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O. V. Sukhova, Yu. V. Syrovatko, K. V. Ustinova*

Oles Honchar Dnipropetrovsk National University, Dnipropetrovsk, Ukraine
**e-mail: aspkat@i.ua*

STRUCTURE FORMATION OF CONVENTIONALLY SOLIDIFIED Al–Co–Ni AND Al–Fe–Ni QUASICRYSTALLINE ALLOYS

The conventionally solidified alloys with nominal compositions of $Al_{73}Co_{16}Ni_{11}$ and $Al_{72}Fe_{15}Ni_{13}$ are studied by X-ray diffraction, optical and scanning electron microscopies, and energy-dispersive X-ray analysis. The microstructural and micromechanical characteristics of their constituent phases are studied in each alloy. Both alloy systems are shown to form stable decagonal quasicrystalline D-phases. In Al–Co–Ni, the primarily solidified phase is D-phase, but, in Al–Fe–Ni alloy, it is the Al_5FeNi phase. Depending on the composition two types of decagonal quasicrystals are observed in the investigated alloys that belong respectively to AlCo-based and AlFe-based phases with Ni dissoluted in binary compounds of $Al_{73}Co_{27}$ and $Al_{86}Fe_{14}$ respectively. Both the quasicrystalline phases are regarded as Hume-Rothery phases differing in *e/a* ratio. The formation of these phases are found to follow the evolution of their corresponding *e/a* constant lines in Al–(Co,Fe)–Ni pseudoternary phase diagram. The structure of all the coexisting crystalline phases is shown to be closely related to those of the decagonal quasicrystals.

Key words: quasicrystalline alloys, microstructural characteristics, structural-and-phase composition, quasicrystal decagonal phases, empirical Hume-Rothery rule.

У роботі досліджено сплави $Al_{73}Co_{16}Ni_{11}$ і $Al_{72}Fe_{15}Ni_{13}$, закристалізовані за звичайних швидкостей охолодження, із застосуванням методів рентгеноструктурного аналізу, оптичної та скануючої електронної мікроскопії, рентгеноспектрального мікроаналізу. Досліджено мікроструктурні та мікромеханічні характеристики структурних складових. Показано, що в досліджених сплавах утворюється стабільна декагональна квазикристалічна D-фаза. У сплаві Al–Co–Ni ця фаза кристалізується безпосередньо з рідини, а у сплаві Al–Fe–Ni першою виділяється фаза Al_5FeNi. Встановлено, що залежно від складу у вивчених сплавах спостерігаються два типи квазикристалічних декагональних D-фаз, які утворюються при розчиненні нікелю в подвійних сполуках $Al_{73}Co_{27}$ (AlCo-тип) та $Al_{86}Fe_{14}$ (AlFe-тип). Ці квазикристалічні фази відносяться до фаз Юм-Розері, що відрізняються відношенням *e/a*. Склад квазикристалічних фаз розташований уздовж ліній із постійним відношенням *e/a*, проведених на перерізі псевдопотрійної діаграми стану Al–(Co,Fe)–Ni. Структура всіх кристалічних фаз у досліджених потрійних сплавах пов'язана зі структурою квазикристалічних фаз, з якими вони співіснують.

Ключові слова: квазикристалічні сплави, мікроструктурні характеристики, структурно-фазовий склад, квазикристалічні декагональні фази, емпіричне правило Юм-Розері.

В работе изучены сплавы $Al_{73}Co_{16}Ni_{11}$ и $Al_{72}Fe_{15}Ni_{13}$, закристаллизованные при обычных скоростях охлаждения, с использованием методов рентгеноструктурного анализа, оптической и сканирующей электронной микроскопии, рентгеноспектрального микроанализа. Исследованы микроструктурные и микромеханические характеристики структурных составляющих. Показано, что в изученных сплавах образуется стабильная декагональная квазикристаллическая D-фаза. В сплаве Al–Co–Ni эта фаза кристаллизуется непосредственно из жидкости, в сплаве Al–Fe–Ni первой выделяется фаза Al_5FeNi. Установлено, что в зависимости от состава в исследованных сплавах наблюдается два типа квазикристаллических декагональных D-фаз, которые образуются при растворении никеля в двойных соединениях $Al_{73}Co_{27}$ (AlCo-тип) и $Al_{86}Fe_{14}$ (AlFe-тип). Эти квазикристаллические фазы относятся к фазам Юм-Розери, различающимся отношением *e/a*. Состав квазикристаллических фаз расположен вдоль линий с постоянным отношением *e/a*, проведенных на разрезе псевдотройной диаграммы состояния Al–(Co,Fe)–Ni. Структура всех кристаллических фаз в исследованных тройных сплавах связана со структурой квазикристаллических фаз, с которыми они сосуществуют.

