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Structural Evolution and Phase Transformation in Nanoquasicrystalline Al-Fe-Cr Alloy: DSC Analysis

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Kinetic parameters for microstructural evolution and phase transformation in water atomized Al-Fe-Cr based alloy with nominal composition $Al_{94}Fe_3Cr_3$ have been examined by means of developed precise method of DSC technique and confirmed by the results of XRD analysis. Two exothermic reactions including that with a maximum at 380 – 400 °C has been ascribed to dislocation reorganisation and recrystallisation process within the Al matrix although the main exothermic reaction with a maximum around 540 °C arose from decomposition of icosahedral quasicrystalline particles and simultaneous formation of the metastable Al_6Fe phase and more stable crystalline particles compositionally corresponded to the θ-$Al_{13}Cr_2$ and θ-$Al_{13}Fe_4$ phases. Activation energy for the main exothermic reaction has been found to be roughly about 53.1 kJ mol^{-1} which is significantly smaller than that for the bulk diffusion of either iron or chromium atoms in aluminium and very close to that for the vacancy migration.

Keywords: Nanoquasicrystals, Al-Fe-Cr Based Alloy, Structural Evolution, Phase Transformation.

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1. INTRODUCTION

Nanoquasicrystalline Al-Fe-Cr based alloys, which belong to the group of metal matrix nanocomposite, show excellent balance between high strength and sufficient ductility [1, 2]. Compared to other commercial Al-based alloys these nanocomposites exhibit better microstructural stability, making them promising for industrial application under elevated temperature and, especially, in the automotive and aircraft industries [1, 2]. These alloys are composed of quasi-spherical icosohedral quasicrystalline particles (i-phase) with sizes around 100 nm embedded in an α-Al matrix [3]. A number of processing routes based on rapid solidification with high cooling rate about 10^5 -10^6 K/s have been developed for creating quasicrystalline phases although powder atomisation technique either with argon-gas [3, 4] or high-pressure inhibited water [5] are thought to be the most effective for mass production. However, quasicrystalline i-phase presented in Al-Fe-Cr based alloys are of metastable nature, retaining in surrounding the α-Al solid solution under heating up to the limited temperatures. On this evidence detailed knowledge concerning the range of temperatures where icosohedral quasicrystalline particles survive in Al-Fe-Cr based alloys of particular elementary composition is of great importance. Evidences concerning structural evolution and phase transformation under heating the melt-spun ribbons of $Al_{93}Fe_{4.2}Cr_{2.8}$ alloy and $Al_{93}Fe_3Cr_2$ (Ti, V, Zr, Nb or Ta)$_2$ have been studied exhaustively by different techniques including differential scanning calorimetry (DSC), X-ray diffraction (XRD) analysis, and transmission electron microscopy (TEM) [6, 7, 8, 9, 10]. Karpets et al. [11] studied phase transformation in Al-Fe-Cr based alloys with nominal composition $Al_{94}Fe_4Cr_2$ and $Al_{88.6}Fe_8Cr_{3.4}$ using XRD analysis. Unfortunately, data related to phase transformation of Al-Fe-Cr based alloys produced by powder atomisation technique are few in number [12]. In the present study, therefore, the kinetic parameters for microstructural evolution and phase transformation in water atomized Al-Fe-Cr based alloy have been examined by means of precise method of DSC technique and confirmed by the results of XRD analysis.

2. EXPERIMENTAL

Quasicrystalline powders of Al-based alloy with nominal composition of $Al_{94}Fe_3Cr_3$ was employed in experimentation and fabricated by water-atomisation technique using inhibited high-pressure water with Ph 3.5 [5]. After atomisation powder was sieved to 40 μm. Oxygen content was dependent on powder mesh fractions and varied in the region from about 0.3 to 0.6 wt. %. Fraction volume of quasicrystalline particles contained by $Al_{94}Fe_3Cr_3$ powders did not exceed 30 % [13]. Quasicrystalline particles with sizes varied from 50 to 200 nm was embedded in an α-Al matrix of $Al_{94}Fe_3Cr_3$ powders although quasicrystalline particles with the size increased up to 1.5 μm have also been revealed in the interior of some powder particles, suggesting variable cooling conditions for water jets [14].

