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$_5$FeNi 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$_{73.4}$Ni$_{13}$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.
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 Al72Ni13Fe15 and Al71.6Ni23Fe5.4 [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 Al13(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 Al72Fe15Ni13 and Al71.6Ni23Fe5.4 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 CuKα 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 Al72Fe15Ni13 alloy are summarized in Fig. 1 and Fig. 2. Two ternary compounds were observed in the structure: monoclinic Al5FeNi and decagonal quasicrystalline (D) phases. Thermal effects represented by DTA results showed the formation of D-phase at 950°C and Al5FeNi 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 quasicrystalline D-Al56Fe14 phase is metastable in Al–Fe system it can be deduced that this phase becomes more stable with the dissolution of Ni.
The solidification of Al–Ni–Fe decagonal quasicrystalline alloys

Fig. 1. The OM images of the as-cast Al$_{72}$Fe$_{15}$Ni$_{13}$ alloy: a – x200; b – x400.

Fig. 2. XRD pattern obtained from the as-cast Al$_{72}$Fe$_{15}$Ni$_{13}$ alloy: a – before DTA; b – after DTA.

Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Identified phases</th>
<th>Reactions temperatures, °C on heating</th>
<th>DTA data a – on heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$<em>{72}$Fe$</em>{15}$Ni$_{13}$</td>
<td>D-phase, Al$_3$FeNi</td>
<td>960, 860</td>
<td>960, 860</td>
</tr>
<tr>
<td>Al$<em>{71.6}$Ni$</em>{23}$Fe$_{5.4}$</td>
<td>D-phase, Al$_3$(Ni,Fe)$_2$, Al$_3$(Ni,Fe)</td>
<td>950, 1020, 865</td>
<td>950, 1020, 865</td>
</tr>
</tbody>
</table>

Metallographic examination of Al$_{71.6}$Ni$_{23}$Fe$_{5.4}$ alloy revealed the existence of the following phases: decagonal D-phase, monoclinic Al$_3$(Ni,Fe)$_2$, 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$_3$(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].

![Fig. 3. The OM images of the as-cast Al$_{71.6}$Ni$_{23}$Fe$_{5.4}$ alloy: a – x200; b – x400.](image1)

![Fig. 4. XRD pattern obtained from the as-cast Al$_{71.6}$Ni$_{23}$Fe$_{5.4}$ alloy: a – before DTA; b – after DTA.](image2)

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

<table>
<thead>
<tr>
<th>Alloy</th>
<th>D-phase volume fraction, pct.</th>
<th>D-phase microhardness, GPa</th>
<th>Total alloy microhardness, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{72}Fe\textsubscript{15}Ni\textsubscript{13}</td>
<td>13.7±0.1</td>
<td>10.8±1.33</td>
<td>6.1±0.7</td>
</tr>
<tr>
<td>Al\textsubscript{71.6}Ni\textsubscript{23}Fe\textsubscript{5.4}</td>
<td>32.0±0.1</td>
<td>9.2±0.47</td>
<td>4.7±0.3</td>
</tr>
</tbody>
</table>

4. Conclusions

From the results presented, it follows that the investigated alloys contain thermodynamically stable decagonal phase. The quasicrystalline phase of Al\textsubscript{72}Fe\textsubscript{15}Ni\textsubscript{13} alloy coexists with Al\textsubscript{5}FeNi. At a temperature of about 940 °C the D-phase of Al\textsubscript{71.6}Ni\textsubscript{23}Fe\textsubscript{5.4} alloy is in equilibrium with Al\textsubscript{3}(Ni,Fe)\textsubscript{2} and the liquid phase, and between 800 and 850 °C it transforms to Al\textsubscript{3}(Ni,Fe), Al\textsubscript{13}(Ni,Fe)\textsubscript{4}, and Al\textsubscript{5}(Ni,Fe)\textsubscript{2}. The alloys microhardness was found to be dependent on the alloy composition, with the Al\textsubscript{72}Fe\textsubscript{15}Ni\textsubscript{13} alloy showing a substantially higher microhardness compared to that of the Al\textsubscript{71.6}Ni\textsubscript{23}Fe\textsubscript{5.4} alloy.

References


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