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

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

THE SOLIDIFICATION OF Al–Ni–Fe DECAGONAL QUASICRYSTALLINE ALLOYS

The formation of quasicrystalline decagonal phase and related crystalline phases in the structure of the Al–Ni–Fe alloys was investigated. The decagonal phase exhibits two modifications (AlFe- and AlNi-based) depending on the composition. In the $Al_{72}Ni_{13}Fe_{15}$ alloy it coexists with monoclinic Al_5FeNi phase. Upon cooling at 50 K/min, only two major exotherms are detected for this alloy in the temperature range of 850–950 °C. In the $Al_{71.6}Ni_{23}Fe_{5.4}$ alloy the crystalline $Al_{13}(Ni,Fe)_4$, $Al_3(Ni,Fe)_2$, and $Al_3(Ni,Fe)$ phases are seen adjacent to the quasicrystalline decagonal phase. With falling temperature the quasicrystalline phase forms between 940 °C and 890 °C and other phases appear at 850 °C, which indicates that this alloy follows a various crystallization path. Stability of the quasicrystalline D-phase up to room temperature was shown to be connected with its incomplete decomposition during cooling at a rate of 50 K/min. Besides, the as-cast alloys contain various quantity of the quasicrystalline D-phase. The $Al_{71.6}Ni_{23}Fe_{5.4}$ alloy has more than twice larger volume fraction of this phase. A dependence on alloy composition was observed as well, with the $Al_{72}Fe_{15}Ni_{13}$ alloy having substantially higher values.

Key words: quasicrystal decagonal phase, phase transformations, thermal effects, microhardness.

Досліджено процеси утворення квазікристалічної декагональної та співіснуючих кристалічних фаз у структурі сплавів Al–Ni–Fe. Встановлено формування двох модифікацій декагональної фази (AlFe- і AlNi-тип) залежно від складу сплаву. У сплаві $Al_{72}Ni_{13}Fe_{15}$ вона співіснує з моноклінною фазою Al_5FeNi. Під час охолодження цього сплаву зі швидкістю 50 К/хв в температурному інтервалі 850–950 °С виявлено лише два основних ендотермічних ефекти. У сплаві $Al_{71.6}Ni_{23}Fe_{5.4}$ квазікристалічна декагональна фаза оточена кристалічними фазами $Al_{13}(Ni,Fe)_4$, $Al_3(Ni,Fe)_2$ і $Al_3(Ni,Fe)$. Зі зниженням температури квазікристалічна D-фаза формується в температурному інтервалі між 940 °С та 890 °С, а інші фази з'являються за температури біля 850 °С, що вказує на різні шляхи кристалізації досліджених сплавів. Показано, що стабільність квазікристалічної декагональної фази до кімнатної температури може бути пов'язана з її неповним розпадом при охолодженні зі швидкістю 50 К/хв. Крім того, литі сплави містять різну кількість квазікристалічної D-фази. Об'ємний вміст цієї фази у сплаві $Al_{71.6}Ni_{23}Fe_{5.4}$ більш ніж у два рази перевищує її вміст у сплаві $Al_{72}Ni_{13}Fe_{15}$. Встановлено залежність цієї характеристики від складу сплаву, а саме суттєве підвищення мікротвердості сплаву $Al_{72}Fe_{15}Ni_{13}$.

Ключові слова: квазікристалічна декагональна фаза, фазові перетворення, температури реакцій, мікротвердість.

Исследованы процессы образования квазикристаллической и сосуществующих кристаллических фаз в структуре сплавов Al–Ni–Fe. Установлено формирование двух модификаций декагональной фазы (AlFe- и AlNi-тип) в зависимости от состава. В сплаве $Al_{72}Ni_{13}Fe_{15}$ она сосуществует с моноклинной фазой Al_5FeNi. При охлаждении этого сплава со скоростью 50 К/мин в температурном интервале 850–950 °С обнаружено только два основных эндотермических эффекта. В сплаве $Al_{71.6}Ni_{23}Fe_{5.4}$ квазикристаллическая декагональная фаза окружена кристаллическими фазами $Al_{13}(Ni,Fe)_4$, $Al_3(Ni,Fe)_2$ и $Al_3(Ni,Fe)$. При понижении температуры квазикристалическая D-фаза формируется в температурном интервале между 940 °С и 890 °С, а остальные фазы появляются при температуре около 850 °С, что указывает на разные пути кристаллизации исследованных сплавов. Показано, что стабильность квазикристаллической декагональной фазы до комнатной температуры может быть связана с ее неполным распадом при охлаждении со скоростью 50 К/мин. Кроме того, литые сплавы содержат разное количество квазикристаллической D-фазы. Объемное содержание этой фазы в сплаве $Al_{71.6}Ni_{23}Fe_{5.4}$ более чем в два раза превышает ее содержание в сплаве $Al_{72}Ni_{13}Fe_{15}$. Установлена зависимость этой характеристики от состава сплава, а именно существенное повышение микротвердости сплава $Al_{72}Fe_{15}Ni_{13}$.

