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Detailed microstructural studies of amorphous Al-Ni-Si and Al-Ni-Si-Cu alloys during crystallization

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Abstract. **Two types of rapidly solidified ribbons were obtained from the systems Al-Ni-Si and Al-Ni-Si-Cu. By XRD, TEM and DSC analysis the ribbons were proved to be amorphous. By annealing at 350ºC nanocrystalline alloys were obtained. It was found that when the amorphous alloys are annealed at 190ºC and 220ºC, an unknown metastable hexagonal phase is presented, which could not be identified when annealing at 350ºC is provided. Both studied alloys $Al_{74}Ni_{16}Si_{10}$ and $Al_{74}Ni_{15}Si_9Cu_9$ show that when annealed at 190°C a residual amorphous phase is observed. It is located mainly at the phase boundaries.**

Keywords: amorphous, nanocrystalline, phase analysis.

I. INTRODUCTION

Amorphous and nanocrystalline alloys from Al-Ni-Si ternary system are of great science interest because of their unique combination of physical and mechanical properties. Many researchers paid attention to the study of the structure and properties of these materials [1] - [4]. However, information on the phase diagram of Al-Ni-Si and alloys based on it is limited [5], [6]. Al_3Ni and Al_3Ni_2 phases, which have orthorhombic and trigonal crystal lattices respectively, are known to exist in the range of increased aluminium content of the Al-Ni-Si phase diagram.

The authors of [7] - [10] had investigate alloy from Al-Ni-Si system and it was clarified that a metastable hexagonal phase is formed in amorphous Al-Ni-Si alloys upon annealing below a temperature of 200ºC. This hexagonal phase is with crystal lattice parameters a = 6.55-6.59 Å, c = 3.83-3.86 Å. It disappears when the alloy is subjected to further annealing above 300ºC.

In our previous work [11], $Al_{74}Ni_{16}Si_{10}$ and $Al_{74}Ni_{15}Si_9Cu_9$ alloys were investigated in the amorphous state and after annealing at 350ºC. In the course of the investigation, it was found that the transformation of the microstructure from amorphous to crystalline proceeded in two steps and an unknown hexagonal phase was released, which disappeared after annealing at 350ºC. To identify this metastable phase, further studies were conducted on the fine structure of the alloys.

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The aim of the study was to investigate the phase characteristics of the amorphous alloys $Al_{74}Ni_{16}Si_{10}$ and $Al_{74}Ni_{15}Si_9Cu_9$ annealed at 190ºC and 220ºC and to determine the presence of the mentioned hexagonal phase at different annealing temperatures in the studied alloys.

II. Materials and Methods

The investigated alloys $Al_{74}Ni_{16}Si_{10}$ and $Al_{74}Ni_{15}Si_9Cu_9$ were synthesised from the metals Al, Ni, Si and Cu with a purity of 99.99%. The ligatures and ribbon fabrication processes (Chill Block Melt Spinning method) were described in detail in our previous publication [12]. Annealing at 190ºC, 220ºC and 350ºC was performed to obtain the crystalline structure and to study the types of phases.

The chemical composition of the ribbons was determined using a HIROX 5500 scanning electron microscope (SEM, HIROX Europe, Limonest, France) with a BRUCKER EXDS system (BRUCKER Co., Germany).

Bruker D8 Advance powder X-ray diffractometer (Karlsruhe, Germany) with Ni-filtered Cu Kα radiation and a LynxEye solid state position sensitive detector was used. The PDF-2 (2021) database of the International Centre for Data Diffraction (ICDD) and the DiffracPlusEVA software package v.4.0 (Bruker AXS 2010-2014, Karlsruhe, Germany) were used for phase analysis.

Differential Scanning Calorimetry (DSC) analysis was performed on a STA 449 F3 Jupiter calorimeter connected to a QMS 403 Aëolos Quadro mass spectrometer in an Ar environment. The protective Ar flow rate in the apparatus during the analysis was 30 mL s-1 and the purge Ar flow rate through the samples studied was 20 mL s-1. The heating rate was 20 K min-1.

