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Structural Characterization of Rapidly Solidified $Al_{71}Ni_{24}Fe_5$ Alloy

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Abstract

The influence of rapid solidification from the liquid state on the structure of $Al_{71}Ni_{24}Fe_5$ alloy was studied. The samples were prepared by induction melting (ingots) and high pressure die casting into a copper mold (plates). The structure was examined by X-ray diffraction (XRD), light microscopy and high resolution transmission electron microscopy (HRTEM). The mechanism of crystallization was described on the basis of differential scanning calorimetry (DSC) heating and cooling curves, XRD patterns, isothermal section of Al-Ni-Fe alloys at 850°C and binary phase diagram of Al-Ni alloys. The fragmentation of the structure was observed for rapidly solidified alloy in a form of plates. Additionally, the presence of decagonal quasicrystalline phase D-$Al_{70.83}Fe_{9.83}Ni_{19.34}$ was confirmed by phase analysis of XRD patterns, Fast Fourier Transform (FFT) and Inverse Fast Fourier Transform (IFFT) of transmission electron microscopy images. The metastable character of D-$Al_{70.83}Fe_{9.83}Ni_{19.34}$ phase was observed because of the lack of thermal effects on the DSC curves. The article indicates the differences with other research works and bring up to date the knowledge about $Al_{71}Ni_{24}Fe_5$ alloys produced by two different cooling rates.

Keywords: Solidification process, Mechanism of crystallization, Rapid solidification, Quasicrystalline structure, Aluminium alloys

1. Introduction

Rapid solidification (RS) technologies are described as very fast extraction of thermal energy during the transition metal from a liquid to solid state. RS technologies include: melt-spinning, plasma spray deposition, rotating electrode process, high pressure die casting to water quenched mold and many others [1–4]. The advantages of RS include structure fragmentation and the formation of new non-equilibrium phases. Fast cooling in various alloy compositions provide the possibility of forming an amorphous, nanocrystalline or quasicrystalline structure, as well as their combinations, which provide a number of properties more favorable than the crystalline structure and strengthening mechanisms [5].

The high-pressure die casting is a method that provides a solidification rate of up to 10^3 °C/s. The process consists in very fast injection (10-100 ms) of liquid metal into a closed die by a piston. The matrix can be cooled by internal water channels [6,7]. The technology of high pressure die casting into a copper mold was used in other works to obtain alloys with a quasicrystalline structure, including: Al-Mn-Cu-(Mg, Si) [8], Al-Cr-Fe-Si [9], Zr-Ti-Nb-Cu-Ni-Al [10].

Quasicrystals, apart from crystalline and amorphous structures, constitute the third state of a solid [11]. The atoms in the quasicrystalline structure do not show the periodicity characteristic for crystal, but long range order [12]. Quasicrystals are characterized by a large extent pentagonal, octagonal, decagonal, dodecagonal and icosahedral symmetries, which are subject to the special principle of quasiperiodicity [13]. Quasicrystalline structures indicate versatile properties like low thermal and electrical conductivity, low coefficient of friction along non-periodic axes, mechanical strength, high hardness, thermal stability and corrosion resistance [14, 15].

According to the literature [16], it is possible to obtain aluminium nanocomposites with combinations of amorphous, crystalline or nano-quasicrystalline phases.

Nano-quasicrystalline phases as reinforcement are the subject of researches, and the importance of composite nanocrystalline alloys as an innovative class of materials was described by Inoue et al. [17]. Many current sources also describe the developing knowledge of amorphous-nanocrystalline composites [18]. Many known articles indicate the presence of quasicrystalline and crystalline phases without the discussed amplification mechanism [19, 20]. Nanocrystalline aluminium alloys reinforced with crystalline nanoparticles are materials that constitute an original class that differs from quasicrystals and nanocrystals. Reinforcement in the form of nano-quasicrystalline particles up to 30% by volume ensures plasticity of aluminium composites [21].