Ключевые слова: квазикристаллическая декагональная фаза, фазовые превращения, температуры реакций, микротвердость.

1. Introduction

In the last decades, much basic and applied research has been dedicated to quasicrystalline alloys. The wide range of applications of this specific set of materials ensures a continuous and prolific interest from the academic and industrial communities [1]. A quasicrystalline decagonal phase was found to form at compositions very close to $Al_{72}Ni_{13}Fe_{15}$ and $Al_{71.6}Ni_{23}Fe_{5.4}$ [2, 3]. Grushko et al. discussed the stability of this phase and argued that it could be as stable as periodic crystalline phases [4]. However, de Laissadiere et al. asserted in a review paper that decagonal quasicrystals in the Al–Ni–Fe system are to be regarded as metastable [5]. It was suggested that the decagonal phase appears as an intermediate state during the formation of $Al_{13}(Fe,Ni)_4$ from the liquid.

Taking into account some discrepancies concerning the stability of the decagonal quasicrystalline phase observed in the Al–Ni–Fe alloys, the aim of the paper is to investigate the solidification reactions involving this phase.

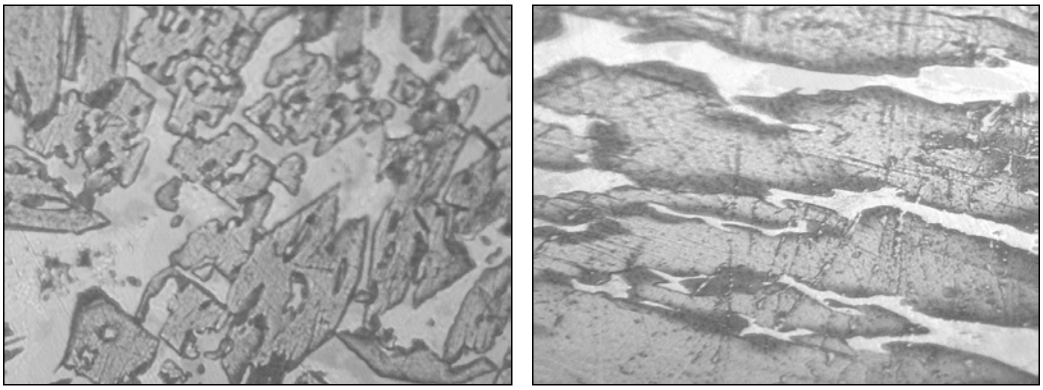
2. Experimental procedure

The alloys with nominal compositions of $Al_{72}Fe_{15}Ni_{13}$ and $Al_{71.6}Ni_{23}Fe_{5.4}$ were prepared of high purity (99.99 pct.) aluminum, nickel, and iron. These elements were put in a graphite crucible and melted using Tamman furnace. The cooling rate of the alloys was 50 K/min. In order to verify the bulk compositions, inductively coupled plasma optical emission spectroscopy was applied for the examination of selected samples. The relative precision of the measurements was better than ± 3 pct.

The instruments used in the microstructural characterization of the investigated alloys were mainly optical microscopes (OM) *Neophot* and *GX-51*, quantitative 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 determined 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. The reactions involving the decagonal quasicrystalline phase were investigated by means of differential thermal analysis (DTA). DTA measurements were carried out using open alumina crucibles. Two heating and cooling curves were recorded for each sample at a heating rate of 50 K/min. The Vickers microhardness was measured with a diamond indenter with a 50 g load. The porosity level was determined by image analysis to be approximately 5 pct.

