, Zr, and Fe-based systems [1-6]. Unfortunately, the limits for application of the most glass forming alloys are requirements for a high purity, high prices of the precursors and low plasticity of the amorphous matrix. A possibility to lower the cost of the manufacture is using the cheaper precursors. However, in order to improve the plastic deformation behavior, composite materials were recently developed consisting of an amorphous matrix and a ductile body-centered cubic-type phase formed by primary crystallization [7, 8]. The feature required for the formation of a two-phased amorphous/crystalline composite is a good glass forming ability of one component and a demixing tendency of the two liquids. It is known that some Ni-P-based and Cu-P-based systems [9, 10] are able to form amorphous structures upon cooling. This does not require a high purity precursors and they can be vitrified relatively easily in the form of ribbons. On the other hand, the available thermodynamic data [11] allow expectations about possible separation of liquids in the Ni-Ag-P system. And this suggests a possibility that the liquids provide the structural constituents that fulfill the above mentioned requirements about the amorphous matrix and a crystalline fcc phase. Therefore, the aim of the work was to study whether it is possible to form such a composite starting from a commercial purity precursors and using a simple and well-known melt spinning technique and to provide some data about the mechanical properties of the material.

2. Experimental

Nickel-silver-phosphorus $Ni_{78}Ag_2P_{20}$ and nickel-phosphorus $Ni_{80}P_{20}$ alloys were prepared starting from commercial powders of 99.95 wt % Ni, 99.95 wt % Ag, 98 wt % P. The powders were mixed, compacted and remelted in arc furnace with argon gettered protective atmosphere. After cutting, grinding and polishing cross-section of the arc melted droplet of the $Ni_{78}Ag_2P_{20}$ alloy its primary microstructure was observed in PHILIPS XL30 scanning electron microscope with EDS (SEM). Then the $Ni_{78}Ag_2P_{20}$ alloy and the reference $Ni_{80}P_{20}$ alloy were modified through the melt spinning method. Then the microstructure observations was made with use of OLYMPUS GX51 optical microscope and PHILIPS CM20 200kV transmission electron microscope. Next the mechanical properties using CSM Instruments nano-scratch Berkovich tester micro-hardness tester were investigated.

3. Results

The results of microstructure examination of the arc melted droplet is presented on Fig. 1. The primary $Ni_{78}Ag_2P_{20}$ alloy microstructure consists of the slightly hypo-eutectic matrix and silver rich spherical particles. The eutectic consists of the nickel phosphide with the chemical composition corresponding to Ni_3P and Ni-based solid solution containing 1.84%at. P. The primary dendrites are also formed by Ni-based solid solution. The results of the microstructue analysis are consistent with the available data about the heats of mixing for liquid binary nickel alloys $\Delta H^{mix}_{\{NiX\}}$ [11]. The value of $\Delta H^{mix}_{\{NiAg\}}$ is +15 $[kJ/mole]$ and the value of $\Delta H^{mix}_{\{NiP\}}$ -26 $[kJ/mole]$. Thus, due to the relatively high positive enthalpy of mixing $\Delta H^{mix}_{\{NiAg\}}$ the immiscibility of Ni-rich and Ag-rich liquids can be expected. There is no available data on $\Delta H^{mix}_{\{AgP\}}$. However, the fact that we observed formation of the phosphide with the chemical composition close to Ni_3P and that we found no silver phosphides may suggest that the most of phosporus is attracted by the Ni-rich slightly hypo-eutectic liquid (that can be transformed into a glass matrix). This in turn, suggest that $\Delta H^{mix}_{\{AgP\}}$ may be higher than $\Delta H^{mix}_{\{NiP\}}$ and possibly higher than $\Delta H^{mix}_{\{NiAg\}}$. In fact, we observe the silver-rich regions containing 96.52at.% of silver and 3.48at.% of nickel with apparently no phosphorus. The result is consistent with the information from Ag-P binary diagram [12].
The right hand corner of the Fig. 1 shows well the differences between the micro-hardness Ag-rich regions and eutectic Ni-P regions of the droplet .

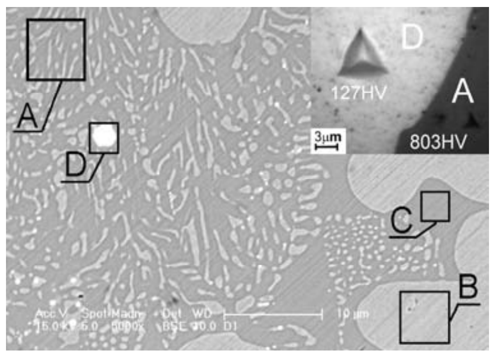

Fig. 1. SEM primary microstructure of the arc melted droplet; exemplary EDS analysis for the structure constituents: A – 80.06at.% Ni, 19.94at.% P; B – 98.16at.% Ni, 1.84at.% P; C – 74.29at.% Ni, 25.71at.% P; D – 96.52at.% Ag, 3.48at.% Ni; micro-hardness indentations in the Ni-P-rich and Ag-rich regions

