

Influence of the chemical composition of rapidly quenched amorphous alloys (Ni, Fe, Cr)-B-Si on its crystallization process

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Abstract. This paper presents results of research of the structure and phase transformations during the multistage crystallization of the metallic glasses with the compositions $\text{Ni}_{71.5}\text{Cr}_{6.8}\text{Fe}_{2.7}\text{B}_{11.9}\text{Si}_{7.1}$ and $\text{Ni}_{63.4}\text{Cr}_{7.4}\text{Fe}_{4.3}\text{Mn}_{0.8}\text{B}_{15.6}\text{Si}_{8.5}$ labeled as AWS BNi-2 according to American Welding Society. Differential scanning calorimetry (DSC), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX) were used as experimental research methods. The influence of the alloys chemical composition (boron, manganese and iron) on the temperatures and the exothermic heat effects of phase transformations, as well as on the phase composition of alloys at three stages of crystallization was analyzed. We present a thermodynamic explanation of the observed heat effects. It has been shown that manganese has the main influence on the phase transformations temperatures and heat effects in these two alloys. It is also assumed that at the final crystallization stage simultaneously with the formation of phases Ni_3B and $\beta_1\text{-Ni}_3\text{Si}$ should occur the nucleation of borides of CrB type with high Cr and low Si content.

1. Introduction

Alloys based on the ternary system Ni-Si-B (AWS BNi-2) in crystalline and amorphous states are widely used as a brazing alloys and corrosion-resistant coatings. It is known [1-4], that crystallization of amorphous BNi-2 alloys proceeds in three stages: the first stage of crystallization (450–500°C) is associated with the formation of solid solution crystals based on nickel ($\alpha\text{-Ni}$). The second stage (500–550°C) is associated with the formation of a metastable τ -phase with M_{23}B_6 -type structure. At the final stage (550–650°C), the formation of Ni_3B and Ni_3Si [2, 4] or $\text{Ni}_{31}\text{Si}_{12}$ [1] as a result of the decomposition of τ -phase was reported. It should be noted that other authors observed another phases in BNi-2 alloys [3]: Ni_4B_3 , CrB, $\text{B}_2\text{Fe}_{15}\text{Si}_3$, CrSi_2 and $\text{Ni}_{45}\text{Si}_2\text{B}$ [5]; Ni_2B , Ni_3Si_2 and $\text{Fe}_3(\text{Si},\text{B})$. Data obtained for the phase composition of such alloys produced by crystallization from the amorphous state, as well as data on the temperatures and heat effects of the phase transformations are slightly different due to different chemical compositions of the investigated BNi-2 alloys.

Therefore, a purpose of this work is to explore the influence of the chemical composition of the alloys on their phase composition at all stages of crystallization, as well as on the temperatures and the exothermic heat effects of phase transformations.



2. Materials and Experimental Methods

The amorphous alloys in the form of tapes with a thickness of 40–50 μm with two similar to BNi-2 compositions $\text{Ni}_{71,5}\text{Cr}_{6,8}\text{Fe}_{2,7}\text{B}_{11,9}\text{Si}_{7,1}$ (STEMET[®] 1301A) and $\text{Ni}_{63,4}\text{Cr}_{7,4}\text{Fe}_{4,3}\text{Mn}_{0,8}\text{B}_{15,6}\text{Si}_{8,5}$ (STEMET[®] 1301) (hereinafter referred to as 1301A and 1301) were produced by the rapid solidification techniques [6]. The main difference between alloys is the content of boron, manganese and iron. Crystallization process of the amorphous alloys was carried out in a vacuum furnace with heating rate of 20°C/min.

Differential scanning calorimetric (DSC) analysis of alloys was performed using the Netzsch STA409CD calorimeter. The samples of the amorphous alloys weighing approximately 20 mg were heated in the scanning calorimeter at a heating rate of 20°C/min under a purified argon atmosphere.

X-ray diffraction phase analysis (XRD) was carried out by means of DRON-3M and D8 DISCOVER (Bruker) at CuK_α -radiation using crystallographic database ICDD PDF-2 and software Bruker AXS DIFFRAC.EVA. Determination of the chemical composition of the phases formed during crystallization was carried out using the scanning electron microscope (SEM) EVO 50 XVP (Zeiss) with an energy-dispersive X-ray microanalysis spectrometer (EDX) INCA x-act (Oxford Instruments).

