Peculiarities of Microstructure of Al-Rich Al-La-Ni-Fe Alloys.

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Abstract

The results of a comprehensive microstructural study of ternary and quaternary phases in air cast $\text{Al}_{85}\text{Ni}_{11-x}\text{Fe}_x\text{La}_4$ (where $x = 2$ and 4 at.%) polycrystalline alloys by means of optical microscopy, scanning electron microscopy, transmission electron microscopy, scanning transmission electron microscopy, energy dispersive X-ray microanalysis, and X-ray diffraction are presented. It was found that these alloys contain several phases, namely fcc-Al, $\text{Al}_{11}\text{La}_3$, $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$, $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$, $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ and $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ in the form of δ -layers in the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particles. High density of other defects in the quaternary $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particles were found and their formation could be caused by dendritic type of growth of this phase. The crystal structure of all these defects was revealed by high resolution scanning transmission electron microscopy together with atomic resolution energy dispersive X-ray microanalysis. The thermal stability of the ternary and quaternary phases were also studied. The $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase is metastable and undergoes an irreversible transformation: $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La} \rightarrow \text{Al}_9\text{Ni}_{2-x}\text{Fe}_x + \text{Al}_{11}\text{La}_3$. On the basis of all these data, a sequence of solid phase reactions in these alloys during cooling and heating is proposed.

Keywords

Intermetallics; rapid-solidification; microstructure; SEM, TEM, STEM

1. Introduction.

Since the seeding studies of A. Inoue et al. ^[1], ^[2] and G.Shiflet et al. ^[3] in 1988, Al-based metal glasses containing rare-earth elements (RE) together with transition metals (TM) have been under intensive study due to their high metallic glasses formation ability combined with excellent mechanical properties such as high strength and corrosion resistance. Two groups of ternary Al-based alloys containing La, namely, Al-La-Ni and Al-La-Fe, were already considered in those pioneer research works. In subsequent studies it was shown that the reported high glass-forming ability and mechanical properties could be substantially improved by the addition of a second transition element ^[4], ^[5], ^[6]. The quaternary alloys with two transition elements, in particular, Fe and Ni, are characterized by a higher thermal stability and better mechanical properties. Studies of the microstructure and phase formation processes in ternary and quaternary alloys during annealing have been carried out mainly by X-ray and electron diffraction (XRD and ED, correspondingly) since these materials were discovered, but in most cases they were limited to ascertaining the presence of fcc-Al and one or more binary phases. Quaternary intermetallic compounds, to the best of our knowledge, were not found and were not considered. To some extent this might be due to the issues related with the completeness of their identification by XRD or ED for a number of reasons. On the one hand, XRD spectra from low-symmetrical binary phases exhibit a significant number of maxima which could conceal the presence of ternary and quaternary phases.

A study of the microstructure of amorphous alloys after thermal treatment or intense plastic deformation was carried out mostly in samples with extremely high mechanical characteristics, when the grain sizes often did not exceed 100 nm ^[4], ^[7], ^[8]. Such grain sizes precluded investigations by ED, on the other hand, although these alloys are most interesting. In addition, during annealing or intensive plastic deformation, along with stable phases, metastable intermetallic ones could appear. If so, for an unambiguous interpretation of the XRD spectra, ED patterns and the phase determination, a comprehensive study of polycrystalline alloys is necessary, just as the case reported in ^[9], ^[10], ^[11], ^[12]. A possible phase composition of the alloys can be determined from the phase diagrams, but quaternary Al-La-Ni-Fe alloys have been insufficiently studied and the corresponding phase diagrams were not found in the literature. The ternary phase diagrams of the Al-Fe-La system are presented in ^[13] ^[14] and of the Al-La-Ni system in ^[15] ^[16]. The Al-Ni-Fe system has been studied much better and the phase diagrams for several isothermal sections were described by Rivlin ^[17] and updated later in papers ^[18], Khaidar

et al. ^[19] as well as in relatively recent works of Budberg et al. ^[20], Raghavan ^[21], Eleno et al. ^[22], Chumak et al. ^[23] and in the works by Zhang et al. ^{[24][25][26]}.

Table 1 summarizes the known intermetallic phases in the Al-Ni-Fe-La system with Al ≥ 70 at%. These alloys contain polycrystalline fcc-Al, several binary and ternary phases. Two Al-Ni binary phases are known in this Al concentration range: the first one is Al_3Ni ^[27] and the second one is Al_9Ni_2 ^[28]. It is assumed that the Al_3Ni phase has a very narrow homogeneity range ^[29] Eleno and co-workers ^[22] defined this range as ~ 23 -26 at.% Ni. Yamamoto and Tsubakino ^[28] found out by ED the Al_9Ni_2 phase which is isostructural to Al_9Co_2 , and turned out to be metastable. Moreover, according to the energy dispersive X-ray (EDX) microanalysis, Al content in the Al_9Ni_2 particles was above the stoichiometric Al/Ni atomic ratio with the value of 4.68. Four basic binary Al-Fe intermetallic phases with different crystal structures and stoichiometry with Al content above 70 at% were discovered. The Al_5Fe_2 phase exhibits an orthorhombic crystal structure (Space Group (*S.G.*) *Cmcm*) ^[30], ^[31]. This compound is isomorphic with the hexagonal compound Al_5Co_2 ^[32] and has a homogeneity range of 70-73 at.% Al ^[22]. The group of Al_3Fe , $\text{Al}_{13}\text{Fe}_4$, $\text{Al}_{3.2}\text{Fe}$ and $\text{Al}_{9.75}\text{Fe}_3$ is characterized by a monoclinic crystal structure with very close unit cell parameters. The homogeneity range is 74.5 - 76.6 at.% Al ^[22]. Several isostructural compounds with a slight difference in the stoichiometric composition have been investigated (see Table 1, the structure parameters are given according to the first reference). A phase designated as Al_9Fe_2 was found by ED in the ternary Al-Fe-Si system (Al-0.5 Fe-0.2 Si wt % alloy) ^[33], it was isostructural with Al_9Co_2 and was shown to be monoclinic with lattice parameters: $a = 0.869$ nm, $b = 0.635$ nm, $c = 0.632$ nm, $\beta = 93.4^\circ$. In other studies it was not detected, and can be regarded as metastable. Another metastable phase Al_6Fe , was first described by Hollingworth et al. ^[34] and refined by ^[35]. The homogeneity range of the latter two phases remains undefined.

Three stable Al-Fe-Ni ternary phases with Al ≥ 70 at% (displayed in the order of Al content increasing in Table 1) were found: 1 - quasicrystalline $\text{Al}_{71}\text{Fe}_5\text{Ni}_{24}$ compound, 2 - hexagonal with the general formula $\text{Al}_{10}\text{Fe}_{4-x}\text{Ni}_x$, and 3 - monoclinic $\text{Al}_9\text{Fe}_{2-x}\text{Ni}_x$. The latter two phases are denoted by τ_1 and τ_2 , and different authors, for example, ^[17] and ^[23] use the opposite notation. The $\text{Al}_{10}\text{Fe}_{4-x}\text{Ni}_x$ and $\text{Al}_9\text{Fe}_{2-x}\text{Ni}_x$ phases were first described in the investigation of Bradley & Taylor ^[36], where it was claimed to be isostructural with Al_5Co_2 and Al_9Co_2 , respectively. Schroder & Hanemann ^[37] shortly afterwards determined the homogeneity range of these compounds: for $\text{Al}_{10}\text{Fe}_3\text{Ni}$, Fe - 18-24.5 at% and for Ni - 4.5-10.5 at% ,for the Al_9FeNi compound - Fe in the range of 4.4-11.1 at% and Ni - 7.0-13.5 at.%. Later on, the structure, composition and homogeneity ranges of compounds with the general formula $\text{Al}_{10}\text{Fe}_{4-x}\text{Ni}_x$ and

Al₉Fe_{2-x}Ni_x were critically evaluated by Mondolfo [38] and Rivlin [17] with amendments in their later study [18], as well as by Raghavan [39], Dubko [29], Budberg et al. (Budberg et al., 2004), updated by, Raghavan [21], Eleno et al. [22], Chumak et al. [23], Zhang et al. [25]. Basing on these studies, the homogeneity range can be extended: for Al₁₀Fe_{4-x}Ni_x: Fe in the range of 14.4-24.5 at% and Ni in the range of 4.5-13.1 at%. For the Al₉Fe_{2-x}Ni_x phase the ranges are: Fe - 3.05-11.1 at% and Ni - 4.5-14.3 at%. According to Chumak and co-workers [23] Al atoms at the 2a site can be substituted by Fe/Ni atoms in the Al₁₀Fe_{4-x}Ni_x compound. The pointed above homogeneity range for the Al₁₀Fe_{4-x}Ni_x compound includes Al₁₀Fe₃Ni determined by [40], confirmed by Khaidar and co-workers [19], and the Al₅FeNi compound discovered by Ellner & Rohrer [41]. However, the composition of the Al₁₀FeNi₃ compound mentioned by Khaidar et al. [19] does not fit this homogeneity region. This paper reported that the particle size of the polycrystalline alloy was too small to determine the structure. This phase was not found in later studies and that was the reason of its absence in Table 1. In a number of studies, namely, [37], [19], [29] it was noted that the Al₉Fe_{2-x}Ni_x phase was formed via the peritectic reaction L+Al₁₃Fe₄+Al₃Ni $\leftrightarrow$ Al₉Fe_{2-x}Ni_x at 809 °C, the transition reaction L+(Al₁₃Fe₄) $\leftrightarrow$ Al₉Fe_{2-x}Ni_x+(Al) at 650°C and the eutectic reaction L $\leftrightarrow$ Al+Al₃Ni+Al₉Fe_{2-x}Ni_x at 638°. Chumak and co-workers [23] reported that the reactions of the Al₁₀Fe_{4-x}Ni_x phase formation are unknown, although Budberg et al. [20] with reference to Khaidar et al. [19], presented an invariant reaction of L+ τ_2 $\leftrightarrow$ Fe₄Al₁₃+Ni₂Al₃, which occurred in a narrow temperature range between 1050°C and 950°C. The Al₁₀Fe_{4-x}Ni_x compound was denoted by τ_2 , in that study.