Ключевые слова: квазикристаллические сплавы, микроструктурные характеристики, структурно-фазовый состав, квазикристаллические декагональные фазы, эмпирическое правило Юм-Розери.

1. Introduction

The ternary Al-rich alloys with Co and Ni or Fe and Ni are the most interesting stable quasicrystalline materials having decagonal rotation symmetry [1–7]. Decagonal quasicrystals combine two different types of order, periodicity along the rotational axis and non-periodic order perpendicular to it. This property sets decagonal phases apart from periodic crystals, as well as from icosahedral quasicrystals. The interest also is prompted due to the finding of quasicrystalline phases of the above alloys when they are cast under conventional solidification techniques. However, there are very few investigations in the literature [2, 7] related to the microstructural characteristics of the decagonal phases. A comparison of the decagonal phases in the above ternary alloy systems can provide important information with respect to the factors governing the formation of quasicrystals in general.

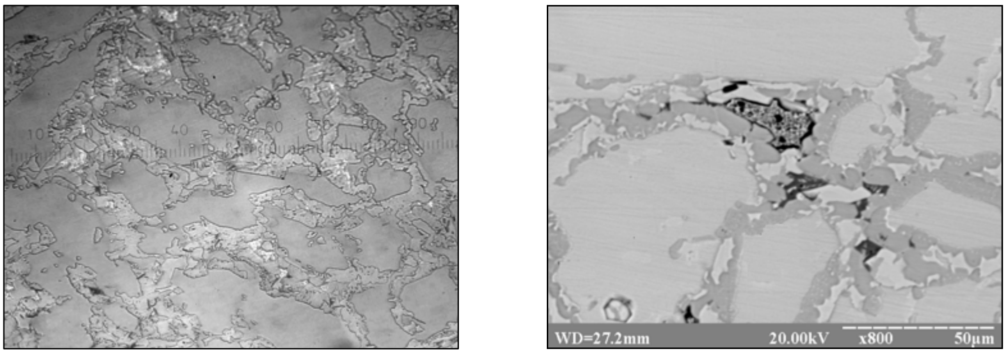
The aim of this paper is to investigate quasicrystalline and crystalline phases observed in Al–Co–Ni and Al–Fe–Ni alloys for chemical compositions set closely to the compositions, where the quasicrystal decagonal phases have been firstly obtained [1, 6].

2. Experimental procedure

The alloys with nominal compositions of $Al_{73}Co_{16}Ni_{11}$ and $Al_{72}Fe_{15}Ni_{13}$ were prepared of high purity (99.99 pct.) aluminium, nickel, cobalt or iron. These elements were put in a graphite crucible and melted using Tamman furnace. The average chemical composition of the produced ingots was obtained with an atomic absorption spectroscopy method. The cooling rate of the alloys was 50 K/s. The instruments used in the microstructural characterization of the investigated alloys were mainly optical microscopes (OM) *Neophot* and *GX-51*, quantative analyzer *Epiquant*, scanning electron microscope (SEM) *РЭМА 102-02*. The alloys were also studied by powder X-ray diffraction (XRD) using CuK_α radiation. The local phase compositions were detemined in SEM by energy dispersive X-ray (EDX) analysis on polished unetched cross sections. The usual scattering of the measurements was about ± 0.25 at. pct.

3. Results and discussion

The microstructure of the Al–Co–Ni alloy is a mixture of quasicrystalline and crystalline phases (Fig. 1).



(a) (b)

Fig. 1. Microstructure of the as-cast Al–Co–Ni alloy: a – OM image (x400); b – SEM image (x800).

From the XRD and the EDX the cast alloy consists of the quasicrystalline decagonal D-phase with composition $Al_{72}Co_{9.5}Ni_{18.5}$ and the crystalline $Al_9(Co,Ni)_2$ phase as shown in Fig. 2. The D-phase formed during solidification remains down to room temperature. The average volume fraction of D-quasicrystals is about 59 pct. of the total alloy volume (Table). Their size ranges from 50 to 80 μm.