3. Results and Discussion

The results of differential scanning calorimetry of 1301A and 1301 alloys are presented on figure 1 (curves 1 and 2 respectively). This figure also shows the DSC curve 3 for alloy of similar composition ($\text{Ni}_{64,4}\text{Fe}_4\text{Cr}_{4,9}\text{Mn}_2\text{B}_{16,2}\text{C}_{0,5}\text{Si}_8$), presented in [1]. It can be seen that curves differ significantly despite the similarity of the compositions of these three alloys. Primary crystallization of 1301 compared to 1301A alloy begins at a slightly higher temperature, while the temperature of formation of τ -phase is below it. Thus, the first and second peaks on the DSC curve of the alloy 1301 are partially overlapped. For the third alloy ($\text{Ni}_{64,8}\text{Cr}_{4,9}\text{Fe}_{4,0}\text{Mn}_2\text{B}_{16,2}\text{Si}_8\text{C}_{0,5}$) this overlap is considerably more visible. Overlapping of the first and second crystallization peaks means that the formation of α -Ni and τ -phase crystals occurs substantially simultaneously.

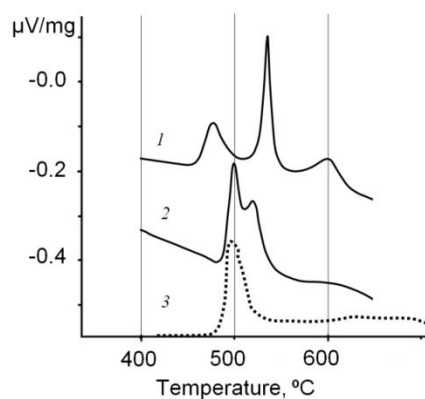


Figure 1. DSC curves of alloys: 1 - 1301A; 2 - 1301; 3 - $\text{Ni}_{64,8}\text{Cr}_{4,9}\text{Fe}_{4,0}\text{Mn}_2\text{B}_{16,2}\text{Si}_8\text{C}_{0,5}$ [1].

Table 1 presents data on the temperatures of the three most high heat peaks (T_1 , T_2 , T_3) on the DSC curves for different stages of crystallization of alloys 1301 and 1301A in comparison with the published data for other amorphous alloys with similar chemical composition. Because the available DSC data were obtained at the various heating rates of the samples, the values were given for the one heating rate (20 °C/min). For this purpose the data on the crystallization temperature dependence of the heating rate for the amorphous alloy $\text{Ni}_{65}\text{Cr}_{6,6}\text{Fe}_3\text{B}_{17,5}\text{Si}_{7,6}\text{C}_{0,3}$ for all three stages of the crystallization process were used [5].

Analysis of these data shows that at the beginning of the primary crystallization generally not boron content, but the amount of manganese and possibly iron affects temperature T_1 . Indeed, alloys No.2 and No.3, which contain a large amount of boron, iron and manganese as compared with other

samples have a maximum value of this temperature (close to 500°C). While sample No.6, which has the high boron content, but do not contain manganese and iron, has a primary crystallization temperature around 480 °C that is typical for the majority of alloys of this type. It also can be seen that alloys with manganese and possibly with increased iron content have the lower values of temperature T_2 and the higher temperature T_3 .

Table 1. Temperatures of highs for the heat peaks on the DSC-curves for three stages of crystallization.

№№	Alloy	Temperatures, °C			Reference
		T_1	T_2	T_3	
1	Ni _{71,5} Cr _{6,8} Fe _{2,7} B _{11,9} Si _{7,1}	478.4	535.5	597.1	our data
2	Ni _{63,4} Cr _{7,4} Fe _{4,3} Mn _{0,8} B _{15,6} Si _{8,5}	499.7	519.1	610	our data
3	Ni _{64,4} Cr _{4,9} Fe ₄ Mn ₂ B _{16,2} Si ₈ C _{0,5}	497.5	509	629	[1]
4	Ni _{69,1} Cr _{6,6} Fe _{2,7} B _{13,7} Si _{7,9}	482	517	583	[4]
5	Ni _{68,7} Cr _{6,6} Fe _{2,65} B ₁₄ Si _{7,8} C _{0,25}	472	520	582	[3]
6	Ni ₆₅ Cr _{6,6} Fe ₃ B _{17,5} Si _{7,6} C _{0,3}	480	525	600	[5]

Note that the relative and total heat effects for three crystallization stages of 1301 and 1301A alloys are approximately the same (table 2). As shown below the relative amount of phases in 1301A and 1301 alloys after the first and second stages are significantly different (the amount of α -Ni in 1301A is approximately 1.4–1.6 times higher, and amount of τ -phase is 1.1–1.3 times lower than in 1301). Thus, formation of the same amount of α -Ni phase in the alloy 1301A is accompanied by a less heat effect than in the alloy 1301, and a larger heat effect for τ -phase formation, respectively.