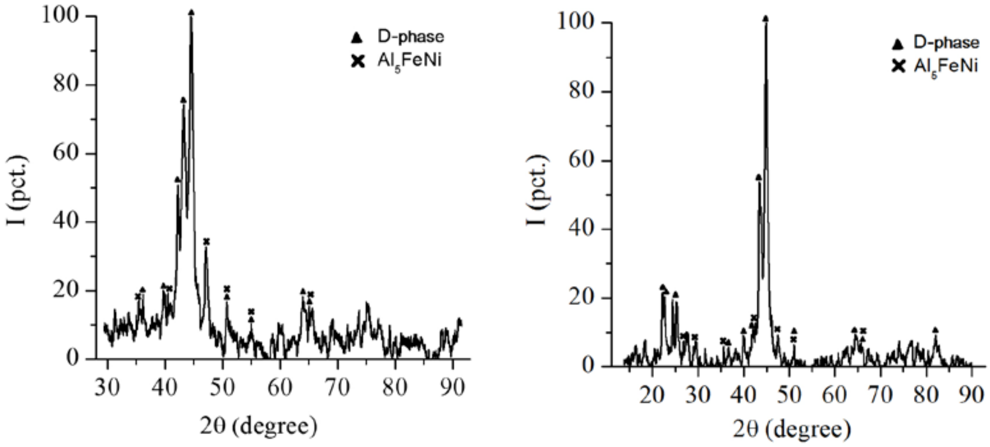
3. Results and discussion

The investigated as-cast alloys exhibited different microstructure. The results of metallographic and XRD analyses of $Al_{72}Fe_{15}Ni_{13}$ alloy are summarized in Fig. 1 and Fig. 2. Two ternary compounds were observed in the structure: monoclininc Al_5FeNi and decagonal quasicrystalline (D) phases. Thermal effects represented by DTA results showed the formation of D-phase at 950°C and Al_5FeNi at 845°C (Table 1). As the D-phase was found at room temperature the stability of this phase with respect to decomposition into its neighboring phases is clearly confirmed. Taking into account the fact that the binary quaiscrystalline D-$Al_{86}Fe_{14}$ phase is metastable in Al–Fe system it can be deduced that this phase becomes more stable with the dissolution of Ni.



(a) (b)

Fig. 1. The OM images of the as-cast $Al_{72}Fe_{15}Ni_{13}$ alloy: a – x200; b – x400.



(a) (b)

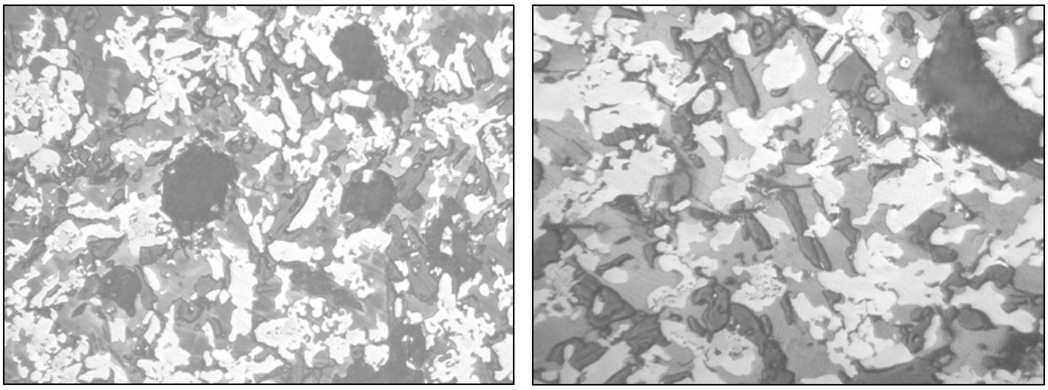
Fig. 2. XRD pattern obtained from the as-cast $Al_{72}Fe_{15}Ni_{13}$ alloy: a – before DTA; b – after DTA.

Table 1

Summary of the identified phases and DTA data of the as-cast Al–Ni–Fe alloys

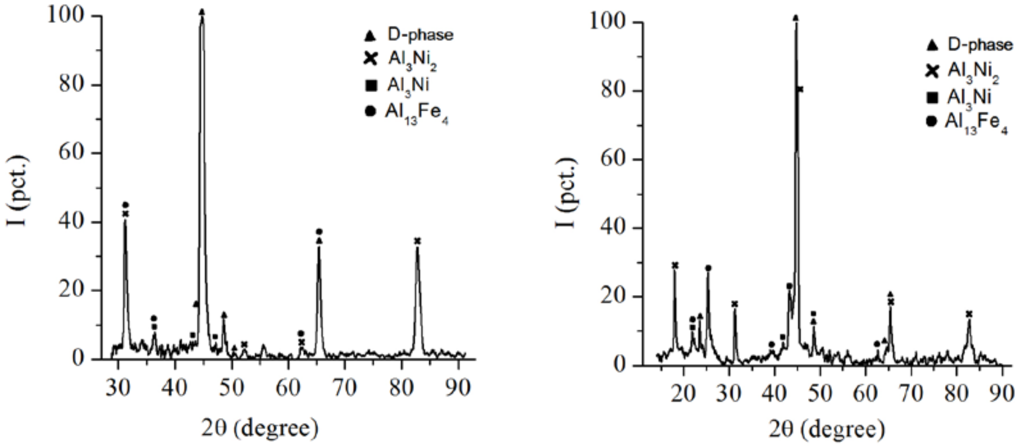
Alloy	Identified phases	Reactions temperatures, °C	
		on heating	on heating
$Al_{72}Fe_{15}Ni_{13}$	D-phase	960	960
	Al_5FeNi	860	860
$Al_{71.6}Ni_{23}Fe_{5.4}$	D-phase	950	950
	$Al_3(Ni,Fe)_2$	1020	1020
	$Al_3(Ni,Fe)$	865	865
	$Al_{13}(Ni,Fe)_4$	865	865