The typical microstructure of the melt spun ribbon is presented on Fig. 2a and Fig. 2d for longitudinal section and cross section, respectively. This consists of a featureless bright matrix containing fine spherullitic grains. The spherullitic particle size distribution revealed for the magnifications of the optical microscope (see Fig. 2b) gave the average particle size of 2.02±0.81μm. The few regions containing more massive spherullitic colonies allowed the hardness measurement of the two structural components. The typical microhardness indentations presented on Fig. 2c show that the spherullitic particles are substantially softer that the matrix. The TEM microstructure of the melt spun ribbon presented on Fig. 3 consists of the featureless amorphous regions that form the matrix of the alloy and the crystalline particles. The diffraction pattern presents a broad diffusive rings typical for an amorphous materials and a dot pattern identified as a crystalline silver-base solid solution. With reference to the mentioned above remark about immiscibility, it was possible in the present work to obtain the crystalline spherullites within the amorhous matrix, during the melt spinning, probably due to the separation of liquids into the Ag-rich and the glass forming Ni-P-rich.

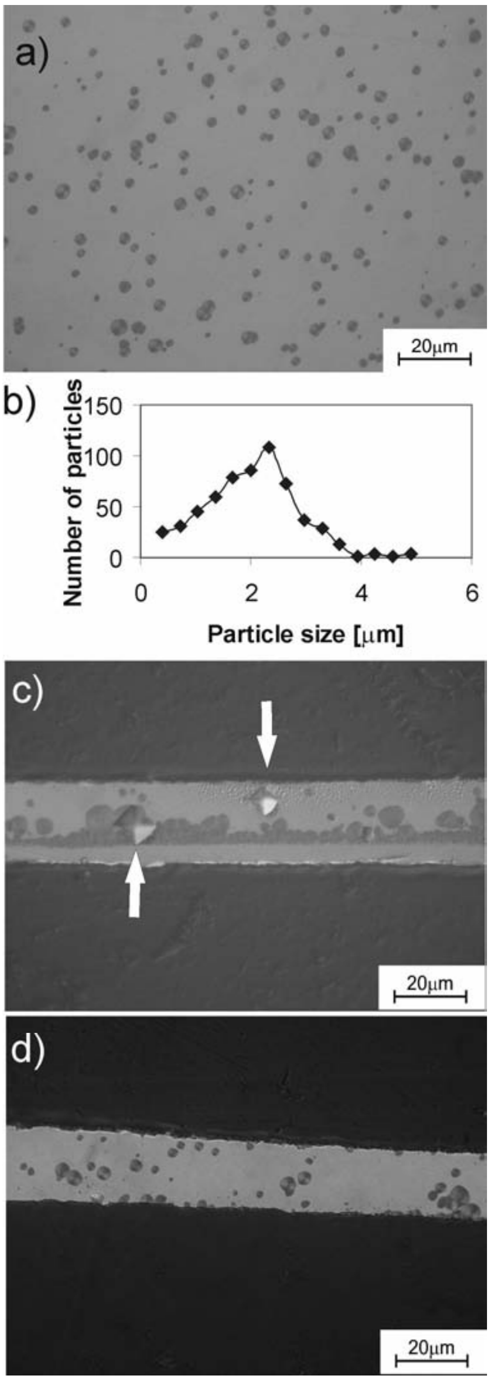

Fig. 2. The typical microstructure of the melt spun ribbon; a) longitudinal section, b) particle size distribution of the spherullitic grains, c) cross-section, d) massive colonies of spherullitic grains in the amorphous matrix with Vickers indenter traces

The plots of indentation force (F_n) versus displacement (P_d) for a nano-indentation test using 100 mN and the values of Young modulus and Vickers hardness are presented on Fig. 4. Comparison between the results shows that in the case of the bulk crystalline samples the Ni-P eutectic constituent is the hardest microstructure constituent presented in the present study (803HV). The hardness values for the crystalline Ni-P matrix are even higher that the maximum hardness obtained for the electroless alloys of the similar composition by Bay and Hu [13-15]. However, the values of the hardness values can vary significantly from 200HV to over 1000HV depending on phosphorus content, deposition bath, and temperature of heat treatment [13, 16-18]. On the other hand silver-rich constituent presents the hardness value on the level of 127HV. This value is relatively high, taking into consideration that the hardness of pure polycrystalline silver corresponds to 26HV [19]. But it is worth to note, that the silver-base solid solution tested in the present work contains 3,48at.% Ni and the droplets after the arc melting are cooled at ca. 100K/s and formation of fine crystals could be favored. On the other hand, the hardness values even for pure Ag can be substantially higher e.g.: 92HV when formation of nano-crystals is observed [20]. The melt spun ribbons have the hardness values slightly lower than the crystalline Ni-P constituent i.e.: 624HV and 721HV $Ni_{78}Ag_2P_{20}$ and $Ni_{80}P_{20}$, respectively. The lower value of hardness observed in $Ni_{78}Ag_2P_{20}$ than in $Ni_{80}P_{20}$ can be attributed to the softening influence of silver addition. It is worth to note that the alloy constituents in a bulk crystalline state present the higher values of elasticity modulus (i.e.: 208 GPa for Ni-P eutectic and 113 GPa for silver-rich solid solution) than it is observed in the melt spun $Ni_{78}Ag_2P_{20}$ and $Ni_{80}P_{20}$ ribbons. The elasticity modulus for the amorphous electroless Ni-P alloys containing ca. 20at.%P was found to be 70GPa [13]. Therefore, this is close to the elasticity modulus 64GPa obtained for the $Ni_{80}P_{20}$ melt spun alloy in the present work. Further, the melt spun $Ni_{78}Ag_2P_{20}$ ribbon has a slightly higher vale of elasticity modulus (85GPa), which can be attributed to the fact that it contains Ag-rich crystalline particles of the higher elasticity modulus probably very close to 113GPa – the value observed for the bulk crystalline samples.

