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STRUCTURAL EVOLUTION AND PHASE TRANSFORMATION IN NANOQUASICRYSTALLINE Al-Fe-Cr ALLOY

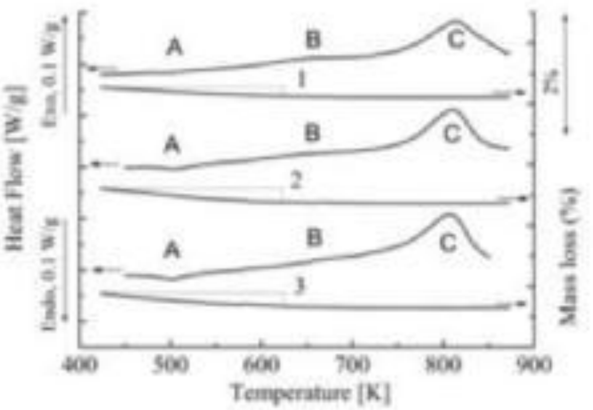
Yurkova A.[1], Byakova A. [2], Kravchenko A. [3]
[1]Doct of Tech. Science, Professor of National Technical University of Ukraine “Kiev Polytechnic Institute”,
Kyiv, Ukraine, (yurkova@iff.kpi.ua)
[2]Doct of Tech. Science, Professor, Institute for Problems in Materials Science, National Academy of
Sciences of Ukraine, Kyiv, Ukraine, (byakova@mail.ru)
[3]Student of National Technical University of Ukraine “Kiev Polytechnic Institute”, Kyiv,
Ukraine (gara346@yandex.ua)

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 alloys, Al-Fe-Cr based alloys show better structural stability, making them promising to be employed at elevated temperatures and, therefore, attractive for industrial application in automotive and aircraft industries [1, 2]. These alloys are composed of icosahedral quasicrystalline particles (i-phase) with sizes about 100 nm embedded in α-Al matrix [3]. However, quasicrystalline particles of i-phase presented in Al-Fe-Cr based alloys are of metastable nature, retaining in surrounding of α-Al solid solution at heating up to ultimate temperatures. On this evidence detailed knowledge concerning the range of temperatures where i-phase particles survive in Al-Fe-Cr alloys of particular elementary composition is of great importance. In the present study, therefore, the kinetic parameters for structural 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.

Quasicrystalline powders of Al-based alloy with nominal composition of $Al_{94}Fe_3Cr_3$ was em-ployed in experimentation and fabricated by water-atomisation technique using inhibited high-pressure water with Ph 3.5 [4]. Fraction volume of quasicrystalline particles contained by $Al_{94}Fe_3Cr_3$ powders did not exceed 30% [5]. DSC measurements were performed using commercial apparatus STA449F1 (Netzsch, Germany). XRD analysis was performed using Cu K_α radiation. The i-phase was indexed using Cahn’s indexation scheme [6].

Fig. 1 shows typical DSC run at constant heating rate of 10 $K \cdot min^{-1}$.

One endothermic and two exothermic reactions are clearly recognised in DSC runs of powdered $Al_{94}Fe_3Cr_3$ alloy detected by DSC measurements. An attention should be paid to the fact that endothermic peak is accompanied by powder mass loss, suggesting dehydration of aluminium hydroxide usually presented on aluminium surface in a form of ultrathin layer. It should be noted that endothermic peak becomes strongly pronounced as powder particles size increases. This is because fraction of pores in the interior of powder particles increases, resulting in bigger length of oxidized surface. Actually, the results of XRD analysis confirm the presence of hydroxide on the surface of powder particles and pores in their interior, as can be seen in fig. 2.



Fig, 1. DSC runs and TGA measurements detected under heating of $Al_{94}Fe_3Cr_3$ powder with different mesh fractions: 1 – particles of 40 μm and less; 2 – particle size ranged from 40 to 63 μm; 3 – particle size ranged from 63 to 100 μm.