The group of Al-Ni-Fe alloys was extensively described in the literature as quasicrystalline structure forming. The literature describes that the presence of thermodynamically stable quasicrystals can only be obtained in a few alloying compositions [22, 23]. Grushko et al. [24] described the existence of a stable decagonal phase for the $Al_{71.5}Ni_{23.5}Fe_5$ alloy in the temperature range 1120÷1200 K. While, the work [23] describes the thermodynamic approach of designing Al-Ni-Fe alloys with a quasicrystalline structure, where the decagonal phase was identified for the $Al_{71}Ni_{24}Fe_5$ composition.

The aim of the study was to characterize the structure of the $Al_{71}Ni_{24}Fe_5$ alloy in a slow-cooled (ingot) and fast-cooled (plate) form. Structure analysis was performed using XRD analysis and transmission electron microscopy. The analysis of DSC curves was performed in order to describe the mechanism of crystallization of individual phases in the studied alloys.

2. Materials and methods

2.1. Alloy preparation

The master alloys (ingots) were prepared by the induction melting of Al, Ni, and Fe (99.9%) under an argon atmosphere in a ceramic crucible. The ingots were re-melted to ensure homogeneity. Then, 1 mm-thick plates were produced with using high-pressure die casting method. The liquid metal was forced under pressure into a flowing-water cooled copper mold. In case of structural tests, the samples were prepared in the form of milled powder.

2.2. Examination

In order to characterize the structure, phase identification was performed using X-ray diffraction (XRD). All samples were powdered and XRD patterns were recorded using a Rigaku Mini Flex 600 equipped with a copper tube as X-ray radiation source and D/TEX strip detector. The microstructure of alloy was described on the basis of light microscopy images in bright-field carried out by Zeiss Axio Observer with magnification of 500X. Additionally, to confirm the presence of quasicrystals, transmission electron microscopy (TEM) was used by S/TEM TITAN 80-300 FEI. The article presents the results of image analysis of the high-resolution transmission electron microscopy images and Fast Fourier Transform (FFT) as well as Inverse Fast Fourier Transform (IFFT) images.

The differential scanning calorimetry (DSC) analysis was performed to determine the crystallization mechanism using thermal analyzer SDT Q600 TA Instruments. The DSC curves were recorded at heating rate of 20°C/min and cooling rate of 10°C/min under a protective argon atmosphere.

3. Results

3.1. X-ray diffraction

X-ray diffraction patterns and identified phases of studied samples were presented in Figure 1 and listed in Table 1. The studied $Al_{71}Ni_{24}Fe_5$ alloy in a form of ingot and plate was characterized by multiphase structure. Quasicrystalline decagonal D-$Al_{70.83}Fe_{9.83}Ni_{19.34}$ phase was observed in rapidly solidified sample. The literature [19] confirmed the presence of Al_3Ni and Al_3Ni_2 phases at the same chemical composition in the as-cast state. The same work [19] also indicates the quasicrystalline D-$Al_{70.83}Fe_{9.83}Ni_{19.34}$ phase, which was identified in the alloy in a form of plate. Moreover, the phase composition of decagonal phase, Al_3Ni_2, Al_3Ni, $Al_{13}Fe_4$ were identified by X-ray diffraction for $Al_{71.6}Ni_{23}Fe_{5.4}$ [5]. Figure 2 shows the isothermal cross-section for Al-rich Al-Ni-Fe alloys at 850°C [25]. The alloys with an atomic fraction of Al 71%, Ni 24% and Fe 5% indicate characteristic region for decagonal quasicrystalline phase D-$Al_{71}Ni_{24}Fe_5$ and Al_3Ni and Al_3Ni_2 crystalline phases. The presence of these phases in the structure is confirmed by the Al-Ni phase equilibrium system shown in Figure 3 [26]. The Al_3Ni_2 phase is transformed during crystallization from the liquid state and then the Al_3Ni phase crystalizes. There is no time to convert Al_3Ni_2 to Al_3Ni with higher cooling rate, therefore only the Al_3Ni_2 phase is present for alloy in a form of plate. The formation of the B2 Fe(Al,Ni) phase may be caused by the reduction of aluminium and nickel from the liquid, because the presence of this phase is characteristic of alloys around Fe at. ≥25%.