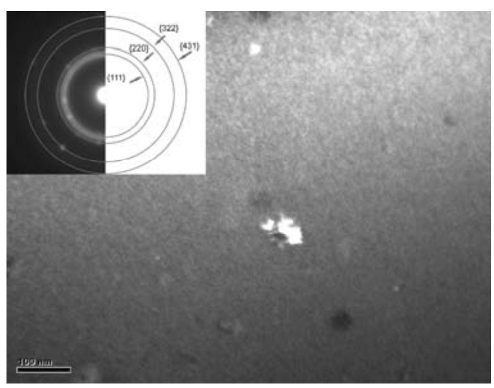

Fig. 3. TEM microstructure with diffraction pattern. Ag-rich particles included in amorphous matrix

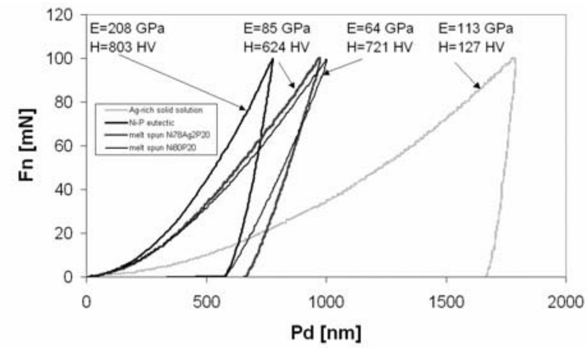

Fig. 4. Indentation curves with Young modulus and hardness results for Ag-rich crystalline solid solution, Ni-P base crystalline matrix, melt spun $Ni_{80}P_{20}$ amorphous alloy, melt spun $Ni_{78}Ag_2P_{20}$ amorphous/crystalline composite

4. Conclusions

1. The solid state microstructure both the droplet and the amorphous/crystalline ribbons of the $Ni_{78}Ag_2P_{20}$ alloy results from the tendency of the alloy for separation into Ni-P-rich and Ag-liquids. This may be explained by the relatively high positive enthalpies of mixing $\Delta H^{mix}_{\{AgX\}}$ for Ag-Ni and probably for Ag-P liquids.
2. The primary microstructure of the $Ni_{78}Ag_2P_{20}$ alloy has the slightly hypo-eutectic matrix and silver rich spherical particles where the eutectic constituent consists of Ni_3P nickel phosphide and Ni-based solid solution. The hypo-eutectic primary dendrites are formed by Ni-based solid solution.
3. The bulk crystalline Ni-P eutectic constituent is a hard constituent of the primary structure with a hardness on the level of 803HV. The silver-rich constituent is the softest constituent with hardness on a level of 127HV, possibly caused by formation of Ag-rich nanocrystals.
4. The microstructure of the $Ni_{78}Ag_2P_{20}$ melt spun ribbon is formed by an amorphous matrix and the crystalline silver reach particles. The spherullitic particle size has the average particle size of $2.02\pm0.81\mu m$.
5. The melt spun ribbons are slightly softer than the crystalline Ni-P constituent (803HV) i.e.: 624HV and 721HV for $Ni_{78}Ag_2P_{20}$ and $Ni_{80}P_{20}$, respectively. The lower value of hardness in $Ni_{78}Ag_2P_{20}$ than in $Ni_{80}P_{20}$ can be attributed to the softening influence of silver.
6. The alloy constituents in a bulk crystalline state present the higher values of elasticity modulus i.e.: 208 GPa for Ni-P eutectic and 113 GPa for silver-rich constituent, than in the melt spun $Ni_{78}Ag_2P_{20}$ and $Ni_{80}P_{20}$ alloys.
7. The $Ni_{78}Ag_2P_{20}$ melt spun alloy has a slightly higher value of elasticity modulus than $Ni_{80}P_{20}$ alloy, probably because it contains Ag-rich crystalline particles of a higher Young modulus.

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