The last ternary phase of the Al-Ni-Fe system with Al $\geq$ 70 at% is a quasicrystal phase with the formula Al₇₁Fe₅Ni₂₄, denoted as τ_3 . This phase was first discovered in 1989 [42]. Later, the parameters were refined in the studies [43], [44], [45]. It was specified that the homogeneity range of this phase is extremely narrow, less than 1 at%, the compound being stable in a slim temperature range between 847 °C and 930 °C and it can be studied only after rapid quenching.

In Al based alloys (Al $\geq$ 70 at.%) with La and transition metals, the binary phase Al₁₁La₃ was discovered [46] as well as the Al₄La phase [47]. Those phases were characterized by very close crystal lattice parameters and S.G. *Immm* and *Imm2*, respectively (Table 1), which, practically, could not be resolved by XRD or ED. Gomes de Mesquita and Buschow [48] asserted that the low-temperature phase (α) should be described by the formula Al₁₁La₃, not by Al₄La. According to Buschow [49] and Gschneidner & Calderwood [50], the transition of α -Al₁₁La₃ to the high-temperature phase (β) - Al₁₁La₃ takes place at the temperature of 915 °C.

In the Al-rich corner of the Al-Fe-La system two ternary compounds were found: Al₈Fe₂La, which was claimed to be an isostructural to Al₈Fe₂Ce [51], and Al₁₀Fe₂La [52].

Thus, the analysis of the results of the microstructural studies of Al-Ni-Fe-La based alloys with Al $\geq$ 70 at% demonstrated a variety of intermetallic phases formed in different concentration ranges of the alloying elements. Moreover, minor deviations of the chemical composition led to a change in the phase composition. Therefore, the ambiguity of the results requires a careful study of the phase content in these alloys.

Previously, we performed a preliminary study of quaternary Al-La-Ni-Fe alloys and discovered the Al₈Fe_{2-x}Ni_xLa phase ^[53], isostructural to Al₈Fe₂Eu ^[54]. However, the atomic structure of defects in that phase was not considered. In this paper, we present the results of a comprehensive microstructural study of ternary and quaternary phases in air cast Al₈₅Ni_{11-_x}Fe_xLa₄ (where x = 2 and 4 at.%) polycrystalline alloys by means of optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray (EDX) microanalysis, and X-ray diffraction (XRD). Defects in the quaternary Al₈Fe_{2-x}Ni_xLa phase together with the thermal stability of the ternary and quaternary phases were studied. On the basis of these data, a sequence of solid phase reactions in these alloys during cooling and heating is proposed.

Table.1. Structural data for Al-rich phases (>70%) in the Al-La-Fe-Ni system.

#	Phase	Space group	Prototype	Crystal class	Lattice parameters (nm)	Reference
1	Al	Fm-3m	Cu	Cubic	a=0.405	[55]
2	Al ₃ Ni	Pnma	Fe ₃ C	Orthorhombic	a=0.661 b=0.736 c=0.481	[27]
3	Al ₉ Ni ₂	P2 ₁ /c	Al ₉ Co ₂	Monoclinic	a=0.62 b=0.85 $\beta=95^0$	[28]
3	Al ₅ Fe ₂	Cmcm	Unknown	Orthorhombic	a=0.767 b=0.64 c=0.42	[31] [30]
4	Al ₃ Fe Al ₁₃ Fe ₄ (Al _{3.2} Fe) (Al _{9.75} Fe ₃)	C2/m	Unknown	Monoclinic	a=1.548 b=0.808 c=1.247 $\beta=107.43^0$	[56] [57][58]
5	Al ₉ Fe ₂	P2 ₁ /a	Al ₉ Co ₂	Monoclinic	a=0.869 b=0.635 c=0.632 $\beta=93.4^0$	[33]
6	Al ₆ Fe	Ccm2 ₁	Al ₆ Mn	Orthorhombic	a=0.646 b=0.744	[35]

					c=0.877	
7	Al ₇₁ Fe ₅ Ni ₂₄			quasi-crystalline decagonal		[43]
8	Al ₅ FeNi Al ₁₀ Fe _{4-x} Ni _x	P6 ₃ /mmc	Al ₅ Co ₂	Hexagonal	a=0.7693 c=0.7657	[36], [41] [23]
9	Al ₉ Fe _{2-x} Ni _x	P2 ₁ /c	Al ₉ Co ₂	Monoclinic	a=0.62406 b=0.62993 c=0.85992 β=95.129	[36], [23]
10	Al ₃ La	P6 ₃ /mmc	Ni ₃ Sn	Hexagonal	a=0.6667 c=0.4619	[59]
11	Al ₁₁ La ₃	Immm	Al ₁₁ La ₃	Orthorhombic	a=0.4431 b=1.3142 c=1.0132	[48]
12	Al ₄ La (β-Al ₁₁ La ₃)	I4/mmm	Al ₄ Ba	Tetragonal	a=0.4422 c=1.021	[60], [49]
13	Al ₄ La	Imm2	-	Orthorhombic	a=0.443 b=1.314 c=1.013	[61]
14	Al ₈ Fe ₂ La	Pbam	Al ₈ Fe ₂ La	Orthorhombic	a=1.257 b=1.445 c=0.4063	[51]
15	Al ₁₀ Fe ₂ La	Cmcm	Al ₁₀ Fe ₂ Yb	Orthorhombic	a=0.9051 b=1.0249 c=0.9122	[62]
16	Al _{6-x} Ni _{1+x} La	P4/mmm	unknown	Tetragonal	a=0.4189 c=0.8032	[63]

2. Experimental

Polycrystalline alloys with the composition determined as Al₈₅Ni₇Fe₄La₄ and Al₈₅Ni₉Fe₂La₄ were obtained from melt as ingots by cooling in air. In order to study the thermal stability, the specimens were annealed under a Ar/H (H-4%) gas mixture at 400, 500 and 600 °C for 3 hours. The heating and cooling rates were 30 °C/min and 50 °C/min, respectively.

An optical microscope Axiovert 40MAT was used at the first stage. The tint etching of the specimens after mechanical grinding and polishing was performed in a mixture which consisted of 3% HF, 4% HNO₃, 3% HCl and 90% H₂O at room temperature for 10 s. Further studies were performed by SEM/EDX microanalysis. A Focus Ion Beam (FIB)/SEM dual beam Helios (FEI, USA) at an accelerating voltage of 2 kV was used for the imaging. Due to the use of through lens detector even in the secondary electron (SE) registration mode a significant fracture of backscattering electrons (BSE) was detected that generated a strong Z-contrast. The microscope was equipped with an EDX spectrometer (EDAX, USA), the spectra and elemental maps were recorded using the accelerating voltage of 15-30 kV. The specimens for TEM, STEM

and ED studies were prepared by 2 methods: A) - by twin-jet electropolishing in a TenuPol-5 facility (Struers USA) using an electrolyte which consisted of 70% butanol, 20% perchloric acid and 10% ethanol at the temperature of 5– 7 °C and the potential of 40 V, cleaning with Ar⁺ ions was accomplished in the PIPS (Gatan, USA) at the acceleration voltage of 0.1-1 kV and B) - by using a standard lift-out FIB technique. Microstructural analyses were performed in a Titan 80-300 TEM/STEM (FEI, USA) equipped with a spherical aberration corrector (probe corrector), with an accelerating voltage of 300 kV. Such a configuration allows one to obtain images in the STEM mode with a resolution of 0.08 nm. The device is equipped with an EDX Si(Li) spectrometer (EDAX, USA), High Angle Annular Dark Field (HAADF) electron detector (Fischione, USA) and Gatan Image Filter (GIF) (Gatan, USA). In addition, part of the STEM images were obtained in an aberration corrected (probe corrected) TITAN 80-200 (FEI, USA) at an accelerating voltage of 200 kV. This instrument is also equipped with a HAADF detector (Fischione, USA) and a silicon drift detector (SDD), which was a Super-X EDX detector (Bruker, USA). Image processing was performed using a Digital Micrograph (Gatan, USA) and TIA (FEI, USA) software, simulations of the ED patterns and images were produced using a Stadelmann's EMS software package ^[64]. The powder X-ray diffraction analysis of the as-received and annealed bulk polycrystalline samples of the two compositions was performed with a Rigaku Miniflex-600 diffractometer (Rigaku Corporation, Tokyo, Japan). The XRD data were recorded using Cu-K α radiation (40 kV, 15 mA, Ni-K β filter) in the 2 θ range 10–90° at a scan rate 0.5°/min. The crystalline phases were identified with integrated X-ray powder diffraction software (PDXL: Rigaku Diffraction Software) and ICDD PDF-2 datasets (Release 2014 RDB). For these experiments the specimens with the size of ~4x10 mm² were polished from one side.

