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Effect of Cr addition on the formation of the decagonal quasicrystalline phase of a rapidly solidified Al-Ni-Co alloy

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The influence of Cr addition in a rapidly solidified Al-Ni-Co alloy was investigated. Melt spun samples of atomic composition $Al_{71}Ni_{20}Co_9$, $Al_{72}Ni_{19}Co_7Cr_2$ and $Al_{72}Ni_{20}Co_5Cr_3$ were studied by X-ray diffraction and transmission electron microscopy. Aiming to develop quasicrystalline compositions enriched in corrosion resistant elements such as Cr and Ni this work presents, for the first time, the effect of Cr addition on the quasicrystalline phase formation of a high-Ni Al-Ni-Co rapidly solidified alloy chosen to be within the range of formation of the decagonal quasicrystalline phase observed in this ternary system. The composition of the quaternary alloys was chosen by reducing the Co content in favor of Cr on the ternary alloy and keeping the average valence electron per atom (e/a) around 1.86. The phase constitution of the ternary alloy consisted of the decagonal phase along with two intermetallic phases, Al_3Ni and Al_3Ni_2. The addition of Cr resulted in the formation of a second quasicrystalline decagonal phase, rich in Cr. This was due to the low Cr solubility on the ternary Al-Ni-Co decagonal and intermetallic phases, which rejected Cr and resulted on the formation of the Cr-rich quasicrystal.

1. Introduction

Quasicrystalline alloys exhibit a variety of interesting properties, including high hardness, low friction coefficient, high corrosion resistance in acid medium, high resistance to oxidation and low thermal conductivity. Such features make the quasicrystalline forming alloys suitable candidates to be used as coatings, for example, in the petrol industry, which has major problems associated with corrosion, wear and formation of organic deposits in ducts during oil transport. Over a 100 systems are known to form quasicrystalline phases and the associated approximants [1]. Most of those systems are aluminum based, such as, Al-Cu-Fe [1–4], Al-Co [5–9], Al-Cr-Fe [10,11], Al-Cu-Fe-Cr [12,13], Al-Co-Ni [14], among other systems.

The Al-Ni-Co system is well known for the formation of decagonal quasicrystals over a wide range of Ni and Co [14–19]. The atomic percentage of Al in which the decagonal phase is stable is between 70 and 72.5% [15]. In the Co-poor composition of the decagonal phase, atomic percentages as low as 5% of Co were found to form the decagonal quasicrystalline phase [15]. Previous studies have reported the effect of Cu addition to the Al-Ni-Co system in a wide range of Ni/Co atomic percentages [20–22] on the formation of the decagonal quasicrystalline phase. It was found that the decagonal structure can be kept even with great amount of Cu addition, up to 10%.

As the corrosion and oxidation resistance of quasicrystalline alloys are mostly dependent on the chemical composition [2], the addition of corrosion resistant elements, such as Cr, on the quasicrystalline phase could improve the corrosion properties of this alloy. One example of this is the addition of Cr on the well-known Al-Cu-Fe quasicrystal, which produces a decagonal or icosahedral quasicrystalline phase. In this sense, the present work shows the effect of Cr addition on the formation of the decagonal phase, based on the ternary composition $Al_{71}Ni_{20}Co_9$.

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2. Materials and methods

Ingots of 5–10 g were fabricated by arc melting of high purity (>99.99%) elements in order to produce three master alloys of the following atomic compositions: $Al_{71}Ni_{20}Co_9$, $Al_{72}Ni_{19}Co_7Cr_2$ and $Al_{72}Ni_{20}Co_5Cr_3$ (samples will be referred in this text as S1, S2 and S3 respectively). These alloys have e/a ratio of 1.86, 1.84 and 1.82 respectively. The valences used for the calculation of e/a were of $+3$ for Al, -1.66 for Co, -0.66 for Ni and -4.66 for Cr and are available in Ref. [23]. The composition of S2 and S3 alloys was chosen based on the ternary alloy (S1), which is within the range of composition of quasicrystalline phase formation [14,24], aiming to reduce the amount of Co in favor of Cr; in addition to that, the e/a ratio was kept around 1.86 which is the value observed for the ternary quasicrystalline composition. The master alloys were then melt-spun under argon atmosphere on a cooper-wheel with velocity of 30 m/s, to produce 30 μm thick ribbons. The melt-spun ribbons were characterized by X-ray diffraction (XRD) with a Rigaku Geiger-Flex X-ray diffractometer using Cu-Kα radiation and by transmission electron microscopy (TEM) using a TECNAI G2 F20 200 kV coupled with EDX detector. Powder samples were used for XRD analysis and the TEM samples were prepared by ion beam milling of the melt-spun ribbons.

3. Results and discussion

Fig. 1 shows XRD patterns of the melt-spun samples. In all the samples, the decagonal quasicrystalline phase was the major phase. In the ternary alloy (sample S1), $Al_{71}Ni_{20}Co_9$, two other phases were identified in the XRD pattern, which are ternary extensions of binary Al-Ni phases; Al_3Ni and Al_3Ni_2, respectively. The Al_3Ni phase is an orthorhombic phase belonging to the space group Pnma and the Al_3Ni_2 phase is a trigonal phase belonging to the space group $P\bar{3}m1$ [19]. The presence of those intermetallic phases was also observed by Grushko et al. [15]. in another high-Ni Al-Ni-Co quasicrystalline alloy ($Al_{71}Ni_{24}Co_5$) after solidification in a water cooled Cu-crucible.

