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COOLING CHARACTERISTIC AND MICROSTRUCTURE OF Ni-Si-B-Ag ALLOY

The aim of this work was to investigate the possibility of obtaining an amorphous/crystalline composite starting from Ni-Si-B-based powder grade 1559-40 and silver powder. The alloy was produced using arc melting of 95% wt. Ni-Si-B-based powder (1559-40) and 5% wt. Ag powder. Ingot was re-melted on a copper plate and observed while cooling using a mid-wave infra-red camera. The alloy was then melt-spun in a helium atmosphere. The microstructure of the ingot as well as the melt-spun ribbon was studied using light microscopy and scanning electron microscopy with energy dispersive spectrometry. Phase identification was performed by means of X-ray diffraction. The observations confirmed an amorphous/crystalline microstructure of the ribbon where the predominant constituent of the microstructure was an amorphous phase enriched with Ni, Si, and B, while the minor constituent was an Ag-rich crystalline phase distributed in a film along the melt-spinning direction.

Keywords: Amorphous/crystalline composite; Scanning electron microscopy; X-ray diffraction; Thermography; Melt spinning

1. Introduction

Metallic glasses are a valued engineering material, mainly due to high elasticity, strength and special magnetic and electric properties [1]. Nevertheless, the main problem while using them as structural applications is the lack of plasticity [2]. One of the possibilities to improve ductility in these materials is producing glass-matrix composites. Recent reports have discussed the formation of two-phased glassy composites in Ni-Ag-P [3], Fe-Cu-Si-B-Nb [4], Ag-Cu-Zr-Al [5], Ag-Ni-Nb [6] or many others. In these, alloys are produced using immiscibility occurring between the elements.

Ni-Si-B-based alloys present a good glass-forming ability (GFA) and mechanical properties [7,8]. However, the addition of Ag to the Ni-based alloy can cause immiscibility in the liquid state, which in turn can reduce the glass-forming ability. Immiscibility in the Ni-Ag system also provides an opportunity for obtaining a composite with silver precipitates in the amorphous Ni-based matrix [3].

This work aims at investigating the possibility of obtaining an amorphous/crystalline composite starting from Ni-Si-B-based powder grade 1559-40 alloy and silver powder and examining its microstructure and phase composition.

TABLE 1

Specification of Ni-Si-B-based 1559-40 grade powder

Particle size, μm	Chemical composition, wt.%				
	C	Si	B	Fe	Ni
53–150	≤0.06	3.0	2.9	0.2	balance

2. Experimental

Chemical composition of Ni-Si-B-Ag alloy was $Ni_{86.75}Si_{2.8}B_{2.7}Fe_{0.2}C_{0.05}Ag_{7.5}$. The mixture of 95 wt. % Ni-Si-B-based commercial 1559-40 grade powder produced by Höganäs and 5 wt.% of silver powder (particle diameter <63 μm) produced by INMET was arc-melted under argon titanium-gettered atmosphere. The specification of 1559-40 powder is presented in Table 1. The $Ni_{86.75}Si_{2.8}B_{2.7}Fe_{0.2}C_{0.05}Ag_{7.5}$ alloy was named Ni-Si-B-Ag in an article.

The cross-section microstructure of the ingot was investigated by Olympus-GX51 light microscope and JEOL 6610 scanning electron microscope (SEM) with energy dispersive spectrometer (EDS). The 2 g ingot was re-melted in the arc furnace and observed with an MWIR FLIR SC7650 camera while it cooled on a copper plate. The sample-to-camera distance was 200 mm. The process was observed through a high transmission CaF_2 window, the room temperature was 25°C. The areas for temperature measurement were selected in order to avoid the narcissus effect and reflection of the hot tungsten electrode.

The Ni-Si-B-based and Ni-Si-B-Ag alloys were melt-spun in a helium atmosphere with a linear velocity of 33 m/s, an ejection pressure of 150 kPa, a crucible and hole diameter of 0.7 mm. The melt-spun temperatures of the Ni-Si-B-Ag ribbon

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were 1250°C and 1390°C. The cross-section microstructure and chemical composition of the Ni-Si-B-Ag ribbon ejected at 1250°C was studied by JEOL 6610 scanning electron microscope (SEM) with EDS analyzer. X-ray diffractions of the ingot and ribbons ware performed using a Rigaku Miniflex-2 diffractometer with CuKα radiation filtered by a LiF bent single crystal on the detector side. The scattering angle 2θ varied between 20° and 90° degrees.