DSC measurements were performed using commercial apparatus STA449F1 (Netzsch, Germany). Powders of $Al_{94}Fe_3Cr_3$ alloy were pre-compacted in form of disk-shaped specimens of 3 mm in diameter and thickness about 2 mm. Each specimen was placed into DSC cell under argon flow rate about 20 ml/min and heated up to 600 °C. Heating rates used in DSC measurements were as great as 2, 5, 10, 20, 30 K min^{-1}.

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As reference samples, pre-compacted disks of water atomized powder were employed in DSC measurements. Aluminium pans were used for precise measurements, and one of the pans was used for the reference sample while another was used for tested specimen.

Precise analysis of DSC measurements was done following the method originally developed by Jena et al [15] and applied by Doan et al. [16] to study precipitation and dissolution reactions in 6061 aluminium alloy. Following the method above two separate DSC runs were recorded under the same conditions. In the first run, discs of aluminium powder were placed on both the sample and reference pans whereas in the second run disc of pre-compacted powdered $Al_{94}Fe_3Cr_3$ alloy and that of aluminium powder were placed on the sample and reference pans. By subtracting the measurements of the first run from those recorded during the second one, the blank effect due to the characteristics of the apparatus was determined to eliminate it during advance analysis of measurement results. The heat of fusion for potassium nitrate (KNO_3), lead (Pb), and cesium chloride (CeCl) was measured as standards in order to determine the calibration constant of apparatus.

The results of XRD analysis for quasicrystalline powder after heat treatment up to specific temperatures were used for interpretation of the heat effects recorded by DSC measurements. XRD analysis was performed using Cu K_α radiation. The i-phase was indexed using Cahn's indexation scheme [17].

3 RESULTS AND DISCUSSION

Two exothermic peaks are clearly recognised in DSC runs of powdered $Al_{94}Fe_3Cr_3$ alloy, as can be seen in Fig. 1.

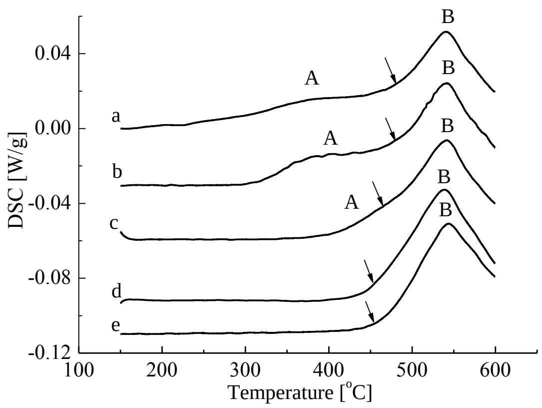

Fig. 1 – DSC runs at the constant heating rate of 10 K min^{-1} for (a) as-received powder of $Al_{94}Fe_3Cr_3$ alloy and that after preliminary heat treatment at (b) 300 °C and (c, d) 400 °C: dwell time is (b, c) 30 min, (d) 1 hour, and (e) 4 hour

Among them there are weak and broad exothermic peak with a maximum at 380 – 400 °C (A) and main exothermic peak around 540 °C (B). The main exothermic peak is commonly associated with i-phase decomposition [6, 7, 8, 9, 10] while the nature of exothermic peak A is thought to be rather different. As opposed to main exothermic peak B the first exothermic peak A is thought to arise from dislocation reorganisation and recrystallisation processes within the Al matrix. This is of common knowledge that the latter processes, which arise from dislocation activity in many other metals and alloys, result in exothermic heat release [18-20]. Actually, the value of the first exothermic peak A is gradually reduced down to complete elimination as the temperature and time of preliminary heat treatment of the powdered $Al_{94}Fe_3Cr_3$ alloy increases, as can be seen in Fig. 1.

The argumentation above is confirmed by the results of XRD analysis. Fig. 2.shows XRD patterns of the $Al_{94}Fe_3Cr_3$ powder before and after heat treatment at different temperatures.