Table 2. Relative and total (per mole of alloy) heat effects of three crystallization stages

Process / Alloy	ΔH (conventional units)	
	1301	1301A
1 $A \rightarrow \alpha\text{-Ni} + A'$	0.31	0.30
2 $A' \rightarrow \tau$ ($M_{23}B_6$)	0.45	0.51
3 $\tau \rightarrow Ni_3B + Ni_3Si$	0.24	0.23
Σ	1.00	1.06

^a A and A' – amorphous phases of different composition

These results of DSC can be explained in terms of thermodynamics. The process of crystallization of the metal glasses is always exothermic and reduces its free energy ΔG . At the first crystallization stage a metastable equilibrium between the amorphous phase and the α -Ni crystal phase is established. The compositions of these phases are determined by the common tangent to the curves of Gibbs free energy dependence on boron concentration (figure 2).

It is known that manganese lowers the melting point of BNi-2 alloy (to 20°C at 2% of Mn) [1]. Therefore, the ΔG curve of the amorphous phase (supercooled liquid) should move down with the addition of manganese. Thus, increase of the manganese content in the amorphous alloy should lead to decrease of the thermodynamic stimulus of α -Ni phase nucleation and to the growth of the onset crystallization temperature.

Increase of the boron content in the amorphous alloy also reduces the thermodynamic factor. However, the crystallization temperature remains nearly unchanged. It can be explained by the fact that not only the thermodynamic, but also kinetic factor affects the nucleation rate. Kinetic factor is determined by the rate of the boron atoms transition through the boundary between crystalline and amorphous phase and increases with the boron concentration increase. Thermodynamic and kinetic

factors compensate each other with the change of the boron concentration, causing the temperature remains unchanged.

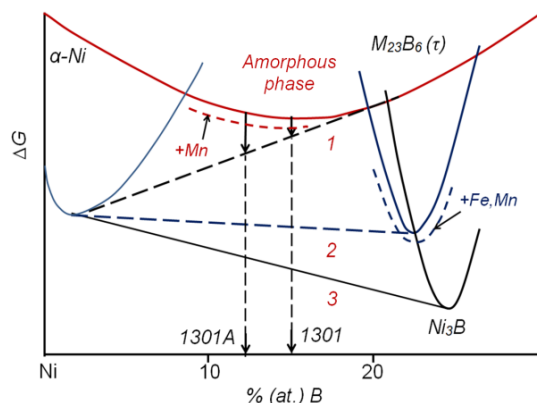


Figure 2. Hypothetical diagram of Gibbs free energy dependences on boron concentration for different phases and phase equilibria in the Ni – B binary system:

- 1 – metastable equilibrium of α -Ni and A;
- 2 – metastable equilibrium of α -Ni and τ -phase ;
- 3 – stable equilibrium of α -Ni and Ni_3B .

It should be noted that increase of the both boron and manganese concentration should reduce the heat effect of the first crystallization stage (per mole of α -Ni phase), because it reduces the difference of enthalpies of the crystalline and initial amorphous phase.

The estimation of the relative volume of the crystalline phase in the alloy 1301A after the first stage of crystallization was carried out. The XRD data from figure 3 and the formula $V_{cr} = I_{cr} / (I_{cr} + \alpha I_a)$, where I_{cr} and I_a – integrated intensities of reflections from the crystalline and amorphous phases, and α – constant (the Huang parameter), were used for this purpose. The values of α for similar alloys ($\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ and $\text{Fe}_{73.9}\text{B}_{13.2}\text{Si}_{10.9}\text{C}_2$) are known: $\alpha \approx 1.05$ and 0.77 [7]. The estimated volume and mole fractions of crystalline phase calculated using these parameters are (49-57) vol. % and (44-52) mol. %. Considering that the solubility of boron in α -Ni is negligible, the boron content in amorphous phase at the metastable equilibrium can be estimated as 21-25 at.%, that is close to τ -phase (M_{23}B_6) composition. On the second stage of crystallization, the formation of τ -phase occurs by the polymorphic transformation without significant change of α -Ni phase amount (Figure 4). In the alloy $\text{Ni}_{64.4}\text{Cr}_{4.9}\text{Fe}_4\text{Mn}_2\text{B}_{16.2}\text{Si}_{18}\text{C}_{0.5}$ with the composition close to 1301 alloy significantly greater amount of τ -phase have been formed (~ 65 vol. %) [1], which is in a good agreement with our data (figure 4).