3. Results and discussion

Figure 1 presents results of light microscopy (Fig. 1a) and scanning electron microscopy observations with EDS analysis (Fig. 1b) of the cross-section microstructure of Ni-Si-B-Ag ingot. Brighter areas on EDS maps represent the areas enriched with Ni, Ag, or Si. Microstructure of Ni-Si-B-Ag ingot basically consists of brighter globular precipitations within the darker eutectic matrix (Fig. 1a). EDS mapping (Fig. 1b) indicates that the globular areas were Ag-rich and matrix mainly consists of nickel-based constituents.

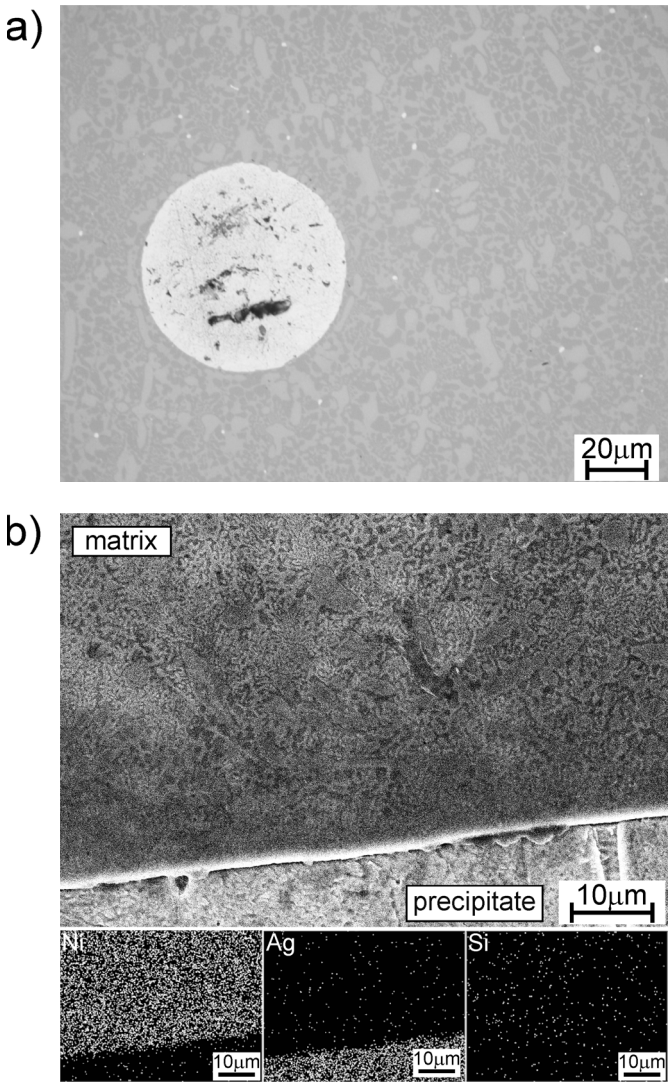

Fig. 1. Microstructure of Ni-Si-B-Ag ingot; a) LM image; b) SEM image with results of EDS analysis for Ni, Ag and Si

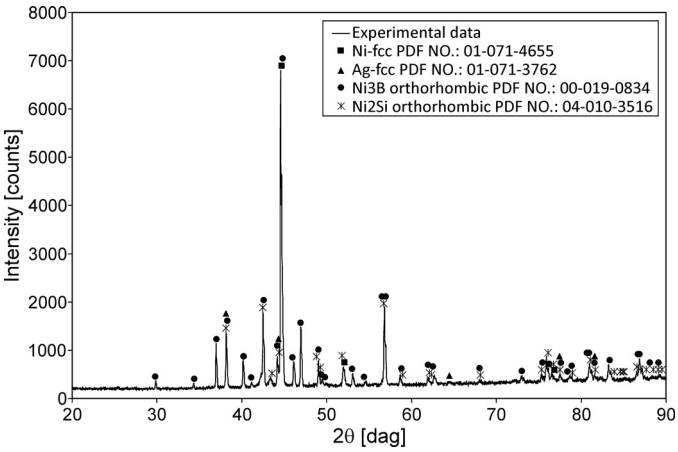

Fig. 2. X-ray diffraction pattern of the Ni-Si-B-Ag arc-melted ingot

The XRD pattern for the arc-melted ingot are shown in Figure 2. The XRD peaks observed on the diffraction can be attributed to four crystalline phases: the fcc Ag-based solid solution (PDF NO. 01-071-3762), the fcc Ni-based solid solution (PDF NO. 01-071-4655), the orthorhombic Ni_3B compound (PDF NO. 00-019-0834) and the orthorhombic Ni_2Si compound (PDF NO. 04-010-3516).