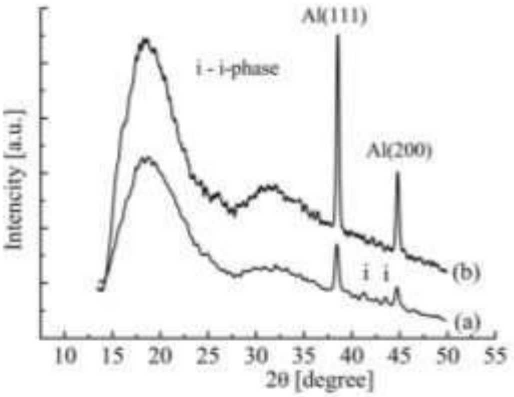


Fig. 2. Sections of XRD patterns of (a) as-received $Al_{94}Fe_3Cr_3$ powder and (b) powder of pure Al.

XRD patterns for $Al_{94}Fe_3Cr_3$ powder shows pronounced halo at the range of small angles that is generally intrinsic to gibbsite $Al_2O_3 \times 3H_2O$ and, thus, strongly suggest the presence of X-ray amorphous hydroxide $Al_2O_3 \times nH_2O$ of variable composition. It should be noted that similar pronounced halo of increased intensity is observed in the XRD patterns for pure Al powder that has smaller corrosion resistance compared to that of $Al_{94}Fe_3Cr_3$ alloy. As evidenced from fig. 2, the mass loss history of $Al_2O_3 \times nH_2O$ hydroxide starts under temperature higher than 453 K, ensuring its transformation into intermediate phases. Among those is boehmite, γ-AlO(OH), which is formed at temperature about 500 K, although it is also gradually decomposed during further heating up to the higher temperatures. These results are in good agreements with the data reported previously [12-14].

There are weak and broad exothermic peaks clearly recognised in DSC curves with a maximum at 653–673 K (B) and a main exothermic peak around 813K (C) commonly associated with i-phase decomposition [7-10]. The nature of the first exothermic peak B is rather different from that of main exothermic peak C. As opposed to the letter first exothermic peak B is thought to arise from dislocation reorganisation and recrystallization processes within the Al matrix. This is of common knowledge that the latter processes arise from dislocation activity and occurred in many other metals and alloys result in exothermic heat release [11-13]. Actually, the value of the first exothermic peak B is gradually reduced down to complete elimination as the temperature of preliminary heat treatment of the powder increases up to 673 K, as can be seen in fig.1. The argumentation above is confirmed by the results of XRD analysis. Fig. 3 shows sections of XRD patterns for $Al_{94}Fe_3Cr_3$ powder prior and after heat treatment at different temperatures. XRD pattern of the $Al_{94}Fe_3Cr_3$ pow-der heat treated at 653 K remain similar to that of the as-received powder. Reflections of the α-Al and quasicrystalline i-phase together with weak diffraction peaks corresponded to the metastable Al_6Fe phase are identified in the XRD pattern of the $Al_{94}Fe_3Cr_3$ powder heat treated at 783 K, suggesting the partial decomposition of i-phase. Gradual dissolution of metastable quasicrystalline particles and simultaneous formation of more stable crystalline particles is still in progress with further increasing the temperature of heat treatment, as was shown by direct observation of TEM images [14]. Coexistence of the quasicrystalline i-phase and metastable Al_6Fe phase with the stable crystalline θ-$Al_{13}Cr_2$ phase becomes true for the $Al_{94}Fe_3Cr_3$ alloy powder heat treated at 803 K, which is in agreement with the data published by other authors [9, 15]. Diffraction peaks of the α-Al together with reflections of the stable crystalline θ-phases compositionally corresponded to the θ-$Al_{13}Cr_2$ and θ-$Al_{13}Fe_4$ are identified in the XRD pattern of the quasicrystalline powder after heat treatment at 873 K.