3. Results.

Below in microscopy section we will describe in more detail the microstructure of the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy, because the phase content and overall microstructure in both alloys are similar. The XRD data and the results of annealing are presented for both alloys.

3.1. OM microstructure study.

Fig.1. Typical microstructure of $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy (OM image). Phases are denoted as: 1 – Al, 2 – $\text{Al}_9\text{Ni}_{1-x}\text{Fe}_x$, 3 – $\text{Al}_{11}\text{La}_3$, 4 – $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$.

The OM image after tint etching of the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy is shown in Fig. 1. The analysis of the contrast and morphology of the particles allows us to conclude that at least 4 phases are present in the alloy. The typical images of the particles of each phase are indicated by numbers from “1” to “4”. A further study has shown that the particles marked by “1” with the light contrast are the fcc-Al. These particles look polycrystalline and reach up to 50 μm in size. The second type of the particles denoted by number “2” looks bluish in OM and they have been identified as $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$. These particles often adopted an elongated morphology with the length of up to 20 μm and width of 1 μm . They are observed in two media: 1 - surrounded by the fcc-Al matrix and 2 - around relatively large elongated particles of the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase designated by “4”. These four component particles are polycrystalline agglomerates with the grain size of 5-20 μm and the total sizes of 100 μm , they have a brown tint in OM images, which, apparently, is

209 due to the presence of Fe. The faceted particles coming in gray color with the sizes up to 25
210 microns are identified as the $\text{Al}_{11}\text{La}_3$ phase, which is indicated by “3” in Fig. 1. According to the
211 paper ^[48] we designated that phase by “11-3”, not by “4-1”, which reflects the stoichiometric
212 Al/La atomic ratios. While evaluating the OM images of different phases we estimated their
213 volume fraction in the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ and $\text{Al}_{85}\text{Ni}_9\text{Fe}_2\text{La}_4$ alloys. A relatively small difference in
214 Fe and Ni contents in the alloys resulted in an approximately two-fold increase of the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$
215 phase in the Ni rich $\text{Al}_{85}\text{Ni}_9\text{Fe}_2\text{La}_4$ alloy. On the contrary, the content of the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase
216 is twice higher in the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy.

Fig.2. SEM image of the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy showing the microstructure at (a) – low and (b) – higher magnifications. Phases are denoted as: 1 – Al, 2 – $\text{Al}_9\text{Ni}_{1-x}\text{Fe}_x$, 3 – $\text{Al}_{11}\text{La}_3$, 4 – $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$, 5- Al- $\text{Al}_{11}\text{La}_3$ - $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ eutectic. The “a-a”, “b-b” and “c-c” sections indicated the areas, where lamellae were cut. Arrows in (b) shows the eutectic microstructure.

Representative SEM images obtained from the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy are presented in Figs. 2 (a and b). Due to an essential Z-contrast the Al particles denoted by “1” look darkest. However, on the high magnification images an unevenness of contrast in these areas is visible. This could be

due to the polycrystalline microstructure, intermetallic precipitates and defect formation during crystallization or specimen preparation.

The particles $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ denoted by “4” in Figs.2 (a and b) exhibit a bright contrast due to the presence of La. It is sometimes difficult to distinguish between these and $\text{Al}_{11}\text{La}_3$, denoted by “3” on SEM images, but the presence of transition metals can be unambiguously detected using EDX microanalysis elemental mapping and these maps are shown in Figs.3 (a-f).

Fig. 3 (a)- SE SEM image of the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy and correspondent EDX elemental maps (b) – Al, (c) – La, (d) – Ni, (e) – Fe, (f) – all elements.

Number “2” denotes the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particles. These particles look brighter than the Al particles and they adopted an elongated morphology with a 2.5:1 mean aspect ratio. As clearly visible in Figs. 2 (a and b), the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particles are oriented in one direction. The particles with the same contrast surround the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ quaternary phase particles forming the core shell and that is also visible in the multiple map (Fig. 2(f)). This microstructure is typical for the initial stage of peritectic transformation in the alloy that was quenched to room temperature and described in the book ^[65] and the corresponding references. The $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particles together with $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ form a two-axis dendritic microstructure. Such dendritic microstructure could be formed at the initial stages of crystallization from the melt. Adjacent to the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particles there are eutectic structures with well-defined dispersed $\text{Al}_{11}\text{La}_3$ particles shown by arrows in Fig. 2(b). Besides, larger eutectic areas looking similar were found and they are denoted by “5” in Figs. 2(a and b). In some areas a more coarse eutectic structure was found. A more detailed study of the eutectic structures was carried out by TEM, STEM and EDX microanalysis, the results are presented below.

Fig. 4. (a) –HAADF STEM image of the specimen prepared by FIB in the area of the “a-a” section (see Fig. 2 (b)): phases are denoted as: 1 – Al, 2 – Al₉Ni_{2-x}Fe_x, 3 - Al₁₁La₃, 4 - Al₈Fe_{2-x}Ni_xLa. (b) – enlarged BF TEM image of the part of the specimen, shown by the red rectangle in (a). Phases are denoted as: 2 – Al₉Ni_{1-x}Fe_x, 4 - Al₈Fe_{2-x}Ni_xLa. Flat defects in the Al₈Fe_{2-x}Ni_xLa particle are indicated by arrows.

The HAADF STEM image of the specimen prepared by FIB from the section denoted by “a-a” in Fig. 2(b) is presented in Fig. 4(a). The contrast variations together with EDX spectroscopy (EDXS) data unambiguously indicated that there are four phases in the cut lamella, namely, fcc-Al, Al₁₁La₃, Al₉Ni_{2-x}Fe_x and Al₈Fe_{2-x}Ni_xLa. The results of EDXS study are presented in Table 2. Below the crystal structure and chemical composition of all the phases starting from quaternary and moving to binary phases are considered in detail. The HAADF STEM image demonstrated clearer than SEM images that there is layer consisted of the Al₉Ni_{2-x}Fe_x particles surrounding the Al₈Fe_{2-x}Ni_xLa particles as shown in the frame in Fig. 4(a). The analysis of BF TEM image of the same area presented in Fig. 4(b) revealed a polycrystalline nature of the Al₈Fe_{2-x}Ni_xLa cluster and the Al₉Ni_{2-x}Fe_x layer. The Al₈Fe_{2-x}Ni_xLa particles exhibit an irregular morphology and grain

sizes ranging between 0.2 and 1 μm . Many of these particles show the contrast characteristic for planar defects, which are arrowed in Fig. 4(b). The defect density was estimated from this and similar images and was up to 10^9 cm^{-2} . The crystal structure of these defects can be determined by HAADF STEM technique, the details are presented below.

Fig. 5. (a) HR HAADF STEM image of a $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle obtained in the [001] zone axis. In between the arrows with numbers “1-4” there are the areas with flat defects. The structural elements shown by red rectangles with La atoms in the corners and the sides, parallel to {310} and {140}, the defects which can be explained using these structural elements are shown by yellow rectangles. (b) - the SADP from a $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle in the [001] zone axis. (c) - the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ 4x4 unit cells in the [001] projection.

A preliminary study of the quaternary $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase indicated that it exhibited an orthorhombic crystal structure isostructural to $\text{Al}_8\text{Fe}_2\text{Eu}$ (S.G. *Pbam*)^[53]. The high resolution (HR) HAADF STEM image of that phase obtained in the [001] zone axis is presented in Fig. 5(a). The most intense spots on the image correspond to La atoms column, Ni and Fe atom columns give rise to spots with a nearly equal intensity. This can prove a substitution of Ni and Fe atoms. The weakest contrast comes from the column of Al atoms. The SADP from a $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle in the [001] zone axis is presented in Fig. 5(b). One of the peculiarities of the SADP are the streaks in the direction parallel to $0k0^*$ that arise from the defects with the habit plane parallel to $\{0k0\}$. The $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ 4x4 unit cells in the [001] projection are shown in Fig. 5(c), one of the unit cells is highlighted by a yellow rectangle. There are structural elements shown by red rectangles with La atoms in the corners and the sides, parallel to $\{310\}$ and $\{140\}$. These rectangles are shifted relative to each other at the distance equal to a and b parameters of the unit cell, their mutual position is very helpful in understanding the crystal structure of the defects in the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase.

Table 2. The results of EDXS study of the areas denoted by “1” – “4” in Fig. 4(a).