Through comparison of the microscopic observations and the XRD measurements, it can be assumed that the microstructure of the ingot consists of fcc Ag-based precipitates and a fine eutectic matrix i.e. the three crystalline phases such as the fcc Ni-based solid solution and compounds isomorphic with the orthorhombic Ni_3B and Ni_2Si compounds.

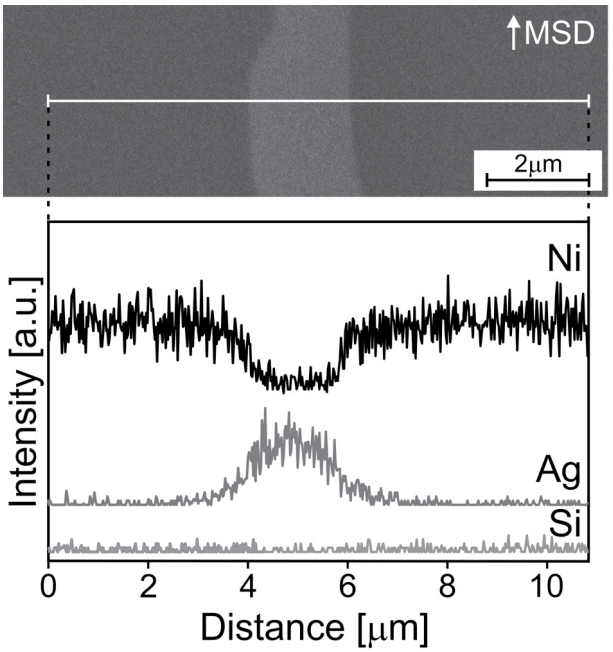

Fig. 3. Cross-section microstructure of Ni-Si-B-Ag amorphous/crystalline composite ejected at 1250°C with EDS profiles of Ni, Ag and Si, MSD – melt-spinning direction

Observation of cross-section microstructure and the results of EDS line scan of Ni-Si-B-Ag ribbon ejected at 1250°C are pre-

sented in Figure 3. Microstructure of Ni-Si-B-Ag ribbon consists of matrix (dark region) and lamellar precipitation (bright area). The results of EDS analysis show that matrix consists mostly of Ni-based constituents and Ag-rich precipitates.

Alloying the Ni-Si-B composition with Ag results in occurrence of liquid immiscibility between nickel and silver. Immiscibility can be affected by a number of factors, but the most important of them is the enthalpy of mixing occurring between the elements. The values of mixing enthalpy for analyzed system were presented in Table 2. The high positive enthalpy between Ni and Ag (ΔH^{mix} = 15 kJ mol^{-1}) and the high affinity of Si and B to Ni (ΔH^{mix} = –23 kJ mol^{-1} and ΔH^{mix} = –24 kJ mol^{-1}) resulted in the Ag-rich precipitates formed as results of liquid immiscibility. The silicon distribution is homogeneous both in the matrix and in the Ag-rich precipitates. In turn, boron distribution due to experimental problems was not included in the results of the EDS analysis. However, on the basis of the Ag-B phase equilibrium system [9], it can be concluded that Ag and B are immiscible elements in liquid state and B is located in an Ni-based matrix.

TABLE 2

Calculated enthalpies of mixing ΔH^{mix} for equiatomic liquids containing Ni, Si, B and Ag in binary systems, kJ mol^{-1} [10]

	Ni	**Si**	**B**	**Ag**
Ni	—	–23	–24	+15
Si		—	+3	–3
B			—	+5

Figure 4a shows a sequence of infra-red images taken while the ingot was cooled after arc melting on a copper plate. These snapshots are presented for six values of time elapsed since beginning of cooling: t = 0 s, t = 0.04 s, t = 0.2 s, t = 0.52 s, t = 0.8 s, t = 1.61 s. The Figure 4b presents the temperature change in the two circular areas – 'A' and 'B' indicated in Figure 4a.