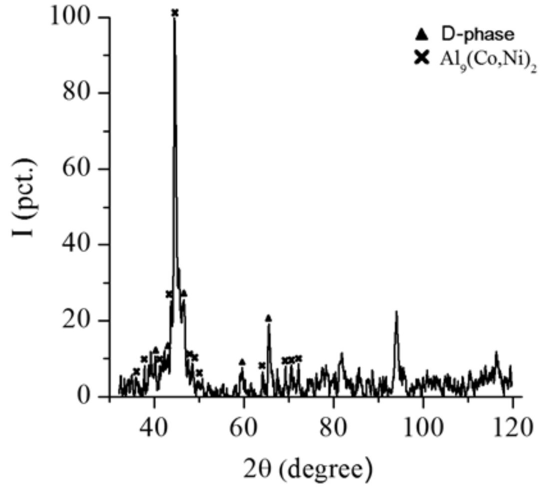


Fig. 2. XRD pattern obtained from the as-cast Al–Co–Ni alloy.

It has been found that the D-phase forms first in the melt as the primary phase during the solidification. Then the crystalline $Al_9(Co,Ni)_2$ phase nucleates on the D-phase and grows by consuming both the D-phase and the melt. The peritectic reaction $L + D \rightarrow Al_9(Co,Ni)_2$ does not proceed completely. The remanent melt is solidified into the $Al_9(Co,Ni)_2$ phase. EDX analysis of Al_9Co_2 reveals that the phase dissolves up to 15 at. pct. of Ni.

Substitution of Co by Fe essentially changes solidification behaviour and the corresponding morphology of the as-cast Al–Fe–Ni alloy (Fig. 3). The Al_5FeNi phase occurs as the primary phase during the solidification. This crystalline phase exhibits a hexagonal morphology. The primary solidification of Al_5FeNi phase is followed by the formation of quasicrystal decagonal D-phase with composition close to $Al_{71.5}Fe_{15}Ni_{13.5}$. Therefore, this phase is seen adjacent to the Al_5FeNi phase, its volume fraction is about 24 pct. (Table). The conclusions made are proved by further examination by X-ray diffraction (Fig. 4). The analysis of Al–Fe–Ni and Al–Co–Ni alloys reveals similarity of the powder X-ray diffraction patterns of the corresponding decagonal phases (Fig. 2, 4).

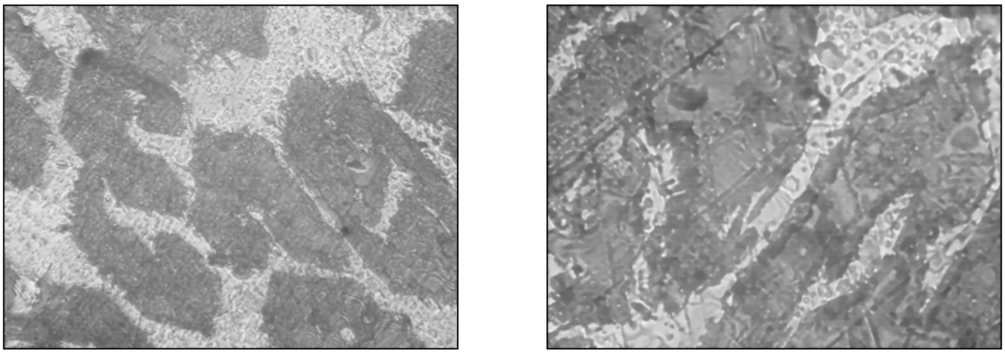
Measurements show that the decagonal D-quasicrystals possess a microhardness of about 8.6 GPa (Table), which is much higher than that for Al_5FeNi phase. Comparison with the intermetallic compounds in the Al–Co–Ni system exhibits the following sequence: H(D-AlCoNi)> H(D-AlFeNi)>H(Al_5FeNi)>H($Al_9(Co,Ni)_2$).

The structural-and-phase compositions of the conventionally solidified Al–Co–Ni and Al–Fe–Ni alloys can be related to quasicrystalline phases via similar *e/a* ratios (the valence electron concentration per atom). This factor is crucial for a large class of so-called electron (Hume-Rothery) phases to which quasicrystalline phases belong. When calculating, the electron contributions for elements Al, Ni, Fe, and Co are taken as 3, 1, -2, and -1.4, respectively [8].

Table

Microstructural characteristics of the as-cast Al–Co–Ni and Al–Fe–Ni alloys

Alloy	Phases	Volume fraction, pct.	Microhardness, GPa	*e/a*
Al–Co–Ni	D-phase	59.2±1.2	8.68±0.44	2.02
	$Al_9(Co,Ni)_2$	40.8±0.5	4.17±0.35	1.99
Al–Fe–Ni	D-phase	23.8±0.1	8.6±1.0	1.84
	Al_5FeNi	76.2±0.1	4.8±0.4	1.86



(a) **(b)**

Fig. 3. Microstructure (OM) of the as-cast Al–Fe–Ni alloy: a –x400; b – x800.