№	Phase	Element content, at%			
		Al	Ni	Fe	La
1	Al	99	1	0	0
2	$\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$	82	15	3	-
3	$\text{Al}_{11}\text{La}_3$	80	-	-	20
4	$\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$,	71	9	11	9

A close inspection of the HR HAADF STEM image presented in Fig. 5(a) and similar images obtained in the same projection revealed a variety of flat defects, denoted by “1”- “4” and dislocation cores, associated with flat defects, denoted by “5”. Flat defects denoted by “1” in Fig. 5(a) are mostly distinctive and these defects are marked by arrows in Fig. 4(b). An enlarged HAADF STEM image of that defect is presented in Fig. 6(a). The analysis of these defects with the habit plane parallel to the a -axis of the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ crystal reveals that these defects are δ -layers of the monoclinic $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ phase with the $\text{Al}_{3.2}\text{Fe}$ structure type (S.G. *C12/m1*)^[56]. Each δ -layer consists of adjacent staggered pentagons with Fe(Ni) atom columns located in the corners and in the center, the pentagons adopted a mirror (m) symmetry position. The pentagons are highlighted in red in Figs. 6(a) and (b). These defects were described in^[53], however, their

composition and, especially, the presence of Ni was not determined. The EDX elemental mapping (Figs. 6 (c-f)) unambiguously reveals the presence of Ni at the Fe sites in these δ -layers without any ordering. A light blur of the image in the δ -layer area could be linked with Al atoms substitution for Ni and Fe. Thus, the chemical content of the phase in the δ -layers can be described as $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$.

Fig. 6. (a) HAADF STEM image of the planar defect «1», which are δ -layers of the monoclinic $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ phase. (b) - the model of the defect and EDX elemental maps: (c) – La, (d) – Al, (e) – Fe, (f) – Ni.

The above mentioned structure elements which are highlighted by red rectangles with columns of La atoms in the corners shown in Figs. 5(a) and (c) are used for the description of planar defects. The stacking fault (sf) forms a triple chain of these structural elements and that sf is confined within arrows marked by number “2”. The model of that defect, which is below denoted as the second type, is presented in Fig. 7(a), its formation was caused by the $a/2$ (half unit cell) shift of the adjacent areas. This defect may be defined as out-of-phase boundaries,

however, typically out-of-phase boundaries are associated with layered compounds [66], [67]. However, the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ crystal structure does not represent a layered structure, but we believe, that we can use that definition in our case.

Fig. 7. The models of the defects marked by arrows in Fig. 5 (a) as: (a) - “2” – the out-of-phase boundary. (b) –and (c) “3” and “4” - shifted mirror twins, respectively .

Defects of the third type are also shown by arrows marked by “3” and “4” in Fig. 5(a). Such defect can be described as a shifted mirror twins. The defect models are presented in Fig. 7(b) and Fig. 7(c), respectively. These defects are located between arrows marked by “3” and “4” formed by the twin formation with a simultaneous shift by $3a/4$ along the a axis. This results in the formation of double chains of the structural units. The defects that are located between the arrows marked by “3” and “4” in Fig. 5(a) are symmetrical relative to the mirror plane parallel to the b axis but with a $b/2$ shift along the b axis. In the junction area of these two defects dislocations are formed without La in the dislocation cores. This was observed on HR HAADF STEM images and supported by EDXS elemental mapping (not presented here).

Two closely spaced dislocation cores are indicated by “5” in Fig.5 (a). The dislocations were formed as a result of the interaction of two flat defects, namely “3” and “4”. It was difficult to construct the Burgers circuit around the dislocation cores, however, the observation of the micrograph at a glancing angle parallel to the a axis of the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ unit cell does not reveal any extra planes. Thus, we proposed that the Burgers vector of the dislocations is parallel to the a axis. Surprisingly, the HR HAADF STEM image unambiguously demonstrated the absence of rare earth La atoms in the dislocation core areas. The cores of screw dislocations in SrTiO_3 , in contrast, demonstrated vacancies in the Ti-O column, not Sr ones [68].

The HR HAADF STEM image of another defect in the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ compound together with the EDXS elemental maps is presented in Fig. 8(a-e), the model is shown in Fig. 8(f). La,

Ni, Fe and Al atoms are presented in the defect area. This defect has a typical zig-zag contrast, the habit plane, parallel to $\{140\}$ and occurs due to overlapping of the defect of the third type

Fig.8. (a) HR HAADF STEM image of the shifted mirror twin overlapping with $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ matrix and EDX elemental maps: (b) – La, (c) – Al, (d) – Fe, (e) – Ni. (f) – The model of the defect.

with the matrix. In Figs. 8 (a) and (f) one can see two adjacent structural elements from the defected part of the specimen marked with pairs of yellow rectangles and the third one belonging to the matrix, which is single and shifted relative to the double structural element. It should be noted that the intensity of the spots corresponding to the La columns in the zig-zag defect area is lighter than that in other parts of the specimen. This is due to a reduced number of atoms in the La columns in the zig-zag defect area relative to other areas, since the defect area is an overlapping of two crystals. The same reduction of the spot intensity is visible in the La elemental map.

The composition of the quaternary phase was measured using EDXS, consistent results were obtained from several particles. The quantification error within the obtained spectra was ~5%. Quantification of the spectra was, however, complicated due to lack of a suitable quaternary standard, a relatively large uncertainty in the composition of the ternary and binary phases containing Fe and Ni, which can substitute each other and a high defect density in the particles. The composition of the quaternary phase is Al:Fe:Ni:La = 8:1.1:0.9:1. A typical EDXS spectrum is presented in Fig. 9. Therefore, the quaternary phase can be described by the general formula $\text{Al}_8\text{Fe}_{1.1}\text{Ni}_{0.9}\text{La}$, which is consistent with the stoichiometry Al:TM: La= 8:2:1.

Fig.9. EDX spectra from a $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle.

For TEM and EDXS investigation of the ternary Al-Ni-Fe compound several lamella in the sections marked by “a-a”, “b-b” and “c-c” and similar to those were prepared from a polished surface shown in Fig. 2(b). First, the “a-a” lamella was sectioned in the area of the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particle, adjacent to the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle, the images are presented in Figs. 4 (a) and (b). The SADP obtained from the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particle is presented in Fig. 10 (a). The analysis of the SADP unambiguously confirmed that the crystal structure of that particle adopted the monoclinic Al_9Co_2 type structure with S.G. $P2_1/c$. That phase was discovered in a number of studies considered above in the introduction. The SADP presented in Fig. 10(a) corresponds to the [011] zone axis, the 100 reflections arise from double diffraction. To estimate lattice parameters of the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ phase we verified the camera length calibration using adjacent Al particles and found out that those were $a=0.857$ nm, $b=0.629$ nm, $c=0.621$ nm, $\beta=97^\circ$, which was close to unit cell parameters of Al_9Co_2 [69]. The EDXS quantification indicated that Fe content in the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particle in our alloys, namely Ni = 15 ± 1 at.%, Fe = 3 ± 1 at.%, was lower than that in the study of Khaidar *et al.* [19] and Chumak *et al.* [23], but corresponded to the homogeneity region determined in the study of Dybkov *et al.* [29] and Eleno *et al.* [22]. The EDXS spectrum is presented in Fig. 10

(b), the quantitative data are shown in Table 2. Thus, the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ phase can be described as $\text{Al}_9\text{Ni}_{1.6}\text{Fe}_{0.4}$.

Fig. 10. (a) - The SADP obtained from the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particle in $[011]$ zone axis.(b) – correspondent EDX spectra.

The lamellas were prepared from elongated $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particles away from quaternary intermetallic particles, like “b-b” sections, shown in Fig. 2(a). The SADP and EDXS investigations demonstrated that the crystal structure also adopted Al_9Co_2 crystal lattice type, its chemical composition was the same as described above.

Occasionally, smaller Al-Ni-Fe particles with another chemical content were found. They have irregular morphology with the size not exceeding $1\mu\text{m}$. The crystal structure is typical for orthorhombic Al_3Ni compound with S.G. $Pnma$ [27]. The SADP obtained in the $[010]$ zone axis is presented in Fig. 11(a), the corresponding EDXS spectra are shown in Fig. 11(b). The EDX quantification pointed to a very low Fe content in the particles: $\text{Al} = 75\pm 1.0\text{ at\%}$, $\text{Ni} = 23.5\pm 1.0\text{ at\%}$ and $\text{Fe} = 1.5\pm 1.0\text{ at\%}$. The general formula for these particles might be $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$, where $x=1.5$. It should be noted that the Al:TM stoichiometry is close to 3:1.

Fig. 11. (a) - The SADP obtained from the $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ particle in [010] zone axis.(b) – correspondent EDX spectra.

A relatively high density of these particles was found during the study of the specimens obtained from the eutectic areas, like “c-c” section in Fig. 2(b). The HAADF STEM image of that sample together with EDXS elemental mapping is presented in Fig. 12 (a-e). A part of a quaternary phase particle surrounded by a $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ shell is visible in the right side of the micrograph. The adjacent eutectic area contains fcc-Al, $\text{Al}_{11}\text{La}_3$ and $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ particles. The content can be confirmed by EDXS elemental mapping, the crystal structure was unambiguously determined by a ED study (the results are not presented here) as orthorhombic Al_3Ni structure type with *S.G.Pnma*.

Fig. 12. The microstructure of the specimen in the area of “c-c”. (a) - the HAADF STEM image of that specimen and EDX elemental maps: (b) – Al, (c) – Ni, (d) – Fe, (e) – La.

The $\text{Al}_{11}\text{La}_3$ particles exhibited two morphology types: the first one is larger faceted particles with the sizes up to 20 μm , found by a SEM study, presented in Fig. 2(a). The second morphology type of the $\text{Al}_{11}\text{La}_3$ particles is observed in the eutectic areas shown in Fig. 12(a).