The alloy is in the liquid state for t = 0 s, t = 0.04 s. The sequence of images clearly shows the difference in the shape of the ingot between the first two images and the other. It is possible to observe a clear division into two liquids on the surface of the ingot. The brighter area of the ingot corresponds to the major component and it can be assumed that it is a Ni-based liquid. The Ag-rich liquid is also clearly visible on the surface of the sample. It is a darker area located at the bottom right side of the sample, this area apparently increases with time. Taking into account the high density of silver (10.49 g/cm^3) compared to nickel (8.9 g/cm^3), or an Ni-based compounds such as Ni_3Si (8.17 g/cm^3) or Ni_3B (8.2 g/cm^3), it can be assumed that the location of the heavier Ag-rich liquid at bottom right side of the sample is due to the gravitational segregation. The upper part of the sample remains liquid until t = 0.2 s.

Eutectic crystallization in Ni-Si and Ni-B binary systems takes place at near 1100°C [9], therefore the thermal effect associated with crystallization (Fig. 4b) can be attributed to the eutectic transformation because the effect observed in areas 'A' and 'B' occurs at a similar temperature, i.e.: 1106°C and 1030°C, respectively. However, the subsequent thermal effects in temperature T_{Ag} = 960°C and T_{Ag} = 807°C indicated on curve 'A' and 'B' (respectively) can be attributed to the crystallization of Ag-based solid solution. For area 'A' we observe a relatively small effect, which is related to the fact that most of the Ag-rich liquid is located in the bottom of the ingot. On the other hand, the lower values of eutectic crystallization temperature and silver crystallization temperature observed in area 'B' are associated with higher undercooling of the bottom part of the ingot, which was intensively cooled by a copper plate.

The XRD patterns recorded for Ni-Si-B-Ag and Ni-Si-B-based ribbons are shown in Figure 5. The Ni-Si-B-Ag composite ribbons are melt-spun from two temperatures: 1390°C and 1250°C. The broad and shallow peaks observed between 40° and 50° recorded for all presented patterns are due to scattering in the amorphous matrix of the alloys. The XRD peaks observed of Ni-Si-B-based ribbon have a very low intensity and they can

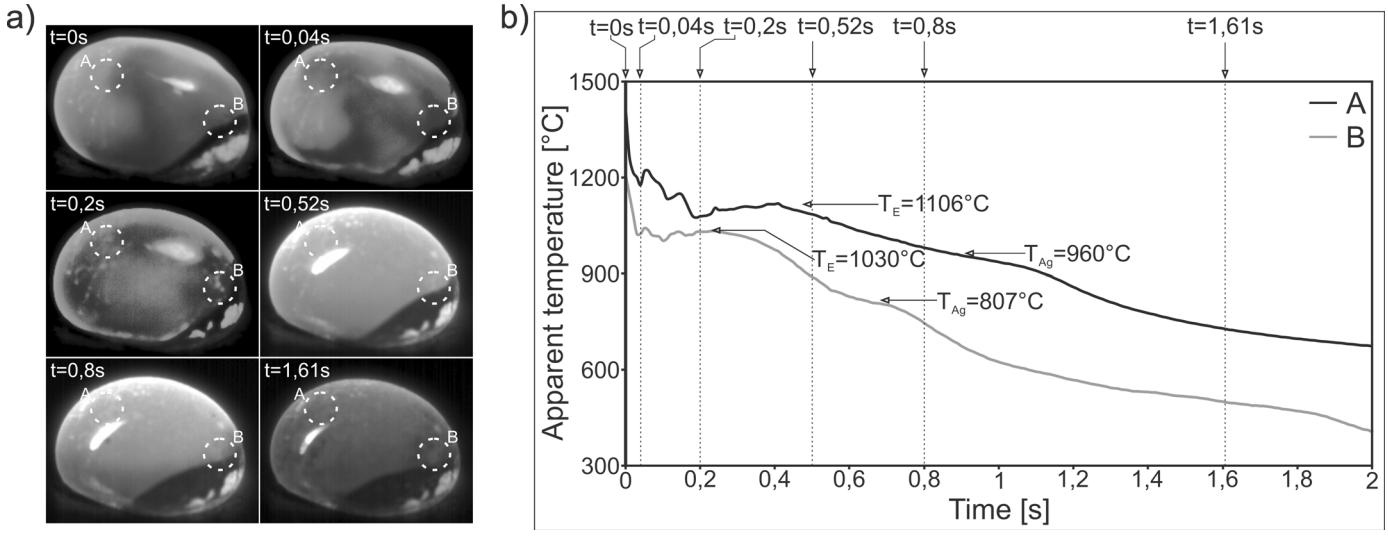

Fig. 4. Course of free cooling of Ni-Si-B-Ag alloy on two areas of arc-melted ingot; a) IR images; b) cooling curves from areas "A" and "B"