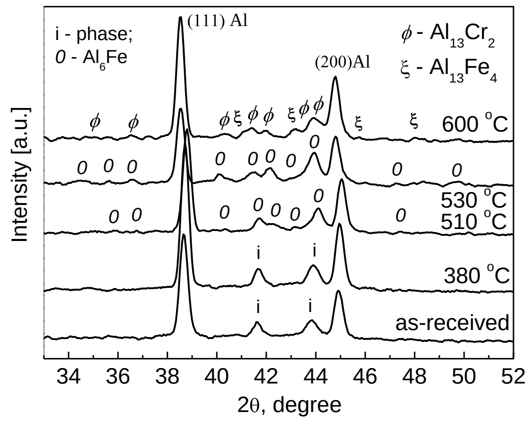

Fig. 2 – XRD patterns of powdered $Al_{94}Fe_3Cr_3$ alloy as-received and heat treated at different temperatures during 30 min

It can be seen that XRD pattern of the $Al_{94}Fe_3Cr_3$ powder heat treated at 380 °C remains similar to that of the as-received powder whereas reflections of the α-Al and diffraction peaks together with those corresponded to metastable Al_6Fe phase are identified in the XRD pattern of the $Al_{94}Fe_3Cr_3$ powder heat treated at 510 °C and 530 °C, suggesting the dissolution of metastable quasicrystalline particles. After heat treatment at 600 °C the metastable Al_6Fe phase is transformed into stable crystalline θ-phases compositionally corresponded to the θ-$Al_{13}Cr_2$ and θ-$Al_{13}Fe_4$, as evidenced from the XRD patterns shown in Fig2. The results of XRD analysis obtained in the present study are in good agreement with those for $Al_{93.7}Fe_4Cr_2$ alloy [11] although coexistence of metastable Al_6Fe phase with the stable crystalline θ-$Al_{13}Cr_2$ phase for melt-spun $Al_{93}Fe_{4.2}Cr_{2.8}$ alloy heat treated at 450 °C was found by Galano et al. [9, 21]

Attention should be drawn to the fact that exothermic heat release B increases with increasing the temperature and time of preliminary heat treatment, as can be seen in Fig.1. This phenomenon is thought to be caused by increasing the fraction volume of quasicrystalline particles during the annealing. As evidenced from [9, 10, 22] coarsening by 150 % of the icosahedral quasicrystalline particles accompanied by extraction of solute Fe and Cr from the Al matrix of melt-spun $Al_{93}Fe_{4.2}Cr_{2.8}$ alloy was found to be true after heat treatment at 450 °C for 30 min, indicating the growth of fraction volume of quasicrystalline particles prior their dissolution. This is because of Al matrix for as-received $Al_{93}Fe_{4.2}Cr_{2.8}$ alloy was oversaturated by solute Fe and Cr compared to that corresponded to the stable equilibrium concentration at liquidus temperature for Al-Fe and Al-Cr [9, 23].

The results of XRD analysis determined in the present study proof the fluctuation of solute Fe and Cr in Al matrix under the influence of preliminary heat treatment. As can be seen in Table, lattice parameter a_o for the α-Al solid solution presented in $Al_{94}Fe_3Cr_3$ alloy powder is gradually reduced with increasing the annealing temperature up to 510 °C, indicating the enrichment of the Al matrix by solute Fe and Cr whose atomic radii are smaller by roughly about 12 % than Al atomic radius. Kinetic of i-phase decomposition is presumably to be faster compared to that for nucleation and growth of Al_6Fe phase. The increase of lattice parameter a_o resulted from extraction of solute Fe and Cr from the Al matrix occurs only after heat treatment at 530 °C when amount of metastable Al_6Fe phase increases in comparison with that indicative of $Al_{94}Fe_3Cr_3$ alloy powder heat treated t 510 °C. This fact is evidenced from increased integral intensity of reflections corresponded to Al_6Fe phase that was detected after heat treatment at 530 °C, as can be seen in Fig. 2. It is noticeable that increasing the temperature of heat treatment up to 530 °C causes the reflections corresponded to Al_6Fe phase to shift towards smaller 2θ, suggesting its alloying by Cr whose atomic radius is greater than that of Fe. However, lattice parameter a_o, for the α-Al somewhat decrease after heat treatment at 600 °C when metastable Al_6Fe phase transforms into conventional crystalline θ-phases such as θ-$Al_{13}Cr_2$ and θ-$Al_{13}Fe_4$.

Table – Lattice parameter a_o of the α-Al solid solution presented in $Al_{94}Fe_3Cr_3$ alloy powder after heat treatment for 30 min at different temperatures

Temperature, °C	As-received	380	510	530	600
a_o, nm	0.40391	0.40369	0.40356	0.40456	0.40434

Another aspect concerns the fact that the start of main exothermic reaction B tends to shift toward lower temperatures with increasing the annealing parameters (temperature and time). Although the reason for this effect is exhaustively not clear at the present, it could be thought that promoting action of dislocation activity on diffusive mobility of Fe and Cr in the Al-matrix under preliminary heat treatment favours the arrangement of solute elements, accelerating dissolution of quasicrystalline particles and simultaneous formation of more stable Al_6Fe phase.

