# UDC 680.18:669.713 PHASE CONSTITUTION OF AI-Ni-Fe ALLOYS IN A COMPOSITIONAL RANGE OF DECAGONAL QUASICRYSTALS FORMATION

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### 1. Introduction

Al–Ni–Fe alloys are promising constructional materials designated for applications in aggressive and oxidizing media under elevated temperatures [1,2]. The alloys of the said system in the concentration range of quasicrystalline decagonal Dphase formation are of a special interest. This phase is a two-dimensional quasicrystal consisting of periodic stacking of atomic layers with a tenfold symmetry within the plane. Decagonal quasicrystals combine two types of crystalline order: they are quasiperiodic in a plane and they are periodic in the direction perpendicular to a plane.

The D-phase stability at room temperature is still under discussion. According to several studies it is stable within a narrow compositional range of  $Al_{71.1-71.7}Ni_{24.6-23.0}Fe_{4.3-5.3}$  [3–5]. In other works [6–8] D-phase is assumed to be thermodynamically stable between 930 and 847 °C, and on further cooling transforms to the mixture of three crystalline phases. Besides, in the study [9] the formation of a single decagonal D-phase by rapid solidification is reported to occur in the concentration range of  $Al_{75.70}Ni_{16-9}Fe_{9-21}$ . Therefore, in this work the phase composition of conventionally solidified Al-Ni-Fe alloys has been investigated to verify the possibility of stable quasicrystalline decagonal D-phase formation in the system.

### 2. Experimental procedure

Al–Ni–Fe alloys were prepared by melting of chemically pure components (<99.99 pct.) in a graphite crucible in a Tamman furnace. The samples were cooled at a rate of 50 K/s. The nominal compositions of Al<sub>70</sub>Ni<sub>145</sub>Fe<sub>15.5</sub> and Al<sub>71</sub>Ni<sub>24</sub>Fe<sub>5</sub> were set close to the compositional range initially reported by Qiang [10] where the decagonal phase had been firstly obtained. The average chemical composition of the alloys was studied by atomic absorption spectroscopy method. The relative precision of the measurements was better than  $\pm$  3 pct. The alloys were examined by light-optical microscope *Neophot*. Quantitative metallography was carried out with structural analyzer *Epiquant*. X-ray diffraction analysis was done to identify the existing phases in produced samples on an X-ray diffractometer  $\square POH-VM$  with CuK<sub>a</sub> source. The local phase compositions were determined in a scanning electron microscope *P* $\ni MMA102-02$  by energy-dispersive X-ray analysis on polished unetched cross-sections. When calculating the valence electron (e) concentration per atom (a) for quasicrystalline D-phases, the electron contributions for elements are taken from [11].

#### 3. Experimental results and discussion

 $Al_{70}Ni_{14.5}Fe_{15.5}$  alloy exhibits two-phase structure (Fig. 1). The sample contains crystals of primary  $Al_5FeNi$  phase separated by secondary quasicrystalline decagonal D-phase. The morphology of  $Al_5FeNi$  crystals corresponds to hexagonal lattice

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that is isostructural to binary  $Al_5Co_2$  (hP28). The phase constitution is presented in X-ray diffractograms of the investigated samples (Fig. 2).



Fig. 1. Microstructure of  $Al_{70}Ni_{14.5}Fe_{15.5}$  alloy: a - x 400; b - x 800



Fig. 2. Diffraction pattern of Al<sub>70</sub>Ni<sub>14.5</sub>Fe<sub>15.5</sub> alloy

Quasicrystalline decagonal D-phase has been identified with results reported in [5] taken into account (Table). Its local chemical composition corresponds to  $Al_{72.5}Ni_{13}Fe_{14.5}$ . The volume fraction of D-phase reaches 30 vol. pct. of a total alloy volume. Decagonal quasicrystals of  $Al_{70}Ni_{14.5}Fe_{15.5}$  alloy are typical Hume-Rothery phases which exhibit compositional range, in which the electron-to-atom ratio e/a equals to 1.89.