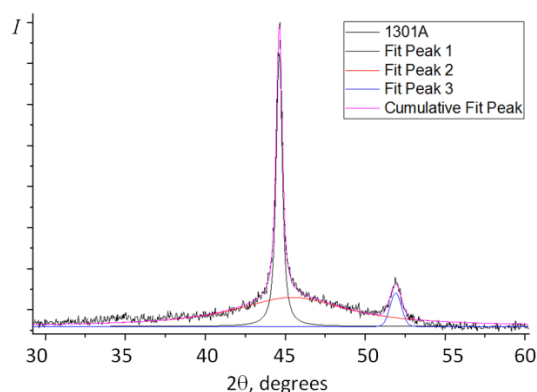


Figure 3. XRD pattern of the 1301A alloy after the first stage of crystallization (annealing at 500 °C, 1 min) with separated peaks of crystalline and amorphous phases.

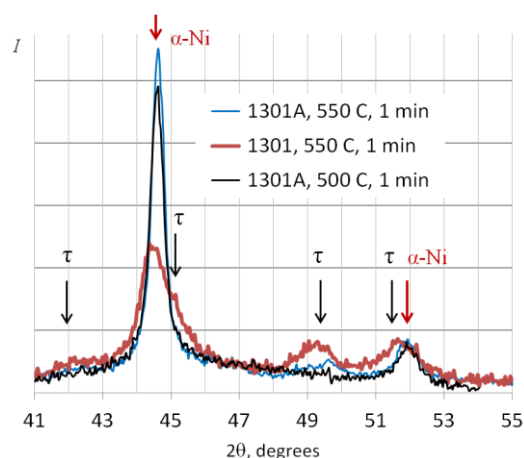


Figure 4. XRD pattern of 1301A and 1301 alloys after the first and second stages of crystallization.

It is also known that in the Ni-B system metastable τ -phase can be fixed by addition of Fe and probably, Cr, into its composition [1]. In the absence of Fe this phase does not form. Note that the formation of compounds of type $M_{23}(B,C)_6$ is typical for such metals as Fe, Cr, Mn, but not Ni. Thus, these metals contribute to the stabilization of τ -phase by decrease of its free energy. This leads to the increase of temperature of τ -phase formation (T_2) and to increase of its decomposition temperature T_3 . Indeed, alloy 1301A completely decomposes at a temperature 600°C, while the alloy 1301 still contains τ -phase at temperatures up to 650°C (figure 5). Annealing at 900°C led to the decomposition of this phase. The presence of two cubic phases (α -Ni and Ni_3Si) with fcc-structure and different lattice parameters at the end of the crystallization process of alloys 1301 and 1301A was observed. Ni_3Si -based phase can hardly be discriminated from α -Ni by XRD since it has the same structure, but the presence of the silicide phase is well observed in XRD pattern of alloy 1301. According to EDX analysis of alloy 1301 annealed at 900°C, in addition to phases mentioned above, formation of chromium boride of CrB type with low Si content can also be observed (figure 6). Application of the EDX method in scanning electron microscope for alloys annealed at low temperatures is limited because of the small size of crystals (30-100 nm). XRD method did not detect the presence of CrB phase in the crystallized amorphous and massive cast alloys, although this phase was detected by EDX analysis [4, 8, 9].