HRTEM JEM 2100, (JEOL Ltd., Japan) with an acceleration voltage of 200 kV in SAED and HRTEM modes was used for microstructural observation of the obtained alloys.

III. Results and Discussion

The base alloy composition of Al-Ni-Si is close to eutectic and is optimal for producing an amorphous alloy. Based on research to combine good GFA, mechanical properties and corrosion resistance [13]-[15], the amount of copper added was set at 2 at. %. Taking into account the chemical analysis provided [11] and based on the results obtained, the designations of the alloys are $Al_{74}Ni_{16}Si_{10}$ and $Al_{74}Ni_{15}Si_9Cu_9$.

TABLE 1. DATA FROM XRD ANALISYS

State of the alloy	Defined phases	
	in $Al_{74}Ni_{16}Si_{10}$	*in $Al_{74}Ni_{15}Si_9Cu_2$*
Amorphous	-	-
Annealed at 190ºC	Al, Al_3Ni, hexagonal	Al, Al_3Ni, hexagonal
Annealed at 220ºC	Al, Al_3Ni, $NiSi_2$, hexagonal,Ni_3SiAl_5, Al_9Ni_2	Al, Al_3Ni, $NiSi_2$, hexagonal, Ni_3SiAl_5, Al_9Ni_2
Annealed at 350ºC	Al, Al_3Ni, $NiSi_2$	Al, Al_3Ni, $NiSi_2$, $Cu_{3.8}Ni$, $(Al,Cu)Ni_3$

The XRD data are given in Table 1. The microstructure of the rapidly solidified $Al_{74}Ni_{16}Si_{10}$ and $Al_{74}Ni_{15}Si_9Cu_2$ ribbons is shown to be completely amorphous. The nature of the crystalline phases in the annealed samples was determined. From the phase composition data it can be seen that only three types of phases are present when annealed at 190ºC - hexagonal metastable, Al and Al_3Ni. The greatest variety of phases is recorded at annealing at 220ºC. The hexagonal phase is present in the alloys at annealing temperatures of 190ºC and 220ºC. At higher annealing temperatures, the amount of hexagonal phase is significantly reduced compared to the lower annealing temperature and is completely absent at annealing at 350ºC. The authors of [7] have shown that the hexagonal phase, which can be clearly determined, is formed from the amorphous phase in the sample annealed at 175ºC. During annealing at higher temperatures the hexagonal phase is transformed into three other phases, namely fcc-Al, Si and Al_3Ni phases.

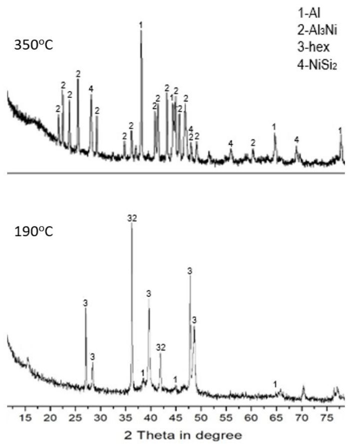
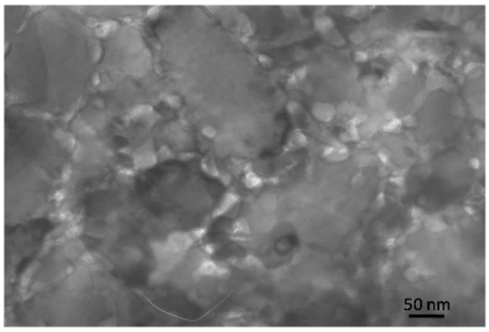
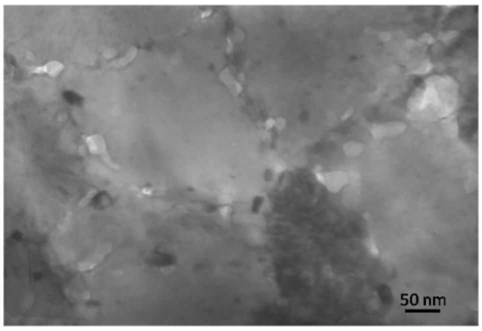


Fig. 1. The fragment of XRD diagrams of $Al_{74}Ni_{16}Si_{10}$ alloy annealed at 190°C and 350°C.