Fig.13. The EDX spectra from a $\text{Al}_{11}\text{La}_3$ particle.

The ED study pointed to an orthorhombic crystal structure of the $\text{Al}_{11}\text{La}_3$ particle of both morphology types and S.G. *Immm* or *Imm2*. The EDXS data (Fig.13) demonstrated that Al:La stoichiometry was close to 4:1. This fact could indicate that those particles corresponded to the Al_4La phase. However, taking into account the study of Gomes de Mesquita and Buschow^[48], we can suggest that the particles are $\text{Al}_{11}\text{La}_3$. A light excess of Al content might arise from Al matrix fluorescence. It is worth noting that we did not observe Ni and Fe peaks on the EDXS spectra (Fig.13) in contrast to the data presented by Huang *et al.*^[46].

3.4. XRD analysis.

The XRD spectra obtained from the alloys $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ (*I*) and $\text{Al}_{85}\text{Ni}_9\text{Fe}_2\text{La}_4$ (*II*) are presented in Fig. 14.

Fig. 14. The XRD patterns of $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ (*I*) and $\text{Al}_{85}\text{Ni}_9\text{Fe}_2\text{La}_4$ (*II*) alloys.

There are many overlapping peaks in the measured patterns that pointed to a multicomponent phase mixture. The most intense peaks represent fcc-Al, $\text{Al}_{11}\text{La}_3$, $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ and $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$. However, the relative intensities disagree because of poor statistics, unequal particle sizes and preferred orientation effects in the measured data. The XRD spectra containing well-defined

peaks which did not match those four phases could be attributed to $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$. The most intense peaks which are typical for the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase, isostructural to Al_8EuFe_2 [54], are identified on both XRD spectra at the angles of $2\theta=28.20^\circ$ ($d=0.316$ nm), $2\theta=31.40^\circ$ ($d=0.29$ nm), $2\theta=34.06^\circ$ ($d=0.26$ nm), and $2\theta=36.10^\circ$ ($d=0.25$ nm). The peak at the angle of $2\theta=20.11^\circ$ ($d=0.44$ nm) is definitely indexed to 110 reflection of monoclinic $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ phase. The peaks arising from $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ overlapped with the peaks from the other phases, that caused uncertainty in phase identification. The noticeable broadening of the peak in the $2\theta=43-45^\circ$ range in the alloy (*I*) could suggest the presence of $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ phase, since the most intense peaks of that phase are observed in that range. According to the OM study, the volume fraction of the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase is higher in the Fe-rich alloy (*I*) relative to the alloy (*II*), therefore, we did not observe any obvious trace of the $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ phase in the alloy (*II*).

3.5. Phase stability and phase transformations.

Fig. 15. Secondary electron SEM image showing the microstructure after 3 h annealing at: - (a) 400 °C of alloy (*I*), the enlarged image of $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle and a eutectic area. (b) - 500 °C of alloy (*I*), (c) - 600 °C of alloy (*I*), (d) - 600 °C of alloy (*II*). Phases are denoted as: 1 – Al, 2 – $\text{Al}_9\text{Ni}_{1-x}\text{Fe}_x$, 3 - $\text{Al}_{11}\text{La}_3$, 4 - $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$, 6- $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$.

476

477 The phase transformations temperature and phase stability were studied after isothermal
 478 annealing in vacuum at 400 °C, 500 °C, and 600 °C during 3 hours. A comprehensive
 479 microstructural study including SEM, TEM/STEM, EDS, and XRD was performed. We also
 480 used part of the data on differential scanning calorimetry (DSC) obtained in the study of
 481 Bakhteeva *et al.* [70]. The DSC scan during heating and cooling was performed at the rate of 20
 482 °C/min.

483 Typical SEM images of the Fe-rich Al₈₅Ni₉Fe₂La₄ alloy (*I*) after annealing at 400 °C, 500 °C,
 484 and 600 °C and the alloy (*II*) (Al₈₅Ni₉Fe₂La₄) after annealing at 600 °C are presented in Fig. 15
 485 (a-d). Coarse particles of different phases can be found in the sample after annealing at 400 °C
 486 (Fig. 15 (a)). However, the eutectic denoted by “5” in Figs. 2 (a) and (b) decomposes. At the
 487 same time, the eutectic reaction starts at the quaternary Al₈Fe_{2-x}Ni_xLa phase particles and that is
 488 shown in the inset of Fig. 15 (a). The aspect ratio of the Al₉Fe_{2-x}Ni_x particles becomes smaller.
 489 The annealing at 500 °C resulted in the eutectoid reaction

491 as shown in Fig. 15(b). Only coarse particles of the three phases, namely, Al, Al₁₁La₃ and
 492 Al₉Ni_{2-x}Fe_x, are visible in SEM images. After annealing at 600 °C coarsening of eutectics takes
 493 place and only relatively large particles of these three phases are visible in Fig. 15(c). The
 494 peculiarities of the contrast and EDXS data indicated that the Al₃Ni_{1-x}Fe_x particles were formed
 495 in the Al₈₅Ni₉Fe₂La₄ alloy (*II*). These particles look slightly brighter than Al₉Fe_{2-x}Ni_x ones in
 496 Fig. 15 (d). The volume fraction of each phase after annealing at 500 °C and 600 °C was
 497 estimated using the difference in contrast on SEM images, the results are presented in Table. 3.

498

499 Table 3. The volume fraction of the phases estimated from OM (before annealing) and SEM
 500 (after annealing) data (the error is ±10%).

Alloy Phase	Al ₈₅ Ni ₇ Fe ₄ La ₄ (<i>I</i>) before annealing	Al ₈₅ Ni ₇ Fe ₄ La ₄ (<i>I</i>) after annealing at		Al ₈₅ Ni ₉ Fe ₂ La ₄ (<i>II</i>) before annealing	Al ₈₅ Ni ₉ Fe ₂ La ₄ (<i>II</i>) after annealing at 600 °C
		500 °C	600 °C		
Al	16	6	11	20	25
Al ₁₁ La ₃	19	37	31	15	32
Al ₉ Ni _{2-x} Fe _x	12	57	58	12	32
Al ₃ Ni _{1-x} Fe _x		-	-		10
Al ₈ LaFe _{2-x} Ni _x	51	-	-	25	-

501

The XRD spectra, obtained from the alloys $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ (**I**) after annealing at 400, 500, 600°C and $\text{Al}_{85}\text{Ni}_9\text{Fe}_2\text{La}_4$ (**II**) after annealing at 600°C are presented in Fig. 15.

The peaks in the spectrum, obtained from the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ (**I**) alloy after annealing at 400°C, located in the range of $2\theta=33\text{--}34^\circ$, on the right and left from the peaks identified as

Fig. 16. The XRD patterns of $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ (**I**) alloy after annealing at 400 °C, 500 °C and 600 °C and $\text{Al}_{85}\text{Ni}_9\text{Fe}_2\text{La}_4$ (**II**) alloy after annealing at 600 °C.

coming from $\text{Al}_{11}\text{La}_3$ phase (denoted by “3”) are clearly visible, these peaks correspond to the $\text{Al}_8\text{LaFe}_{2-x}\text{Ni}_x\text{La}$ phase (“4”). After annealing at 600°C these peaks vanish. The intensity of the peak $2\theta=36.10^\circ$ ($d=0.249$ nm) considerably lowers mostly due to the impact of the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase (“4”). The peak at $2\theta=36.7^\circ$ ($d=0.244$ nm) associated with the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ (“4”) and $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ (“6”) phases disappeared after annealing at 500 °C or higher temperatures. Along with that, the intensity of the peaks associated with the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ phase (“2”) in the angles of $2\theta=37.4^\circ$ ($d=0.240$ nm) and $2\theta=40.0^\circ$ ($d=0.225$ nm) substantially increases. The intensity of the peak $2\theta=42.15^\circ$ ($d=0.214$ nm) coming from the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ phase (“2”) increases after annealing up to 500°C, but then unexpectedly goes down. Again, this may be due to poor statistics, unequal particle sizes and preferred orientation effects in the measured data. The extensive growth of the intensity of the peaks associated with the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ (“2”) and $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ (“6”) at $2\theta=43.55^\circ$ ($d=0.207$ nm) and $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ (“2”) at $2\theta=44.4^\circ$ ($d=0.203$ nm) was observed after annealing at

600 °C. This pointed to the growth and/or coarsening of the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ phase. The growth of the volume fraction of the $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ phase seems unlikely, since we did not find that phase in the SEM study. The intensity of the peak at $2\theta=49.4^\circ$ ($d=0.184$ nm), associated with the $\text{Al}_{11}\text{La}_3$ (“3”), $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ (“4”) and $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ (“6”) phases going down with the temperature growth in the alloy (*I*), might occur due to the eutectoid reaction $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La} \rightarrow \text{Al}_{11}\text{La}_3 + \text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ and the invariant reaction $\text{Al} + \text{Al}_3\text{Ni}_{1-x}\text{Fe}_x \rightarrow \text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$.

The intensity of the (220) Al peak at $2\theta= 65.17^\circ$ ($d=1.43$ nm) in the alloy (*I*) after the annealing at 600 °C decreased. Using SEM data (Table.3) we associated that observation with the growth of the volume fraction of the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ phase. In contrast to that, we found an enormous growth of that peak intensity in the alloy (*II*) after annealing at 600°C, which might arise from a relatively high Al and $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ phases content in the sample (See Table 3).