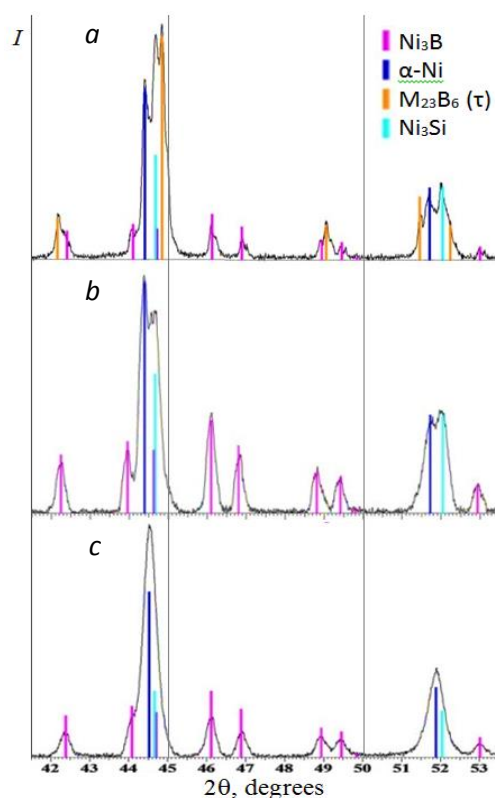


Figure 5. XRD phase analysis of alloys 1301 and 1301A after annealings: *a* – 1301, 650°, 1 h; *b* – 1301, 900°, 1 h; *c* – 1301A, 600°C, 1 h.

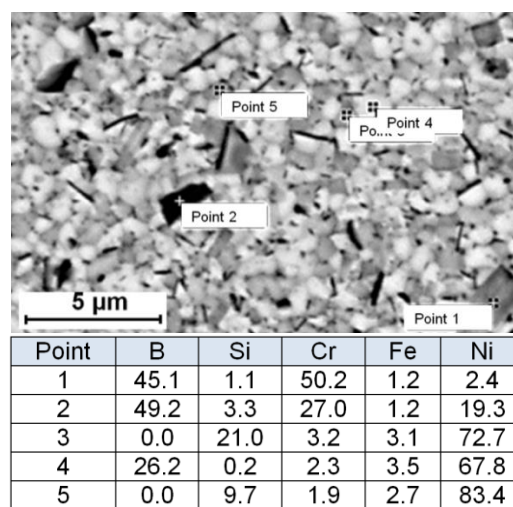


Figure 6. Surface microstructure and EDX results (in at.%) of alloy 1301, annealed at temperatures of 900°C for 1 hour.

Assuming that Ni_3B does not contain silicon and Ni_3Si does not contain boron, the concentration of silicon in α -Ni and Ni_3Si corresponds to the Ni-Si diagram, and iron is not redistributed between the phases, the phase compositions of alloys were estimated from material balance equations. These estimations were carried out for two cases: considering of formation CrB and without it (table 3). The obtained estimations of phase composition do not contradict to the rigorous thermodynamic calculations for alloy BNi-2 at 650 °C performed using the program ThermoCalc [4]. We can conclude

that even a small increase of the boron content in the alloy leads to a mentioned increase of the amount of Ni_3Si and reduce of $\alpha\text{-Ni}$. Note that the amounts of $\alpha\text{-Ni}$ and Ni_3Si phases in the crystallized alloy 1301 are comparable as shown in figure 1 *a, b*. The observed high amount of $\alpha\text{-Ni}$ phase in the alloy 1301 and low amount of Ni_3Si phase in the alloy 1301A after the complete crystallization cannot be explained without assumption of the formation of phase CrB.

Table 3. The phase composition of alloys, calculated according to different models.

Phase amount, % (wt.)	1301A		1301A		BNi-2 ThermoCalc [4]
	with CrB	without CrB	with CrB	without CrB	
$\alpha\text{-Ni}$	16.2	33.3	39.6	66.2	43.9
Ni_3B	50.0	31.8	43.8	18.9	29.1
Ni_3Si	33.8	25.2	16.6	6.4	18.8
CrB	–	9.7	–	8.5	8.2

3. Conclusion

The influence of the alloys chemical composition (boron, manganese and iron) on the temperatures and the exothermic heat effects of phase transformations, as well as on the phase composition of alloys at three stages of crystallization were analyzed.

It is shown that the onset crystallization temperature is practically independent of the boron content in alloys, but it increases with the increase of manganese content. The manganese and iron stabilizes a metastable τ -phase, resulting in decrease of the onset temperature of the second crystallization stage (τ -phase formation) and increase of the onset temperature of the third stage (decomposition of τ -phase). The thermodynamic explanation of these phenomena is proposed.

It is assumed that at the final crystallization stage simultaneously with the formation of Ni_3B and Ni_3Si phases the nucleation of borides of CrB type with high Cr and low Si content should occur.

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