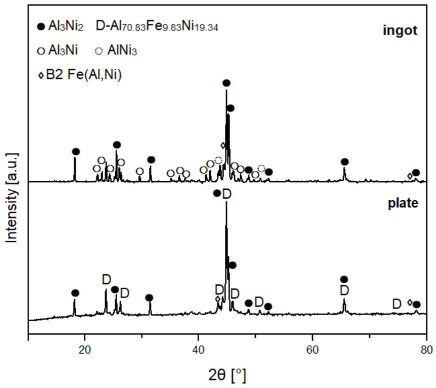


Fig. 1. X-ray diffraction (XRD) patterns of $Al_{71}Ni_{24}Fe_5$ in a form of ingot and plate

Table 1.
Identified phases of $Al_{71}Ni_{24}Fe_5$ alloy in a form of master alloy and plate

	Identified phases
Ingot	Al_3Ni_2+Al_3Ni+ B2 Fe(Al,Ni)+ ($AlNi_3$)
Plate	**D-$Al_{70.83}Fe_{9.83}Ni_{19.34}$**+$Al_3Ni_2$+B2 Fe(Al,Ni)

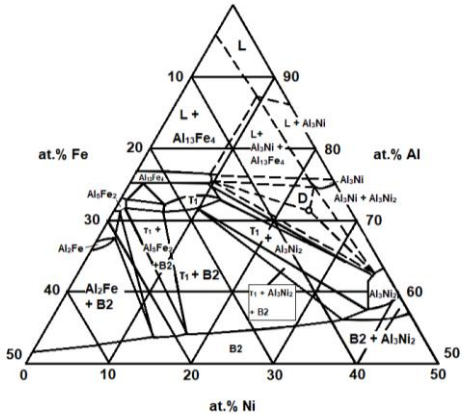


Fig. 2. Isothermal section of Al-Ni-Fe alloys with high Al content at 850°C [25]

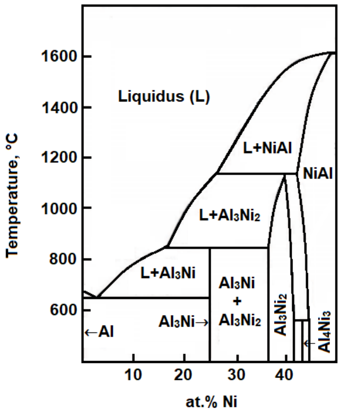
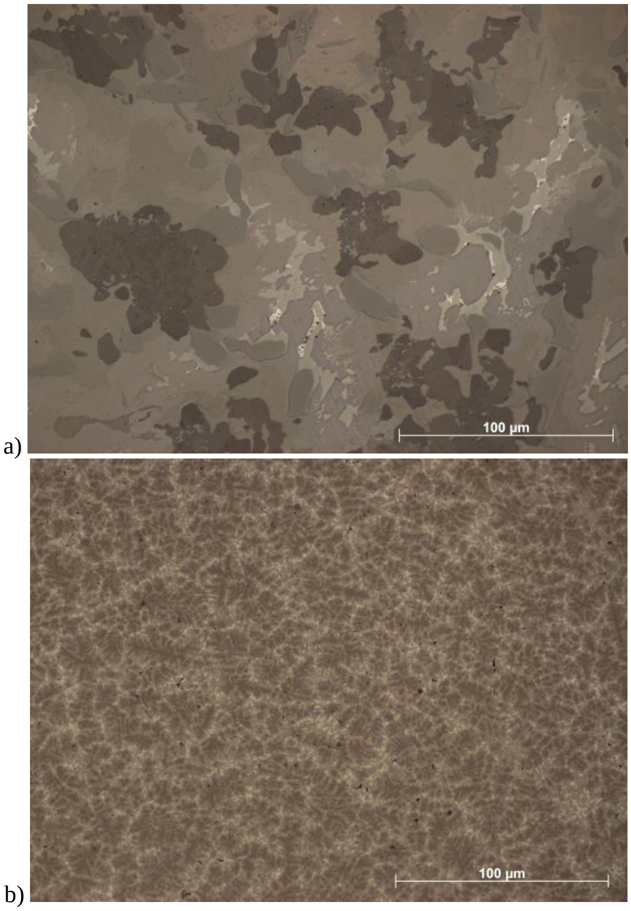