4. Discussion.

In order to reveal the details of the microstructure formation in two air cast $\text{Al}_{85}\text{Ni}_{11-x}\text{Fe}_x\text{La}_4$ (where $x = 2$ or 4 at.%) polycrystalline alloys, which exhibited the number of phases with definite morphology and different structural defects, it seems necessary to determine the sequence of phase transformations. The results of the study of two air cast $\text{Al}_{85}\text{Ni}_{11-x}\text{Fe}_x\text{La}_4$ (where $x = 2$ or 4 at.%) polycrystalline alloys together with isothermal annealing of these samples by means of microscopic and microanalysis methods allow us to suggest a number of phase transformation reactions which take place during cooling of the samples to room temperature in the air. In this consideration we also took into account the DSC data obtained by our group previous to this investigations^[70] for isochronal annealing to the temperatures up to 1000 °C with subsequent cooling down to room temperature (see Fig. 16). As the isothermal annealing experiments demonstrated, the $\text{Al}_8\text{LaFe}_{2-x}\text{Ni}_x$ phase is metastable and undergoes irreversible eutectectoid reaction during heating. Thus, the transformation of cooled melts in the air and the isochronally cooled alloys after heating must be different. The available reference sources were also used for a tentative description of the reaction. Thus, the following phase transformation reactions of the $\text{Al}_{85}\text{Ni}_{11-x}\text{Fe}_x\text{La}_4$ (where $x = 2$ or 4 at.%) melts are proposed during cooling to room temperature in the air:

1. $L \rightarrow L_1 + \text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ primary intermetallic phase solidification.
2. $L_1 \rightarrow L_2 + \beta\text{-Al}_{11}\text{La}_3$ primary intermetallic phase solidification.
3. $\beta\text{-Al}_{11}\text{La}_3 + L_2 \rightarrow \alpha\text{-Al}_{11}\text{La}_3 + L_2$ phase transformation (invariant reaction).
4. $L_2 + \text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La} \rightarrow L_3 + \text{Al}_9\text{Ni}_{2-x}\text{Fe}_x + \text{Al}_{11}\text{La}_3$ peritectic reaction.
5. $L_3 \rightarrow \text{Al}_{11}\text{La}_3 + \text{Al}_3\text{Ni}_{1-x}\text{Fe}_x + \langle \text{Al} \rangle$ eutectic reaction.

In the studied hyper-eutectic alloys the excess of the alloying elements surpassing the eutectic concentration leads to a rapid solidification of primary intermetallic phases in the form of separate particles or their complexes. The growth rate of such primary intermetallic phases is higher than eutectic growth. The solubility limit for binary Al-La alloys is <1 at.% of La^[50] (0.01 at.% at 640 °C^{[71], [50]}), Al-Fe – 1.7 - 2.5 at.% of Fe^[22], and for Al-Ni; 1.7 at.% of Ni) (solid solubility of Ni in Al decreases from 0.11 at.% at 639.9°C to 0.01 at.% at 500°C). In the course of rapid solidification processing the enhancement of the solid solubility is observed up to 7.7 at.% of Ni^[72]. The growth rates of these primary intermetallic phase particles are much higher than the eutectic one. A close inspection of OM and SEM images (See Fig. 1 and Fig. 2) pointed to two scenarios:

A. Solidification of the high-temperature β -Al₁₁La₃ phase after solidification of the Al₈Fe_{2-x}Ni_xLa phase. This assumption was supported by the SEM observations mentioned above, where relatively large Al₁₁La₃ (5-20 μ m in size) faceted particles surrounded the Al₈Fe_{2-x}Ni_xLa/Al₉Ni_{2-x}Fe_x core shell particles or were located in between the Al₉Ni_{2-x}Fe_x particles. The latter ones formed during cooling in a peritectic reaction from the Al₈Fe_{2-x}Ni_xLa particles. Thus, two transformations occurred at the first step:

1. $L \rightarrow L_1 + \text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ primary intermetallic phase solidification followed by.
2. $L_1 \rightarrow L_2 + \beta\text{-Al}_{11}\text{La}_3$ primary intermetallic phase solidification.

B. The eutectic reaction $L \rightarrow L_1 + \text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La} + \beta\text{-Al}_{11}\text{La}_3$. According to Cambell^[65], when an alloy composition departs from eutectic, or when a third alloying element is present, the interface can become unstable for the same reason as in the case of a simple solid-liquid interface. If one of the phases is faceted, which is Al₁₁La₃ in our case, the growth of this phase (and, consequently, of the eutectic) is slower at a given undercooling, whereas dendrites (Al₈Fe_{2-x}Ni_xLa particles) may then grow more rapidly than the eutectic at the eutectic composition. The larger Al₁₁La₃ particles are faceted, while Al₈Fe_{2-x}Ni_xLa before decomposition adopted a dendritic microstructure, therefore, the described eutectic transformation looks highly likely.

This situation occurred in both alloys, **(I)** and **(II)**. The dendrites located on the primary dendritic axis are assemblies of the Al₈Fe_{2-x}Ni_xLa particles. The dendritic microstructure forms in the supersaturated solution under an unstable temperature and element concentration conditions with the influence of crystallographic factors^[73]. The dendritic solidification of the Al₈Fe_{2-x}Ni_xLa phase explains the high density of the defects found in TEM/STEM like twins, share bands and the formation of the Al_{3.2}Fe_{1-x}Ni_x δ -layers. **Since the Al₈Fe_{2-x}Ni_xLa phase is new one, we will discuss the formation of structural defects in this phase in more details.**

The formation of the $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ δ -layers could be caused by a concentration inhomogeneity in the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particles. Extended $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ δ -layers with flat morphology are associated with layered crystal growth during crystallization from the liquid phase. This type of crystallization proposed to be a general phenomenon of crystal growth ^[74] regardless of the composition. If so, an excessive amount of alloying elements, which are Fe and Ni, was dislodged to the liquid/solid interface, and when the critical concentration is reached, a $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ δ -layer is formed in the absence of La. The density of the $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ δ -layers in the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ intermetallic compound is relatively high, which is due to the excess content of Fe and Ni and their relatively high diffusion mobility, in comparison with that of La atoms.

The out-of-phase boundary (defect “2”) and shifted mirror twins (defects “3” and “4”) are associated with dislocations (defects “5”) and the $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ δ -layers. These defects could form during the crystallization of the particle. In an ordered structure, a defect in the atomic arrangement caused by the presence of a dislocation can cause the atomic sequence to be out of step and thus generate an out-of-phase boundary ^[65]. In its turn, there are several possible reasons for the formation of dislocations. The first is due to the heterogeneity of the concentration of the elements in the non-equilibrium crystallization of a solid solution of a multicomponent alloy with atomic radii of different sizes, and that is quite similar to the formation of $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ δ -layers. Successive layers have somewhat different composition and parameters of the crystal lattice. At the boundaries of such layers elastic stresses arise which, when the yield strength is reached as a result of relaxation, lead to the appearance of dislocations. The second reason can be the stresses arising at the interface between two phases, namely, the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ and the Al solid solution of aluminum or the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ and $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$. And third, in addition, the high density of thermal vacancies could result in the formation of dislocations.

Twinning (defects “3” and “4”) could also appear due to the stress in the particle. However, we cannot settle down that out-of-phase boundaries and twins are generated by dislocations or vice-versa.

We suppose that the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase after the primary solidification forms assemblies of particles along the second (and, probably, the third) dendritic axis. However, the peritectic reaction “4”

results in a partial dissolution and transformation of $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ to the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ phase. This is clearly visible in the areas near the surface of the larger $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particles located along the primary dendritic axes, this leads to the formation of core shell structures similar to those described in papers ^[75] and ^[65]. The $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particles, which are located along the second

(third) crystallization axis and are smaller in size, transform to the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particles completely according to the reaction “4”. SEM images demonstrated that the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particles are elongated in the direction perpendicular to the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particles, which is very typical for dendritic crystallization [65] and support the suggestion on quaternary phase crystallization. Therefore, primary crystallization reactions or eutectic reaction occur at temperatures higher than 1000 °C and they were not observed during DSC experiment in [70].

In conformity with the binary Al-La phase diagram [50], [76] and ternary Al-Ni-La phase diagram [16] the solidification of $\beta\text{-Al}_{11}\text{La}_3$ started at the temperature $t=1170^\circ\text{C}$ and underwent a polymorphic transformation $\beta\text{-Al}_{11}\text{La}_3 \rightarrow \alpha\text{-Al}_{11}\text{La}_3$ at $t=915^\circ\text{C}$. Certainly, minor changes of crystallization temperature may occur in the quaternary system, however, it is unlikely to expect a considerable drop of the transformation temperature. Thus, the first peak at $t=913^\circ\text{C}$ in the DSC curve found by Bakhteeva *et al.* [70] (Fig. 16) in the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy during cooling appeared due to the polymorphic transformation $\beta\text{-Al}_{11}\text{La}_3 \rightarrow \alpha\text{-Al}_{11}\text{La}_3$ - reaction “3”.

Fig.16. The DSC curves of the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy [70].