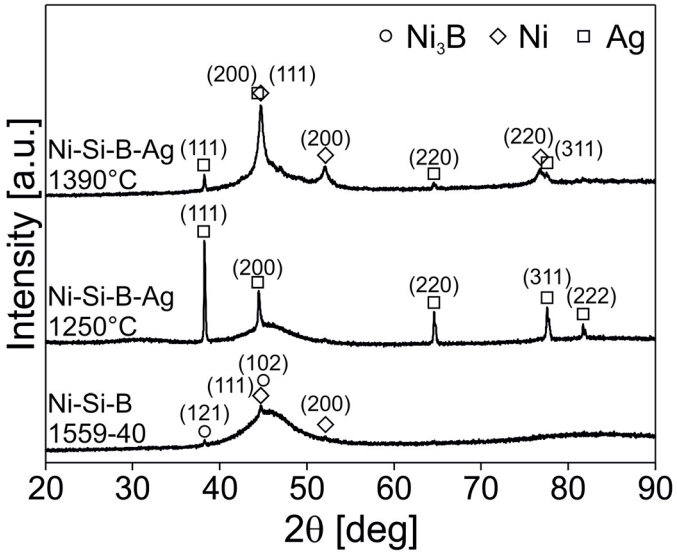

Fig. 5. XRD patterns of Ni-Si-B-Ag ribbon melt-spun from 1390°C and 1250°C and Ni-Si-B ribbon

be attributed to two crystalline phases: the fcc Ni-based solid solution (PDF no. 01-071-4655) and the orthorhombic Ni_3B compound (PDF no. 00-019-0834). The peaks observed on the diffraction patterns for Ni-Si-B-Ag composite ribbons can be attributed to the two crystalline phases: the fcc Ni-based solid solution (PDF no. 01-071-4655) and the fcc Ag-based solid solution (PDF no. 01-087-0718). On the XRD pattern presented for composite ribbons melt-spun from 1250°C there are peaks near the values corresponding to the fcc Ag-based solid solution. However, for the XRD pattern of the ribbon melt-spun from higher temperature there are also peaks that can be attributed to the Ni-based solid solution.

4. Conclusions

1. The Ni-Si-B-Ag alloy presents liquid immiscibility. The Ag in the Ni-Si-B-Ag alloy presents a strong tendency for gravitational segregation, sinking down to the bottom of the ingot. However, the majority of the Ni-Si-B-Ag alloy crystallizes as a Ni-rich eutectic component at near 1100°C.
2. Microstructure of Ni-Si-B-Ag ingot consisted of the eutectic matrix enriched in nickel with globular Ag-rich precipitations. However the cross-section microstructure of the Ni-Si-B-Ag composite ribbon consisted of the Ni-rich matrix and the Ag-rich lamellar precipitation.
3. The phase composition of the Ni-Si-B-Ag composite ribbon ejected at 1250°C consisted of the amorphous Ni-rich phase and the Ag-rich (FCC) crystalline precipitation. The occurrence of amorphous constituent in the Ni-Si-B-Ag alloy was due to the high glass-forming ability of the Ni-rich eutectic.

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REFERENCES

[1] M.F. Ashby, A.L. Greer, Scripta Materialia **54**, 321-326 (2006).
[2] Y. Zhang, Materials Science and Technology **24** (4), 379-391 (2008).
[3] K. Ziewiec, Journal of Non-Crystalline Solids **355** (52-54), 2540-2543 (2009).
[4] T. Kozieł, J. Latuch, S. Kąc, Journal of Alloys and Compounds **586**, S121-S125 (2014).
[5] A. Castellero, G. Angella, M. Vedani, M. Baricco, Journal of Alloys and Compounds **586**, S111-S116 (2014).
[6] J. He, H. Jiang, S. Chen, J. Zhao, L. Zhao, Journal of Non-Crystalline Solids **357** (21), 3561-3564 (2011).
[7] B. Shen, A. Inoue, Materials Transactions **44** (7), 1425-1428 (2003).
[8] I.W. Donald, H.A. Davies, Journal of Material Science **15**, 2754-2760 (1980).
[9] T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak, Binary Phase Diagrams, Second Edition, ASM International, USA 1990.
[10] A. Takeuchi, A. Inoue, Intermetallics **18** (9), 1779-1789 (2010).