Activation energy for the main exothermic reaction B was obtained according to Kissenger method procedure [16, 24] by using DSC measurement results recorded at various heating rate. Following expression between the temperature for a fixed stage of transformation and, in particular, that corresponded to the start of i-phase decomposition T_x and the heating rate V_i is given in the form:

$$\ln\left(\frac{V_i}{T_x^2}\right) = -\frac{Q}{RT_x} + C \qquad (1)$$

where Q is activation energy in J mol^{-1}, V_i is heating rate in K min^{-1}, T_x is the temperature for the start of i-phase decomposition in K, R = 8.31 J mol^{-1} K^{-1} is the gas constant, C is numerical constant.

Activation energy is determined from the relationship:

$$Q = -\operatorname{tg}\phi R, \qquad (2)$$

where tg ϕ is the slope of the strain line obtained by plotting ln (V_i/T_x^2) *vs* $1/T_i$.

Fig. 3 show the data for ln (V_i/T_x^2) plotted against the inverse absolute temperature for main exothermic reaction B.

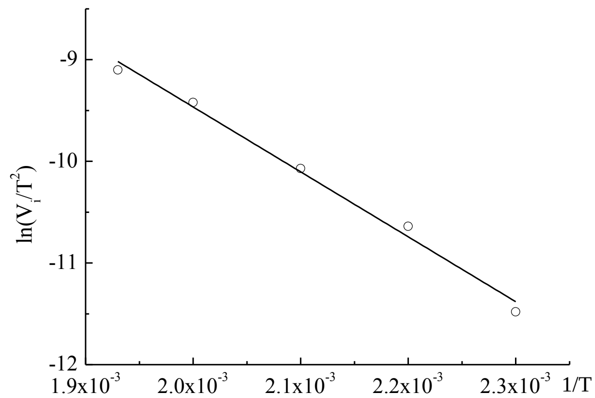

Fig. 3 – Relationship between ln (V_i/T_x^2) and temperature T in the main exothermic reaction

The results of calculations indicate that the activation energy for the main exothermic reaction B is about 53.1 kJ mol^{-1}. The important point concerns the fact that the value of activation energy for the exothermic reaction B is significantly smaller than that for the bulk diffusion of either iron or chromium atoms in aluminium and very close to that for the vacancy migration. By considering the evidence above the main exothermic reaction may be explained as the formation of vacancy cluster. Kestenbach al. [22] and Galano et al. [9] observed the existence of cluster-like contrast of several nanometres in diameter by TEM observation of rosette-like quasicrystals with two-fold rotation axis when they gradually dissolved under heating.

4 CONCLUSIONS

By using water atomised powder of $Al_{94}Fe_3Cr_3$ alloy efficient application of newly developed precise method of DSC analysis for examination of phase transformation and microstructural stability of nanoquasicrystalline Al-Fe-Cr based alloys composed of metastable quasicrystalline particles embedded in an Al matrix was justified.

Two exothermic reactions during continuous heating of powdered $Al_{94}Fe_3Cr_3$ alloy up to 600 °C were detected by DSC measurements. Weak and broad exothermic peak with a maximum at 380 – 400 °C can be explained by dislocation reorganisation and recrystallisation process within the Al matrix whereas the main exothermic peak around 540 °C was believed to arise from decomposition of icosahedral quasicrystalline particles and simultaneous formation of the metastable Al_6Fe phase and more stable crystalline particles compositionally corresponded to the θ-$Al_{13}Cr_2$ and θ-$Al_{13}Fe_4$ phases.

Promoting action of dislocation activity on diffusive mobility of Fe and Cr in the Al-matrix under preliminary heat treatment is thought to favour the arrangement of solute elements, accelerating dissolution of quasicrystalline particles and simultaneous formation of more stable Al_6Fe phase.

Activation energy for the main exothermic reaction calculated as great as about 53.1 kJ mol^{-1} was found to be significantly smaller than that for the bulk diffusion of either iron or chromium atoms in aluminium and very close to that for the vacancy migration.

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