The other two peaks, namely, 2nd and 3rd, appearing on the DSC curve during cooling in the alloy (I) (737 °C and 686 °C, respectively) or in the alloy (II) (749 °C and 691 °C, respectively) [70] did not correspond to the known phase transformation in ternary or even binary systems. There are several phases which were found in the alloys and they can be considered as candidates for a reaction in the temperature range of the 2nd and 3rd DSC peaks. These phases are $\text{Al}_9\text{Fe}_{2-x}\text{Ni}_x$ and $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$. The peritectic reaction $\text{L} + \text{Al}_{13}\text{Fe}_4 + \text{Al}_3\text{Ni} \rightarrow \text{Al}_9\text{Fe}_{2-x}\text{Ni}_x$ in the ternary Al-Ni-Fe system takes place at 809 °C. According to Budberg *et al.* [20], this phase forms in the temperature range of 850 and 750 °C. In our study the $\text{Al}_{13}\text{Fe}_4$ phase, which is isostructural to $\text{Al}_{3.2}\text{Fe}$, contains Ni and this can increase the reaction temperature. We observed this phase

denoted above as $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ in the form of δ -layers in the quaternary alloy particles. The formation of separate $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ as primary particles could occur at the initial stages of crystallization, as observed by Kattner^[77] in the binary Al-Fe system at 1160 °C. The Al_3Ni phase could form in the Al-Ni-Fe system in a number of reactions starting from 866 °C^{[37], [19], [29], [20] [22], [24]}. The increase of Fe content lowers the transformation temperature^[22], thus, the peaks during cooling could be linked with these two reactions. The $\text{Al}_{13}\text{Fe}_4$ phase in the reactions mentioned above could appear during primary crystallization at temperatures higher than 1000 °C.

There is, however, the peritectic reaction denoted by “4” $\text{L}_2 + \text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La} \rightarrow \text{L}_3 + \text{Al}_9\text{Ni}_{2-x}\text{Fe}_x + \text{Al}_{11}\text{La}_3$, which might correspond to one of the peaks. The quaternary $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase was unknown and it was not considered in the literature. The $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase is metastable and could decompose completely upon heating up to 1000 °C in DSC experiment, as we observed at isothermal heating at 600 °C for 3 hours. Therefore, if the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particles were not decomposed completely during the heating, one of the peaks could appear due to this peritectic reaction.

The last 4th peak at 612 and 620 °C for the alloys (*I*) and (*II*), respectively corresponds to Al crystallization.

This eutectic reaction (the fourth DSC peak in the study of Bakhteeva et al^[70]) resulted in the formation of three phases $\text{L}_3 \rightarrow \text{Al}_{11}\text{La}_3 + \text{Al}_3\text{Ni}_{1-x}\text{Fe}_x + \langle \text{Al} \rangle$ (the reaction denoted above by “5”) starts at the temperature of 634 °C which is close to 625 °C, found in the study of Godecke *et al.*^[15] and mentioned by Raghavan^[16] for the Al-Ni-La systems.

At the isochronal annealing of the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy up to 1000 °C with the constant rate of 20 °C/min on the DSC scans four peaks with a complicated shape were also observed^[70]. However, the intensity and shape of the peaks differed from the peaks appeared during cooling. This obviously indicated a diversity of reactions during heating and cooling of the sample in the same temperature range.

The first endothermic effect was found in the temperature range between 627 and 675 °C with the peak maximum at $t_{\text{m}}=647$ °C. The complicated shape of the peak with the shoulder in the low temperature part pointed to numerous reactions. The lowest melting temperature phases are an Al solid solution and Al/ $\text{Al}_{11}\text{La}_3$ / $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ eutectic^{[76], [78], [22]}, which melt in this temperature range.

In the temperature range from 712 to 810 °C, two overlapping endothermic peaks of a complex shape were observed.

The SEM study of the air cast alloys after annealing at 400 °C for 3 hours (Fig. 15a) showed that eutectic colonies designated by “5” in Fig. 2b in air cast sample disappeared, but fine-dispersed Al₁₁La₃ grains were still noticeable in the areas of the assumed location of the eutectic. This indicates that the thermally activated dissolution reaction does not end in the process of isothermal annealing, which is probably due to insufficient annealing time. In the same sample at the edges of the interface regions of the Al₈Fe_{2-x}Ni_xLa phase, the onset of the eutectoid reaction Al₈Fe_{2-x}Ni_xLa → Al₁₁La₃+Al₉Ni_{2-x}Fe_x is noticeable (Fig. 15a, inset). Isothermal annealing at 500 °C for 3 hours leads to the completion of this reaction (Fig. 15 (b)). Based on these data, we may assume that the second intense peak on the DSC curve detected in the temperature range 712-736 °C [70] can be due to this reaction. Again, these results confirm the metastable nature of the Al₈Fe_{2-x}Ni_xLa phase.

The third peak on the DSC curve observed upon heating of this alloy is due to reactions occurring in the temperature range from ~ 750 °C to 789 °C. The nature of this peak could be linked to the transformation of the Al₉Ni_{2-x}Fe_x phase, since it was found at 750 °C [19], [22] but not at 850 °C.

The observed fourth peak, T_{p4} = 933 °C, could correspond to a polymorphic transformation of the α-Al₁₁La₃ → β-Al₁₁La₃ phase transition. Interestingly, there is a relatively strong difference in the temperatures corresponding to the fourth peak in the alloys (*I*) and (*II*), namely, 933 °C and 877 °C, respectively. However, the phase diagram in papers [15] and [16] shows that β-α transformation takes place due to peritectic reaction and the transformation temperature depends on Ni content: a higher Ni content, that is the alloy (*II*), decreases the transformation temperature and vice versa with Fe content in the alloys.

The DSC spectra of the Al₈₅Ni₉Fe₂La₄ alloy (*II*) are similar to those described above with four endothermic and four exothermic peaks during heating and cooling, respectively. The peaks corresponding to the beginning of Al melting in both cases (t=627) °C are related to a close chemical composition of the alloys (*I*) and (*II*). The decrease in Al content in the alloy (*II*) after the annealing at 600 °C results in the formation of the Al₃Ni_{1-x}Fe_x phase together with Al₉Fe_{2-x}Ni_x. and that is clearly visible in Fig. 15 (c,d). The reaction L+ Al₉Fe_{2-x}Ni_x→Al₃Ni_{1-x}Fe_x+Al₁₁La in the alloy (*II*) causes an increase of the volume fraction of the Al₃Ni_{1-x}Fe_x phase after annealing at 600 °C.

The third DSC peak appeared on the DSC scan during cooling of the Al₈₅Ni₇Fe₄La₄ alloy in the temperature range of 693 °C -686 °C. We cannot unambiguously determine the nature of the peak and consider two possibilities: 1. The reaction which was described by [22] and [23], L+Fe₄Al₁₃→FeNiAl₉+<Al>. However, this reaction occurred at 650°C. According to our

observations, the $\text{Al}_{13}\text{Fe}_4$ phase, isostructural to $\text{Al}_{3.2}\text{Fe}$, contains Ni and this can increase the reaction temperature. We observed this phase denoted above as $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ in the form of δ -layers in the quaternary alloy particles. The formation of separate $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ as primary particles could occur at the initial stages of crystallization, as observed by Kattner^[77] in the binary Al-Fe system at 1160°C. 2. The second scenario is the crystallization of proeutectic Al followed by eutectic reaction $\text{L}_3 \rightarrow \text{Al}_{11}\text{La}_3 + \text{Al}_3\text{Ni}_{1-x}\text{Fe}_x + \langle \text{Al} \rangle$. The crystallization of proeutectic Al looks very likely because we observed bubble-like Al grains (see Fig. 2(b) adjacent to $\text{Al}_9\text{Fe}_{2-x}\text{Ni}_x$ particles crowd out the Al- $\text{Al}_{11}\text{La}_3$ - $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ eutectics.

This eutectic reaction (the fourth DSC peak) resulting in the formation of three phases $\text{L}_3 \rightarrow \text{Al}_{11}\text{La}_3 + \text{Al}_3\text{Ni}_{1-x}\text{Fe}_x + \langle \text{Al} \rangle$ starts at the temperature of 634 °C which is close to 625 °C, found in the study of Godecke *et al.*^[15] and mentioned by Raghavan^[16] for the Al-Ni-La systems.