Attention should be drawn to the fact that main exothermic heat release C increases with increasing the temperature of preliminary heat treatment up to 673 K for 10 min, as can be seen in Fig.1. Again, the main exothermic heat release B increases essentially with increasing the annealing time up to 4 hours during heat treatment at 673 K. These phenomena are thought to be caused by increasing the fraction volume of quasicrystalline particles. As evidenced from [9, 10] 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 723 K for 30 min, indicating the increased fraction volume of quasicrystalline particles. This is because of Al matrix for as-spun $Al_{93}Fe_{4.2}Cr_{2.8}$ alloy was oversaturated by solute Fe and Cr compared to that corresponded to the stable equilibrium concentration at liquidus temperature [9, 16].

In the present study, the results of XRD analysis proof of the evidence above. As can be seen in Table, lattice parameter *a* 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 783 K, indicating the enrich-ment 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* resulted from extrac-tion of solute Fe and Cr from the Al matrix occurs only after heat treatment at 803 K when amount of metastable Al_6Fe phase increases in comparison with that indicative of $Al_{94}Fe_3Cr_3$ alloy powder heat treated at 783 K. This fact is evidenced from increased integral intensity of reflections corre-sponded to Al_6Fe phase that was detected after heat treatment at 803 K, as can be seen in Fig. 3. It is noticeable that increasing the temperature of heat treatment up to 803 K 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*, for the α-Al somewhat decrease after heat treatment at 873 K when metastable Al_6Fe phase transforms into conventional crystalline θ-phases such as θ-$Al_{13}Cr_2$ and θ-$Al_{13}Fe_4$.

Another aspect concerns the fact that the start of main exothermic reaction tends to shift toward lower temperatures with increasing the annealing parameters (temperature and time). Although the reason for this effect is not clear at the present, it could be thought that promoting action of dislocation activity under preliminary heat treatment favours the achievement of a stable equilibrium concentration of solute elements in the α-Al and growth of the metastable quasicrystalline particles, accelerating their further dissolution and simultaneous formation of more stable crystalline particles.

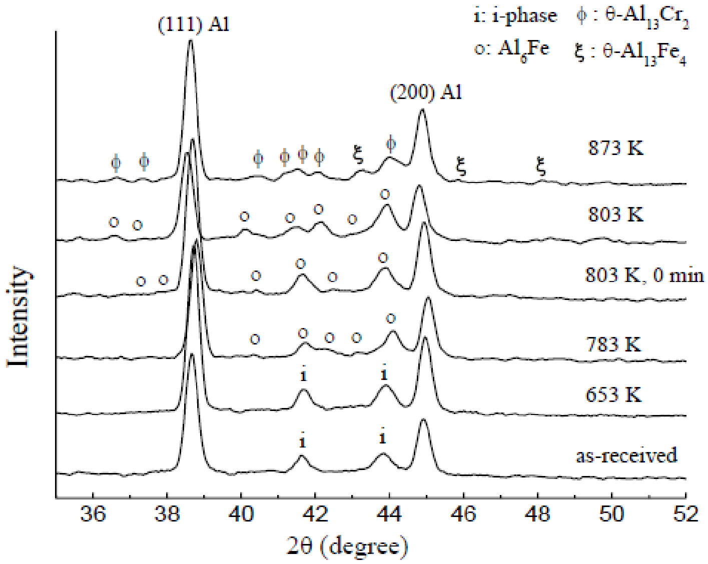


Fig. 3. Sections of XRD patterns for $Al_{94}Fe_3Cr_3$ powder (a) prior and (b-e) after heat treatment at different temperatures during 30 min.

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

Tempera-ture, K	As-received	653	783	803	873
a, nm	0.40391	0.40369	0.40356	0,40456	0.40434

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 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 873 K were detected by DSC measurements. Weak and broad exo-thermic peak with a maximum at 653–673 K can be explained by dislocation reorganisation and recrystallization process within the Al matrix whereas the main exothermic peak around 813 K 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 simultane-ous formation of more stable Al_6Fe phase.

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