Sample S2, fabricated with composition of $Al_{72}Ni_{19}Co_7Cr_2$ showed a remarkable decrease in the intensities of the peaks associated with those two intermetallic phases, showing the XRD pattern of an almost single decagonal quasicrystalline phase. The third alloy, of composition $Al_{72}Ni_{20}Co_5Cr_3$, however, showed an increase in the intensities of the same XRD peaks that were absent in the previous case.

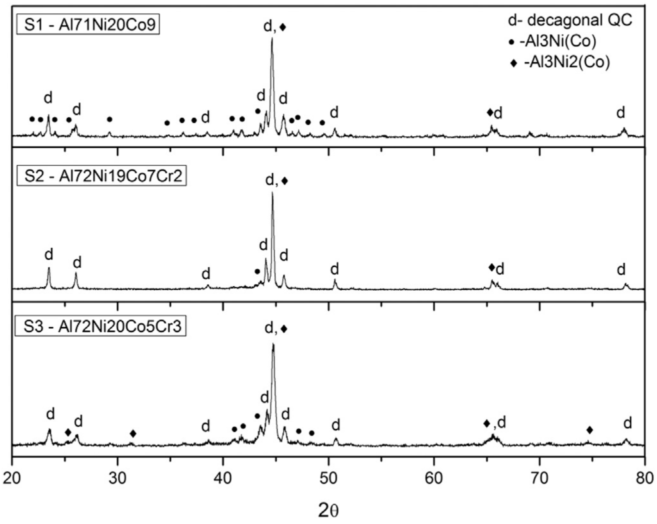

Fig. 1. XRD patterns obtained for melt-spun samples S1, S2 and S3.

Fig. 2 (a) shows TEM bright field image of the microstructure of sample S1. The grains of the quasicrystalline phase and the intermetallic phases in the melt-spun sample are very similar, being difficult to differentiate one from another only by means of morphology. The selected area electron diffraction (SAED) pattern of the Al_3Ni phase is shown in Fig. 2 (b), corresponding to the [011] zone axis. Fig. 2 (c) is the SAED pattern of the quasicrystalline phase, showing a two-fold rotational symmetry and also showing a periodic stacking in one of the directions, while it is quasiperiodic in the orthogonal direction, a characteristic of the decagonal structure.

Fig. 3 (a) shows bright field TEM image of the microstructure of the $Al_{72}Ni_{19}Co_7Cr_2$ alloy (sample S2). Confirming the XRD pattern, the decagonal phase was observed in greater amount than in the sample S1. Along with the quasicrystalline matrix, another quasicrystalline phase, rich in Cr, was also observed at the grain boundaries. Table 1 shows the average chemical composition of the phases measured by EDX. The EDX results clearly show that the solubility of Cr in the ternary Al-Ni-Co decagonal quasicrystal is very limited (about 0.2%, in atomic percentage).

Fig. 3 (b) shows the SAED pattern corresponding to the ten-fold axis from the Cr-poor quasicrystal, which is confirmed to belong to a decagonal quasicrystal in Fig. 3 (c), where the convergent beam electron diffraction (CBED) pattern shows a ten-fold rotational symmetry. Fig. 3 (d) shows SAED pattern of the Cr-rich phase, showing a pseudo-three fold rotational symmetry, which is actually a two-fold rotational symmetry. This pattern shows quasiperiodicity in one of the directions and is similar to one of the electron diffraction patterns shown in Ref. [25] for a $Al_6Cr_{0.5}Ni_{0.5}$ alloy where a decagonal phase was observed. This Al-Cr-Ni composition is very similar to the chemical composition (except for the Co content obviously) measured by means of EDX presented in Table 1 for the Cr-rich phase.

In both S1 and S2 samples, the later stages of solidifications occur with Al segregation. This can be inferred from the binaries Al-Co and Al-Ni [14,26]; the slope in the liquidus line leads to Al enrichment in the liquid at the later stages of solidification. This is observed by the formation of the Al_3Ni phase in the ternary composition and by the formation of the Cr-rich quasicrystalline phase in the sample S2. Both phases have higher Al content than the Al-Ni-Co decagonal phase and thus were formed due to Al segregation in the solidification process. It is interesting to note that in the sample S2, the presence of Cr reduced the formation of the Al_3Ni phase in favor of the formation of the Cr-rich quasicrystal. Al content of the phases presented in Table 1 is greater than the nominal composition of the S2 sample, and this is attributed to the fact that TEM-EDX analysis is performed in an extremely small area; in this sense, some deviation of chemical composition of the phases will be present in each individual grain analyzed, even more intensely in the case of rapid solidified alloys, where metastability is present.

Fig. 4 shows bright field TEM image of the microstructure of the $Al_{72}Ni_{20}Co_5Cr_3$ alloy (sample S3). In this alloy, the presence of the Al_3Ni was more pronounced than in sample S2. The ternary Cr-poor decagonal quasicrystal and the Cr-rich quasicrystal were also present. These three phases are indicated in Fig. 4. The SAED pattern of the Cr-poor quasicrystal, in Fig. 4 (b) shows a two-fold rotational symmetry. The SAED pattern of the Cr-rich quasicrystal, in Fig. 4 (c) also shows a two-fold rotational symmetry although it resembles a ten-fold rotational symmetry. This pattern was also observed in Ref. [25] for the decagonal quasicrystal in a $Al_6Cr_{0.5}Ni_{0.5}$ alloy.

Table 2 shows the average chemical composition of the phases indicated in Fig. 4, measured by EDX. Similarly to the EDX results presented in Table 1, the Cr-poor decagonal quasicrystal shows

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