At the isochronal annealing of the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy up to 1000°C at a constant rate of 20 °C/min four peaks with complicated shape were also observed on the DSC scans^[70]. However, the intensity and shape of the two central peaks differed from the peaks appeared during cooling. This obviously indicated a diversity of reactions during heating and cooling of the sample in the same temperature range. The first endothermic effect was found in the temperature range between 627 and 675 °C with the peak maximum at $t_{\text{H1}}=647$ °C. The complicated shape of the peak pointed to numerous reactions. The lowest melting temperature phases are an Al solid solution and Al/ $\text{Al}_{11}\text{La}_3$ / $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ eutectic^{[76], [78], [22]}, which melt in this temperature range. The samples were isothermally annealed at 400, 500, 600 °C, for comparison. The EM study of the specimen annealed at 400°C demonstrated the absence of typical Al/ $\text{Al}_{11}\text{La}_3$ / $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ eutectics which were found in the cast alloys and are shown in Fig. 2 (a,b), but only fine $\text{Al}_{11}\text{La}_3$ particles were observed. That is the evidence of unfinished thermo activated solution reaction and diffusion process during annealing due to limited time. In that specimen the eutectoid reaction $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La} \rightarrow \text{Al}_{11}\text{La}_3 + \text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ started, which is clearly visible in the inset of Fig. 15(a) on the surface of the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particles. The isothermal annealing at 500°C completes the reaction which is shown in Fig. 15(b). Basing on that data we can assume that the second peak found during DSC scan in the temperature range of 712-736°C^[70] originated from that reaction. That observation, again, proves the fact that the quaternary $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase is metastable. The third peak on the DSC scan obtained during heating in the temperature range of ~ 750÷789°C remains undetermined because the experiments on isothermal annealing did not reveal additional phases. The fourth peak $\text{Tp4}=933^\circ$ most likely is related with the polymorph transition $\alpha\text{-Al}_{11}\text{La}_3 \rightarrow \beta\text{-Al}_{11}\text{La}_3$

The DSC spectra of the $\text{Al}_{85}\text{Ni}_9\text{Fe}_2\text{La}_4$ alloy (**II**) are similar to those described above with four endothermic and four exothermic peaks during heating and cooling, respectively. The peaks correspondent to the beginning of Al melting in both cases ($t=627^\circ\text{C}$) are related to a close chemical composition of the alloys (**I**) and (**II**). The decrease in Al content in the alloy (**II**) after the annealing at 600°C results in the formation of the $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ phase together with $\text{Al}_9\text{Fe}_{2-x}\text{Ni}_x$, which is clearly visible in Fig. 15 (c,d). The reaction $\text{L} + \text{Al}_9\text{Fe}_{2-x}\text{Ni}_x \rightarrow \text{Al}_3\text{Ni}_{1-x}\text{Fe}_x + \text{Al}_{11}\text{La}_3$ in the alloy (**II**) causes an increase of the volume fraction of the $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ phase after annealing at 600°C .

Conclusion

Complex microstructural investigations of two Al alloys, namely, $\text{Al}_{85}\text{Ni}_{11-x}\text{Fe}_x\text{La}_4$ ($x=2$ or 4 at.%) were carried out by means of electron and optical microscopy, EDXS, and XRD. It was found that these alloys contain several phases, which are fcc-Al, $\text{Al}_{11}\text{La}_3$, $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$, $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$, $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ and $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ in the form of δ -layers in the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particles. The OM demonstrated that relatively small difference in Fe and Ni contents in the alloys resulted in significant increase of the volume fraction of the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ phase in the Ni rich $\text{Al}_{85}\text{Ni}_9\text{Fe}_2\text{La}_4$ alloy. On the contrary, the content of the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ phase is twice higher in the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy. The microstructure of $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ was studied in more detail. Except the δ - $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ inclusions with the habit plane parallel to the a -axis, flat defects caused by the $a/2$ (half unit cell) shift, similar to out-of-phase boundaries, shifted mirror twins and dislocations were found. A defect with a zig-zag contrast appeared due to the overlapping of the shifted mirror twins with the matrix.

The high density of the defects in this phase was caused by dendritic growth. The composition of the quaternary phase measured by EDXS is $\text{Al}:\text{Fe}:\text{Ni}:\text{La} = 8:1.1:0.9:1$. Therefore, the quaternary phase can be described by the general formula $\text{Al}_8\text{Fe}_{1.1}\text{Ni}_{0.9}\text{La}$. The heating experiments demonstrated that this phase is metastable and undergoes an irreversible transformation: $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La} \rightarrow \text{Al}_9\text{Ni}_{2-x}\text{Fe}_x + \text{Al}_{11}\text{La}_3$.

The $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ ternary phase contains $\text{Ni}=15\pm1$ at.%, $\text{Fe}=3\pm1$ at.%, and the $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ phase contains $\text{Ni}=23.5\pm1.0$ at.% and $\text{Fe}=1.5\pm1.0$ at.%.

Based on the microstructural data with the use of the results obtained under isothermal and isochronous annealing, a sequence of the development of reactions determining the phase composition of alloys upon cooling and heating was proposed.

The influence of Fe within 2-4 at% on the phase content was not revealed in the air cast alloys. However, after isothermal annealing at 600°C in the alloy containing 4 at% of Fe the

784 $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ phase was not found and in the alloy containing 2 at% of Fe this phase is present in
785 the amount of ~10 vol. %.

786

787 **Acknowledgments**

788 The alloy formation and OM work was carried out under state assignment No 007-00129-18-00
789 (IMET RAS). The XRD and EM experiments were supported by the Federal Agency of
790 Scientific Organizations (Agreement No 007-GZ/C3363/26).

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Figure captions

Fig.1. Typical microstructure of $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy (OM image). Phases are denoted as: 1 – Al, 2 – $\text{Al}_9\text{Ni}_{1-x}\text{Fe}_x$, 3 – $\text{Al}_{11}\text{La}_3$, 4 – $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$.

Fig.2. SEM image of the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy showing the microstructure at (a) – low and (b) – higher magnifications. Phases are denoted as: 1 – Al, 2 – $\text{Al}_9\text{Ni}_{1-x}\text{Fe}_x$, 3 – $\text{Al}_{11}\text{La}_3$, 4 – $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$, 5- Al- $\text{Al}_{11}\text{La}_3$ - $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ eutectic. The “a-a”, “b-b” and “c-c” sections indicated the areas, where lamellas were cut. Arrows in (b) shows the eutectic microstructure.

Fig. 3. (a)- SE SEM image of the $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ alloy (phases are denoted as: 1 – Al, 2 – $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$, 3 – $\text{Al}_{11}\text{La}_3$, 4 – $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$) and correspondent EDX elemental maps (b) – Al, (c) – La, (d) – Ni, (e) – Fe.

Fig. 4. (a) –HAADF STEM image of the specimen prepared by FIB in the area of the “a-a” section (see Fig. 2 (b)): phases are denoted as: 1 – Al, 2 – $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$, 3 – $\text{Al}_{11}\text{La}_3$, 4 – $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$. (b) – enlarged BF TEM image of the part of the specimen, shown by the red rectangle in (a). Phases are denoted as: 2 – $\text{Al}_9\text{Ni}_{1-x}\text{Fe}_x$, 4 – $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$. Flat defects in the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle are indicated by arrows.

Fig. 5. (a) HR HAADF STEM image of a $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle obtained in the [001] zone axis. In between the arrows with numbers “1-4” there are the areas with flat defects. The structural elements shown by red rectangles with La atoms in the corners and the sides, parallel to {310} and {140}, the defects which can be explained using these structural elements are shown by yellow rectangles. (b) - the SADP from a $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle in the [001] zone axis. (c) - the $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ 4x4 unit cells in the [001] projection.

Fig. 6. (a) HAADF STEM image of the planar defect «1», which are δ -layers of the monoclinic $\text{Al}_{3.2}\text{Fe}_{1-x}\text{Ni}_x$ phase. (b) - the model of the defect and EDX elemental maps: (c) – La, (d) – Al, (e) – Fe, (f) – Ni.

Fig. 7. The models of the defects marked by arrows in Fig. 5 (a) as: (a) - “2” – the out-of-phase boundary. (b) - “3” and “4” - shifted mirror twin.

Fig.8. (a) HR HAADF STEM image of the shifted mirror twin overlapping with $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ matrix and EDX elemental maps: (b) – La, (c) – Al, (d) – Fe, (e) – Ni. (f) – The model of the defect.

Fig.9. EDX spectra from a $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle.

Fig. 10. (a) - The SADP obtained from the $\text{Al}_9\text{Ni}_{2-x}\text{Fe}_x$ particle in [011] zone axis.(b) – correspondent EDX spectra.

Fig. 11. (a) - The SADP obtained from the $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$ particle in [010] zone axis. (b) – correspondent EDX spectra.

Fig. 12. The microstructure of the specimen in the area of “c-c”. (a) - the HAADF STEM image of that specimen and EDX elemental maps: (b) – Al, (c) – Ni, (d) – Fe, (e) – La.

Fig. 13. The EDX spectra from a $\text{Al}_{11}\text{La}_3$ particle.

Fig. 14. The XRD patterns of $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ (**I**) and $\text{Al}_{85}\text{Ni}_9\text{Fe}_2\text{La}_4$ (**II**) alloys.

Fig. 15. Secondary electron SEM image showing the microstructure after 3 h annealing at: - (a) 400 °C of alloy (**I**), the enlarged image of $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$ particle and a eutectic area. (b) - 500 °C of alloy (**I**), (c) - 600 °C of alloy (**I**), (d) - 600 °C of alloy (**II**). Phases are denoted as: 1 – Al, 2 – $\text{Al}_9\text{Ni}_{1-x}\text{Fe}_x$, 3 - $\text{Al}_{11}\text{La}_3$, 4 - $\text{Al}_8\text{Fe}_{2-x}\text{Ni}_x\text{La}$, 6- $\text{Al}_3\text{Ni}_{1-x}\text{Fe}_x$.

Fig. 16. The XRD patterns of $\text{Al}_{85}\text{Ni}_7\text{Fe}_4\text{La}_4$ (**I**) alloy after annealing at 400 °C, 500 °C and 600 °C and $\text{Al}_{85}\text{Ni}_9\text{Fe}_2\text{La}_4$ (**II**) alloy after annealing at 600 °C.