Fig. 3. Binary phase diagram of Al-Ni alloys (Ni at. ≤60%) [26]

3.2. Light microscopy

The observations by light microscopy were carried out to characterize the influence of solidification process on structure changes. The microstructures of alloys in a form of ingot and plate were illustrated in Figure 4. It could be seen the clear effect of higher cooling rate of molten alloy on structure fragmentation in case of plate. The alloy in a form of ingot was characterized by grain grow. The rapidly solidified alloy in a form of plate indicated a dendritic kind of microstructure. Sukhova et al. [5] presented in the article the microstructure of rapidly solidified $Al_{71.6}Ni_{23}Fe_{5.4}$ alloy with phase composition of decagonal phase, Al_3Ni_2, Al_3Ni and $Al_{13}Fe_4$. Despite the use of a casting rate of 50K/min, the presented microstructure at 400x magnification is similar to the ingot (Fig. 4a) due to grain growth.



a)

b)

Fig. 4. Microstructure of $Al_{71}Ni_{24}Fe_5$ alloy in a form of a) ingot, b) plate

3.3. High-resolution transmission electron microscopy

In order to present the atomic structure and confirm the presence of a quasicrystalline structure, observations were carried out using transmission electron microscopy for sample in a form of plate (Figure 5). The HRTEM image (Figure 5a) presents the area of IFFT (Figure 5c). The FFT and IFFT images (Figure 5b,c) indicated characteristic for quasicrystals arrangements and 5-fold axis symmetry characteristic for the quasicrystalline phase D–$Al_{70.83}Fe_{9.83}Ni_{19.34}$. Additionally, nano-scaled grains of crystalline phases could be observed on IFFT image.

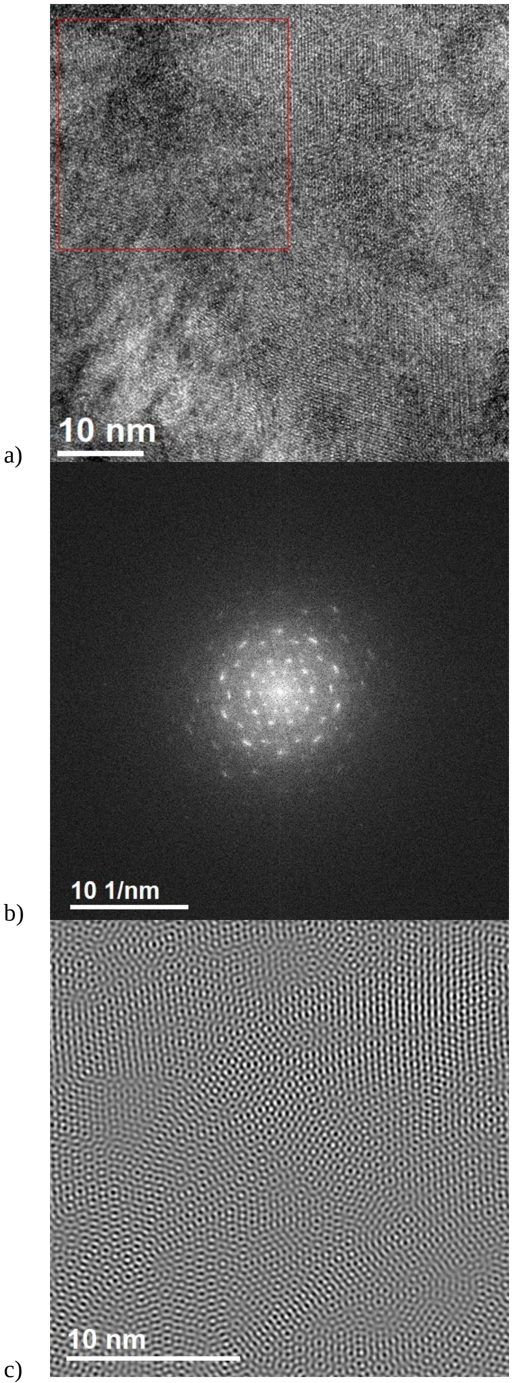


Fig. 5. HRTEM image (a), FFT patterns (b) and IFFT image (c) of $Al_{71}Ni_{24}Fe_{5}$ in a form of plate