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Examination by light-optical microscopy as well as by SEM reveals that  $AI_{71}Ni_{24}Fe_5$  alloy consists of three phases identified as quasicrystalline decagonal D-phase, crystal hexagonal  $AI_3Ni_2$  phase, crystal orphorombic  $AI_3Ni$  phase (Fig. 3). The described phase composition is confirmed by X-ray investigations (Fig. 4). After etching dark-colored quisicrystalline D-phase takes about 15 pct. of a total alloy volume. Its local chemical composition is close to  $AI_{70.5}Ni_{19.5}Fe_{10}$ . As compared with D-phase revealed in  $AI_{70}Ni_{14.5}Fe_{15.5}$  alloy the iron content of this phase decreases but nickel content increases. This quasicrystalline phase can be also regarded as Hume-Rothery phase stabilized by the energy band factor. In this case e/a ratio decreases from 1.89 to 1.79. This difference in e/a may be due to differences in structure between the above two stable decagonal phases. Besides, in the X-ray diffraction pattern the shift of the peaks belonging to D-phase towards higher  $\theta$  angle side is observed (Table). It should be noted that the shift may indicate the increase in lattice parameter.



Fig. 3. Microstructure of  $Al_{71}Ni_{24}Fe_5$  alloy: a - x 400; b - x 800

It is obvious from present investigation that some quantity of the quasicrystal decagonal D-phase formed during solidification is thermodynamically stable and can remain down to room temperature when the investigated Al–Ni–Fe alloys are cooled at a rate of 50 K/s. Depending on alloys composition two types of decagonal quasicrystals are observed. D-phase of  $Al_{70}Ni_{14.5}Fe_{15.5}$  alloy corresponds to a solid solution of nickel in  $Al_{86}Fe_{14}$  (D-AlFe type), and D-phase of  $Al_{71}Ni_{24}Fe_5$  alloy corresponds to a solid solution of iron in  $Al_{80}Ni_{20}$  (D-AlNi type). With the addition of a third element to quasicrystalline binary compounds, e/a ratios change and D-phase becomes more stable at an ideal composition in the ternary Al–Ni–Fe alloys. The above findings also indicate that the Hume-Rothery rule, which is effective in most quasicrystalline alloy systems, is applicable to the present Al–Ni–Fe alloys.



**Fig. 4.** Diffraction pattern of  $Al_{71}Ni_{24}Fe_5$  alloy

Table

Results of X-ray analysis of quasicrystalline decagonal D-phase
of Al–Ni–Fe alloys

Al <sub>70</sub> Ni <sub>14.5</sub> Fe <sub>15.5</sub> alloy			Al <sub>71</sub> Ni <sub>24</sub> Fe <sub>5</sub> alloy		
d <sub>HKL</sub> , nm		τ. θ/	d <sub>HKL</sub> , nm		T 04
exp.	ref.	1, 70	exp.	ref.	1, 70
0.2496	0.2440	20	0.2086	0.2092	3
0.2277	0.2267	20	0.2051	0.2045	6
0.2152	0.2131	50	0.2028	0.2020	100
0.2104	0.2095	75	0.2002	0.2002	30
0.2046	0.2055	100	0.1986	0.1976	7
0.1938	0.1924	35	0.1932	0.1938	2
0.1805	0.1771	17	0.1874	0.1879	6
0.1676	0.1675	10	0.1753	0.1749	3
0.1457	0.1441	18	0.1427	0.1421	35
0.1429	0.1423	16			
0.1337	0.1335	12			