Metallographic examination of $Al_{71.6}Ni_{23}Fe_{5.4}$ alloy revealed the existence of the following phases: decagonal D-phase, monoclinic $Al_{13}(Ni,Fe)_4$, hexagonal $Al_3(Ni,Fe)_2$, and orthorhombic $Al_3(Ni,Fe)$ (Fig. 3). As shown in Fig. 4, the XRD patterns confirmed this conclusion. At 940 °C the decagonal phase was in equilibrium with the liquid and $Al_3(Ni,Fe)_2$, and at 850 °C with $Al_{13}(Ni,Fe)_4$, $Al_3(Ni,Fe)_2$, and $Al_3(Ni,Fe)$ due to its decomposition to the mentioned three crystalline phases upon cooling. A summary of the reactions temperatures derived from DTA data is given in Table 1. The decagonal phase is based on D-$Al_{80}Ni_{20}$ compound and stabilized with the addition of Fe, which is in excellent agreement with the conclusions made in Ref. [2].



(a) (b)

Fig. 3. The OM images of the as-cast $Al_{71.6}Ni_{23}Fe_{5.4}$ alloy: a – x200; b – x400.



(a) (b)

Fig. 4. XRD pattern obtained from the as-cast $Al_{71.6}Ni_{23}Fe_{5.4}$ alloy: a – before DTA; b – after DTA.

Thus, analysis of the as-cast $Al_{72}Fe_{15}Ni_{13}$ and $Al_{71.6}Ni_{23}Fe_{5.4}$ alloys revealed that some quantity of the decagonal phase formed during solidification can remain down to room temperature, as microstructurally evidenced in Fig. 1 and Fig. 3. These results point to the possibility of extending the compositional limits of the decagonal phase by cooling at 50 K/min. Besides, measurements showed that the decagonal D-quasicrystals of $Al_{72}Fe_{15}Ni_{13}$ alloy possess a higher microhardness than that of D-phase of $Al_{71.6}Ni_{23}Fe_{5.4}$ alloy (Table 2). Despite the lower volume fraction of the D-AlFe type phase the total microhardness of $Al_{72}Fe_{15}Ni_{13}$ alloy exceeds that of $Al_{71.6}Ni_{23}Fe_{5.4}$ alloy. The role of alloy composition in increasing microhardness is most probably a microstructural effect.

Table 2

Summary of the quantitative metallographic analysis and microdurometric measurements of the as-cast Al–Ni–Fe alloys

Alloy	D-phase volume fraction, pct.	D-phase microhardness, GPa	Total alloy microhardness, GPa
$Al_{72}Fe_{15}Ni_{13}$	13.7±0.1	10.8±1.33	6.1±0.7
$Al_{71.6}Ni_{23}Fe_{5.4}$	32.0±0.1	9.2±0.47	4.7±0.3

4. Conclusions

From the results presented, it follows that the investigated alloys contain thermodynamically stable decagonal phase. The quasicrystalline phase of $Al_{72}Fe_{15}Ni_{13}$ alloy coexists with Al_5FeNi. At a temperature of about 940 °C the D-phase of $Al_{71.6}Ni_{23}Fe_{5.4}$ alloy is in equilibrium with $Al_3(Ni,Fe)_2$ and the liquid phase, and between 800 and 850 °C it transforms to $Al_3(Ni,Fe)$, $Al_{13}(Ni,Fe)_4$, and $Al_3(Ni,Fe)_2$. The alloys microhardness was found to be dependent on the alloy composition, with the $Al_{72}Fe_{15}Ni_{13}$ alloy showing a substantially higher microhardness compared to that of the $Al_{71.6}Ni_{23}Fe_{5.4}$ alloy.

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