3.3. Differential scanning calorimetry

The crystallization mechanisms of ingot and plate were described on the basis of DSC heating and cooling curves in Figure 6, 7. The crystallization mechanism was similar for both kind of alloys due to the metastable nature of the decagonal phase, for which no thermal effect was observed. The ingot was characterized by higher values of the enthalpy of changes. Based on the literature, it is known that the Al_3Ni_2 phase dissolves at ~1060°C , while the Al_3Ni phase at ~860°C [5, 27]. On the basis of DSC curves, thermal effects characteristic of these transformations can be distinguished. Due to the low iron content in the $Al_{71}Ni_{24}Fe_{5}$ alloy, the high-melting intermetallic phase B2 Fe(Al,Ni) is lower, which was also described in the literature [28]. Probably, the two thermal effects at temperatures 920°C and 965°C for heating are related to the transformations for B2 Fe(Al,Ni) due to the drawing of a common baseline and the effect at a temperature of ~1000°C for cooling. For the alloy in the form of an ingot, when heated, there was a thermal effect at the temperature of ~804°C, which may be related to the transformation of the residual $AlNi_3$ phase.

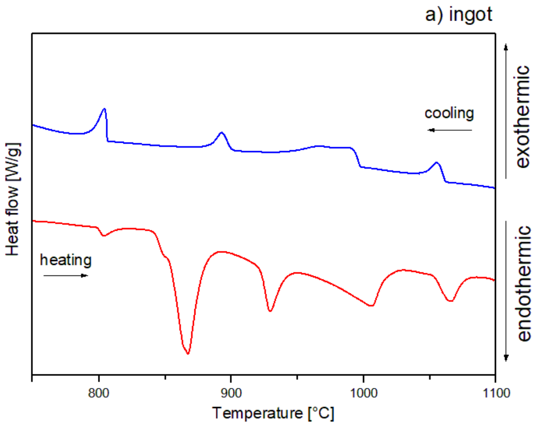


Fig. 6. DSC patterns of $Al_{71}Ni_{24}Fe_{5}$ alloy in a form of ingot

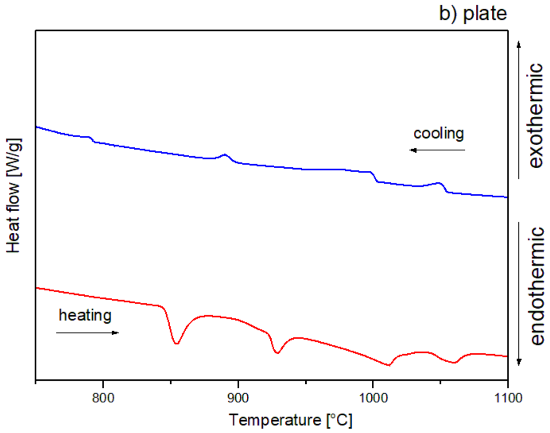


Fig. 7. DSC patterns of $Al_{71}Ni_{24}Fe_{5}$ alloy in a form of plate

4. Conclusions

The decagonal quasicrystalline phase D-$Al_{70.83}Fe_{9.83}Ni_{19.34}$ was identified in high-pressure die casted $Al_{71}Ni_{24}Fe_5$ alloy in a form of plate. High pressure die casting method allowed to obtain nanocrystalline structure and nano-sized quasicrystals. However, quasicrystalline phase was metastable, which could be observed in the DSC curves due to the lack of a characteristic thermal effects. The obtained results extended the actual knowledge about the crystallization mechanism and the structure of $Al_{71}Ni_{24}Fe_5$ alloys due to differences in the phase composition for the crystalline phases described in other works. In the future, experiments may focus on the search for the chemical composition of Al-Ni-Fe that will ensure the formation of a stable quasicrystalline phase.

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References

[1] Tsai, A.P., Inoue, A. & Masumoto, T. (1989). New decagonal Al–Ni–Fe and Al–Ni–Co alloys prepared by liquid quenching. *Materials Transactions, JIM*. 30(2), 150-154. DOI: 10.2320/matertrans1989.30.150.