## 4. Conclusions

On the basis of the above results can be concluded that quasicrystalline decagonal D-phase is thermodynamically stable in the investigated Al–Ni–Fe alloys cooled at a rate of 50 K/s. This phase of Al<sub>70</sub>Ni<sub>14.5</sub>Fe<sub>15.5</sub> alloy is based on binary quasicrystalline Al<sub>86</sub>Fe<sub>14</sub> compound and at room temperature coexists with crystalline hexagonal Al<sub>5</sub>FeNi phase, and D-phase of Al<sub>71</sub>Ni<sub>24</sub>Fe<sub>5</sub> alloy is based on Al<sub>80</sub>Ni<sub>20</sub> coexists with two crystalline phases: hexagonal Al<sub>3</sub>Ni<sub>2</sub> and orthorombic Al<sub>3</sub>Ni. D-phases of the above alloys are stabilized respectively at compositions of Al<sub>72.5</sub>Ni<sub>13</sub>Fe<sub>14.5</sub> and Al<sub>70.5</sub>Ni<sub>19.5</sub>Fe<sub>10</sub>. The stable decagonal D-phase of Al<sub>70</sub>Ni<sub>14.5</sub>Fe<sub>15.5</sub> alloy has an electron concentration of about e/a=1.89, whereas the stable decagonal D-quasicrystals of Al<sub>71</sub>Ni<sub>24</sub>Fe<sub>5</sub> alloy occur at e/a=1.79. This difference in e/a may be due to two types of decagonal quasicrystals observed in the investigated Al–Ni–Fe alloys, the D-AlFe type with dissoluted Ni and D-AlNi type with dissoluted Fe.

## REFERENCES

- 1. Trebin H. R. Quasicrystals. Structure and properties / H. R. Trebin.– Weinheim: Wiley VCH GmbH & Co. KGaA, 2003. 665 p.
- Stadnik Z. M. Physical properties of quasicrystals / Z. M. Stadnik.– Berlin Heidelberg: Springer-Verlag, 1999. – 438 p.
- Grusko B. A comparative study of decagonal quasicrystalline phases / B. Grushko, E. K. Urban // Phil. Mag. – 1994. – Part B, Vol. 70, No. 5. – P. 1063–1075.
- Grusko B. Formation of quasiperiodic and related periodic intermetallics in alloy system of aluminum with transition metals / B. Grushko, T. Velikanova // Computer Coupling of Phase Diagrams and Thermochemistry. – 2007. – No. 31. – P. 217–232.
- Chumak I. The Fe–Ni–Al phase diagram in the Al-rich (>50 at.% Al) corner / I. Chumak, K. W. Richter, H. Ipser // Intermetallics. – 2007. – No. 15. – P. 1416–1424.
- Zhang L. Phase equilibria of the Al–Ni–Fe system at 850 °C and 627 °C / L. Zhang, Y. Du, H. Xu, C. Tang H. Chen, W. Zhang // Alloys and comp. – 2008. – No. 454. – P. 129–135.
- Lemmerz U. Study of decagonal quasicrystalline phase formation in the Al–Ni– Fe alloy system / U. Lemmerz, B. Grushko, C. Freiburg, E. M. Jansen // Phil. Mag. Let. – 1994. – Vol. 69, No. 3. – P. 141–146.
- Grusko B. The low-temperature instability of the decagonal phase in Al–Ni–Fe / B. Grushko, U. Lemmerz, K. Fischer, C. Freiburg // Phys. Stat. Sol. – 1996. – Vol. 155, No. 17. – P. 17–30.
- Setyawan A. D. Phase composition and transformation behavior of rapidly solidified Al–Ni–Fe alloys in α-Al-decagonal phase region / A. D. Setyawan, D. V. Louzguine, K. Sasamori etc. // J. Alloys and Compounds. – 2005. – Vol. 399. – P. 132–138.
- Qiang J. B. Formation rule for Al-based ternary quasi-crystals: example of Al-Ni–Fe decagonal phase / J.-B.•Qiang, D.-H. Wang, C. M. Bao // J. Mater. Res. – 2001. – Vol. 16, No. 9. – P. 2653–2660.
- Pettifor D. G. Theory of energy bands and related properties of 4d transition metals: I. Band parameters and their volume dependence / D. G. Pettifor // J. Phys. F: Metal. Phys. – 1977. – Vol. 7, No. 4. – P. 613–633.