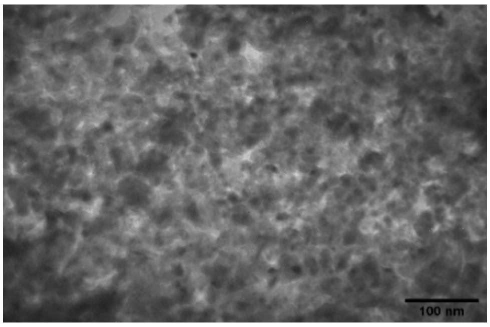
The TEM observations of the structure of alloys (Fig. 2) after annealing at 190°C contains small light inclusions, mainly at the phase boundaries. The presence of inclusions is not observed in the structures of the alloys during annealing at 220°C and 350°C. These inclusions could be a residual amorphous phase [7].



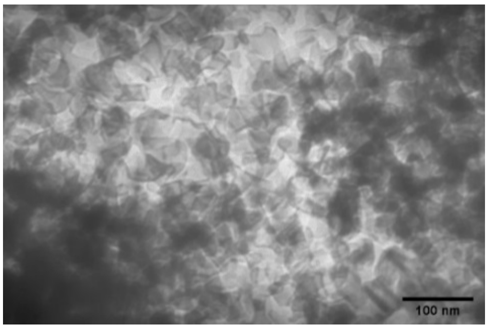
(a)



(b)



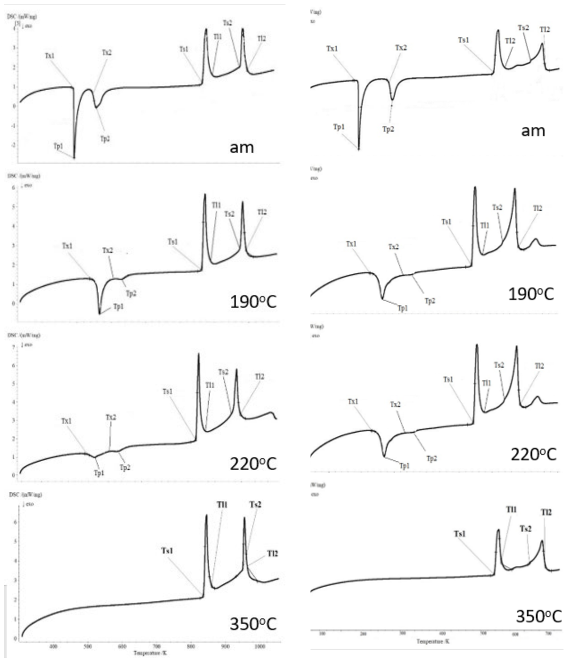
(c)



(d)

Fig. 2. Fig. 2 TEM images of (a) annealed at 190°C $Al_{74}Ni_{16}Si_{10}$ alloy; (b) annealed at 190°C $Al_{74}Ni_{15}Si_9Cu_2$ alloy; (c) annealed at 220°C $Al_{74}Ni_{16}Si_{10}$ alloy; (d) annealed at 220°C $Al_{74}Ni_{15}Si_9Cu_2$ alloy

Differential scanning calorimetry (DSC) studies were provided to determine the thermal resistance, transformation temperature intervals, phase transition temperatures and the crystallization mechanism in heating mode of the new $Al_{74}Ni_{16}Si_{10}$ and $Al_{74}Ni_{15}Si_9Cu_2$ alloys. Fig. 3 shows the results from DSC analysis of the alloys in the amorphous (a) and crystalline state after annealing in an argon atmosphere at temperatures of 190°C (463K) (Fig. 3 (b)), 220°C (493K) (Fig. 3 (c)) and 350°C (623 K) (Fig. 3 (d)) respectively. According to [7], the first peak at DSC diagrams corresponds to the crystallization of the amorphous phase and the crystallization of the hexagonal phase is presented between the first and the second endothermic peaks.