[2] Lin, Y., Mao, S., Yan, Z., Zhang, Y. & Wang, L. (2017). The enhanced microhardness in a rapidly solidified Al alloy. *Material Science and Engneering: A*. 692, 182-191. DOI: 10.1016/j.msea.2017.03.052.

[3] Kula, A., Blaz, L. & Lobry, P. (2016) Structure and properties studies of rapidly solidified Al-Mn alloys. *Key Engineering Materials*. 682, 199-204. DOI: 10.4028/www.scientific.net/KEM.682.199.

[4] Lavernia, E.J. & Srivatsan, T.S. (2010). The rapid solidification processing of materials: Science, principles, technology, advances, and applications. *Journal of Materials Science*. 45, 287-325. DOI: 10.1007/s10853-009-3995-5.

[5] Sukhova, O.V., Polonskyy, V.A. & Ustinova, K.V. (2017). Structure formation and corrosion behaviour of quasicrystalline Al-Ni-Fe alloys. *Physics and Chemistry of Solidstate*. 18(2), 222-227. DOI: 10.15330/pcss.18.2.222-227.

[6] Kridli, G.T., Friedman, P.A. & Boileau, J.M. (2010). Manufacturing processes for light alloys. In P.K. Mallick (Eds.), *Materials, Design and Manufacturing for Lightweight Vehicles* (pp. 235-274). Woodhead Publishing.

[7] Bonollo, F., Gramegna, N. & Timelli, G. (2015). High-pressure die-casting: Contradictions and challenges. *JOM: The Journal of the Minerals, Metals & Materials Society*. 67, 901-908. DOI: 10.1007/s11837-015-1333-8.

[8] Naglič, I., Samardžija, Z., Delijić, K., Kobe, S., Dubois, J.M., Leskovar, B. & Markoli, B. (2017). Metastable quasicrystals in Al–Mn alloys containing copper, magnesium and silicon. *Journal of Material Science*. 52, 13657-13668. DOI: 10.1007/s10853-017-1477-8.

[9] He, Z., Ma, H., Li, H., Li, X. & Ma, X. (2016). New type of Al-based decagonal quasicrystal in Al60Cr20Fe10Si10 alloy. *Scientific Reports*. 6, 22337. DOI: 10.1038/srep22337.

[10] Kühn, U., Eckert, J., Mattern, N. & Schultz, L. As-cast quasicrystalline phase in a Zr-based multicomponent bulk alloy. *Applied Physics Letter*. 77, 3176-3178. DOI: 10.1063/1.1326036.

[11] Avar, B., Gogebakan, M., Yilmaz, F. (2008). Characterization of the icosahedral quasicrystalline phase in rapidly solidified Al-Cu-Fe alloys. *Zeitschrift Für Kristallographie- Crystalline Materials*. 223, 731-734. DOI: 10.1524/zkri.2008.1077.

[12] Surowiec, M.R. (2017). *Quasicrystals*. Warsaw: Polish Scientific Publishers PWN. (in Polish)

[13] Ishimasa, T. (2016). Mysteries of icosahedral quasicrystals: How are the atoms arranged? *IUCrJ*. 3, 230-231. DOI: 10.1107/S2052252516009842.

[14] Pedrazzini, S., Galano, M., Audebert, F., Siegkas, P., Gerlach, R., Tagarielli, V.L. & Smith, G.D.W. (2019). High strain rate behaviour of nano-quasicrystalline Al93Fe3Cr2Ti2 alloy and composites. *Materials Science and Engineering: A*. 764, 138201. DOI: 10.1016/j.msea.2019.138201.

[15] Shadangi, Y., Shivam, V., Singh, M.K., Chattopadhyay, K., Basu, J. & Mukhopadhyay, N.K. (2019). Synthesis and characterization of Sn reinforced Al-Cu-Fe quasicrystalline matrix nanocomposite by mechanical milling. *Journal of Alloys and Compounds*. 797, 1280-1287. DOI: 10.1016/j.jallcom.2019.05.128.