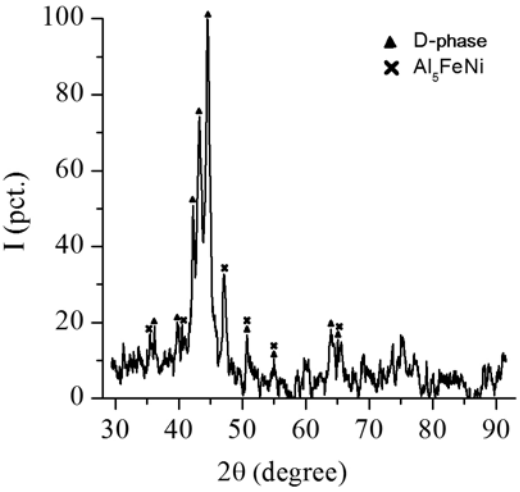


Fig. 4. XRD pattern obtained from the as-cast Al–Fe–Ni alloy.

The phase formation follows the Hume-Rothery rule in the Al–Co–Ni alloy system: their main constituents are D-AlCoNi phase with $Al_9(Co,Ni)_2$. Both the phases possess the almost similar *e/a* ratios as shown in Table. When Co is substituted by Fe in the Al–Fe–Ni alloy, the compositions of the constituent phases change toward D-AlFeNi phase and Al_5FeNi with the same *e/a* ratios. On the basis of the rule, it can be assumed that D-phases of the investigated ternary alloys belong to two types differing in *e/a* ratios. One is based on D-$Al_{73}Co_{27}$ (AlCo-type) and the other is based on D-$Al_{86}Fe_{14}$ (AlFe-type). With the addition of Ni, the D-AlCo is stabilized at the composition of $Al_{72}Co_{9.5}Ni_{18.5}$ (the *e/a* ratio is 2.02). Similarly, the D-AlFe phase becomes stable with the dissolution of Ni at the composition of $Al_{71.5}Fe_{15}Ni_{13.5}$, where the *e/a* ratio is 1.84.

4. Conclusions

The investigations performed on conventionally solidified Al–Co–Ni and Al–Fe–Ni alloys confirm that both alloy systems form stable decagonal quasicrystalline phases. In Al–Co–Ni, the primarily solidified phase is D-phase, but, in Al–Fe–Ni alloys, it is the Al_5FeNi phase. Regions of the quasicrystal D-phase can be seen in the spacing between the hexagonal Al_5FeNi areas.

The Hume-Rothery empirical rule can be applicable to explain the structural-and-phase composition of the investigated alloys. The quasicrystalline and crystalline phases are *e/a* constant phases belonging to a group of Hume-Rothery phases with similar *e/a* ratios. By applying the rule it can be concluded that quasicrystal decagonal D-AlCoNi and D-AlFeNi phases correspond to two different types respectively with *e/a* ratios of 2.02 and 1.84. The quasicrystals exhibit compositional ranges in which the electron-to-atom ration *e/a* varies within certain limits typical of every structure.

References

1. **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. – V. 155, No. 17. – P. 17–30.

2. **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. – V. 399. – P. 132–138.

3. **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. – V. 16, No. 9. – P. 2653–2660.

4. **Yokoyama, Y.** Production of Single Quasicrystals / Y. Yokoyama, R. Note, A. P. Tsai etc. // Sci. Rep. RITU. – 1996. – V. A42, No. 1. – P. 185–190.

5. **Mihalkovic, M.** Cell-Constrained Melt-Quench Simulation of D-AlCoNi: Ni-Rich Versus Co-Rich Structures / M. Mihalkovic, M. Widom, C. L. Henley // Phil. Mag. – 2010. – V. 91, No. 19. – P. 2557–2566.

6. **Hiraga, K.** The Structural Characteristics of Al–Co–Ni Decagonal Quasicrystals and Crystalline Approximants / K. Hiraga, T. Ohsuna, W. Sun, K. Sugiyama // J. Alloys and Compounds. – 2002. – V. 342. – P. 110–114.

7. **Stadnik, Z. M.** Physical Properties of Quasicrystals / Z. M. Stadnik.– Berlin Heidelberg: Springer-Verlag, 1999. – 438 p.

8. **Pettifor, D. G.** Theory of Energy Bands and Related Properties of 4d Transition Metals: I. Band Parameters and Their Volume Dependence / D. G. Pettifor // Phys. F: Metal Phys. – 1977. – V. 7, No. 4. – P. 110–114.

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