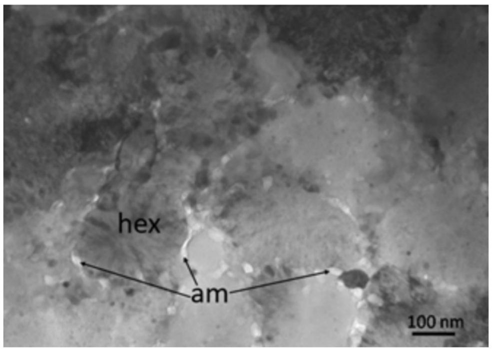
(a) (b)

Fig. 3. DSC diagrams of (a) $Al_{74}Ni_{16}Si_{10}$ and (b) $Al_{74}Ni_{15}Si_9Cu_2$ alloys in amourphous state and annealed at different temperatures.

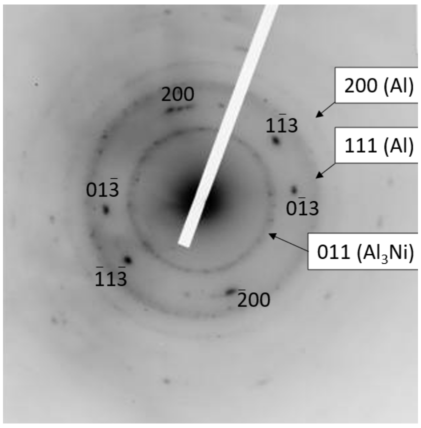
The peaks proving the content of amorphous part in the specimens of $Al_{74}Ni_{15}Si_9Cu_2$ annealed at 190°C are smaller than those of the specimens of $Al_{74}Ni_{16}Si_{10}$ annealed at the same temperature.

In [10] it was shown that the hexagonal phase has a specific outlines. In our TEM observations (fig. 4) a phase, whose morphology strongly resembles the one studied in [10], is observed in our structures.

Diffraction reflections correspond to a hexagonal close-packed structure, the reciprocal lattice plane (031), which may indicate the presence of a hexagonal phase. Diffraction rings can belong to different phases, fig.4 (b).



(a)



(b)

Fig. 4. TEM observations of $Al_{74}Ni_{15}Si_9Cu_2$ annealed at 190°C - (a) BF image; (b) SEAD pattern

IV. CONCLUSIONS

The crystallisation of the amorphous alloys $Al_{74}Ni_{16}Si_{10}$ and $Al_{74}Ni_{15}Si_9Cu_9$ obtained by the CBMS method during continuous heating in the DSC proceeds in two stages in the temperature ranges (452÷453)K and (529÷535)K. In the first stage, the amorphous phase is transformed into fcc-Al and hexagonal phase, and in the second stage, fcc-Si and orthorhombic Al_3Ni phase are formed from the hexagonal phase. These processes were demonstrated by DSC heating of the alloys at 463K (190^{o}C) and 493K (220^{o}C). TEM structural observations of both $Al_{74}Ni_{16}Si_{10}$ and $Al_{74}Ni_{15}Si_9$Cu9 alloys annealed at 190°C showed a residual amorphous phase located at the phase boundaries of both the fcc-Al and hexagonal phases. It was found that after annealing at 350oC the transformation of the microstructure from amorphous to crystalline was complete and the metastable hexagonal phase was not observed.

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