[16] Audebert, F., Prima, F., Galano, M., Tomut, M., Warren, P.J., Stone, I.C. & Cantor, B. (2002). Structural characterisation and mechanical properties of nanocomposite Al-based alloys. *Materials Transactions*. 43, 2017-2025. DOI: 10.2320/matertrans.43.2017.

[17] Inoue, A. & Kimura, H. (2000). High-strength aluminum alloys containing nanoquasicrystalline particles. *Materials Science and Engineering: A*. 286, 1-10. DOI: 10.1016/S0921-5093(00)00656-0.

[18] Li, F.C., Liu, T., Zhang, J.Y., Shuang, S., Wang, Q., Wang, A.D., Wang, J.G. & Yang, Y. (2019). Amorphous–nanocrystalline alloys: fabrication, properties, and applications. *Materials Today Advances*. 4, 100027. DOI: 10.1016/j.mtadv.2019.100027.

[19] Qiang, J., Wang, D., Bao, C., Wang, Y., Xu, W. & Song, M. (2001). Formation rule for Al-based ternary quasi-crystals : Example of Al–Ni– Fe decagonal phase. *Journal of Materials Reserach*. 16(9) 2653-2660. DOI: 10.1557/JMR.2001.0364.

[20] Audebert, F. (2005). Amorphous and nanostructured Al-Fe and Al-Ni based alloys. In Idzikowski B., Švec P., Miglierini M. (Eds.) *Properties and Applications of Nanocrystalline Alloys from Amorphous Precursors. NATO Science Series (Series II: Mathematics, Physics and Chemistry)*. Dordrecht: Springer.

[21] Milman, Y.V., Sirko, A.I., Iefimov, M.O., Niekov, O.D., Sharovsky, A.O. & Zacharova, N.P. (2006). High strength aluminum alloys reinforced by nanosize quasicrystalline particles for elevated temperature application. *High*

Temperature Materials and Processes. 25(1-2), 19-29. DOI: 10.1515/HTMP.2006.25.1-2.19.

[22] Yadav, T.P., Mukhopadhyay, N.K., Tiwari, R.S. & Srivastava, O.N. (2007). Studies on Al-Ni-Fe decagonal quasicrystalline alloy prepared by mechanical alloying, *Philosophical Magazine*. 87(18-21), 3117-3125. DOI: 10.1080/14786430701355208.

[23] Babilas, R., Młynarek, K., Łoński, W., Lis, M., Łukowiec, D., Kądziołka-Gaweł, M., Warski, T., Radoń, A. (2021). Analysis of thermodynamic parameters for designing quasicrystalline Al-Ni-Fe alloys with enhanced corrosion resistance. *Journal of Alloys and Compounds*. 868, 159241. DOI: 10.1016/j.jallcom.2021.159241.

[24] Grushko, B., Lemmerz, U., Fischer, K. & Freiburg, C. (1996). The low-temperature instability of the decagonal phase in Al-Ni-Fe. *Physica Status Solidi (a)*. 155, 17-30. DOI: 10.1002/pssa.2211550103.

[25] Raghavan, V. (2009). Al-Fe-Ni (Aluminum-Iron-Nickel). *Journal of Phase Equilibria and Diffusion*. 30(4), 85-88. DOI: 10.1007/s11669-008-9452-3.

[26] Konieczny, M., Mola, R., Thomas, P. & Kopcial, M. (2011). Processing, microstructure and properties of laminated Ni-intermetallic composites synthesised using Ni sheets and Al foils. *Archives of Metallurgy and Materials*. 56(3), 693-702. DOI: 10.2478/v10172-011-0076-y.

[27] Čelko, L., Klakurková, L. & Švejcar, J. (2010). Diffusion in Al-Ni and Al-NiCr interfaces at moderate temperatures. *Defect and Diffusion Forum*. 297-301, 771-777. DOI: 10.4028/www.scientific.net/DDF.297-301.771.

[28] Titran, R.H., Vedula, K.M. & Anderson, G.G. (1984). High temperature properties of equialomic FeAl with ternary additions. *MRS Proceedings*. 39(309), 1471-1478. DOI: 10.1557/PROC-39-309.