Quasicrystals Formation in Ball-Milled Al-Cu-Cr Powders

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Abstract. Al$_{67}$Cu$_{20}$Cr$_{13}$ and Al$_{75}$Cu$_{10}$Cr$_{15}$ alloys were produced by mechanical alloying from elemental powders. As-milled samples consist of the initial elemental phases. Phase transformations at heating were analyzed by differential scanning calorimetry and X-ray diffraction analysis. Annealing of as-milled powders in the temperature range of 500 to 550 °C results in the formation of binary and ternary compounds including the decagonal quasicrystalline phase that was found to be stable at least up to 800 °C.

1. Introduction

Starting from [1], a number of stable and metastable quasicrystals were obtained in several binary and multicomponent systems [2, 3]. The peculiarities of electron configuration of QC phases cause their unusual properties, which may be useful for industrial application. QC phases are expected to possess high antifriction properties, because they are very hard and, simultaneously, have very low friction coefficient. Quasicrystals offer promise as a reinforcing phase for composite materials. Al-Cu-Fe system has attracted particular attention, because a thermodynamically stable QC phase can form in this system [4-6]. Al-Cu-Fe quasicrystalline phase is widely applied as the reinforcement [7-9] to obtain the composites that combine high mechanical and tribological properties; however, the corrosion resistance of QC in the Al-Cu-Fe system is not high [10]. This is a reason to search for the QC phases in other Al-based systems, for example, in the Al-Cu-Cr system.

The QC in this system can be formed by melt quenching; in some cases, quasicrystals are formed by annealing of quenched alloys [11-13]. No data on the thermodynamic stability of the QC phases in this system are available. It is known that both icosahedral [11, 12] and decagonal [12, 13] crystalline phases can be obtained in the Al-Cu-Cr system. The phase formation in the Al-Cu-Cr system by mechanical alloying was studied for the Al$_{65}$Cu$_{20}$Cr$_{15}$ [4] and Al$_{67}$Cu$_{22}$Cr$_{11}$ [14] compositions. It was found that annealing of the mechanically alloyed composition resulted in the formation of a single-phase alloy with icosahedral [4] or decagonal [14] quasicrystalline structure, respectively. Here, we use a combination of mechanical alloying and subsequent annealing to obtain the quasicrystalline phases in the Al-Cu-Cr powders with various element contents.

To choose the compositions, we used the data on the composition of quasicrystalline phases in the related systems (for example, in the Al-Cu-Fe system, icosahedral quasicrystalline phase is formed for the Al$_{60}$Cu$_{25}$Fe$_{15}$ composition), and the experimental results for stable diagram of the system under investigation. In [12], three quasicrystalline phases were observed under various conditions of annealing. Selected Al$_{65}$Cu$_{20}$Cr$_{13}$ and Al$_{75}$Cu$_{10}$Cr$_{15}$ compositions are the average compounds of compositions of several quasicrystalline phases obtained in [12].
2. Experimental
Elemental powders of aluminum (99.5 %), copper (99.5 %) and chromium (99.85 %) were used as the starting materials. Mechanical alloying was carried out using an AGO-2M high-energy ball mill with the water cooling. DSC-111 SETARAM setup was used for the calorimetric analysis. The annealing was conducted in the tube resistance furnace. Samples in the crucibles were placed into the quartz flask in the argon atmosphere, and the flask was loaded into the furnace.

For the element analysis of the samples, QUANTA 200 3D scanning electron microscope was used. The structure of specimens was examined using the X-ray diffraction analysis with DRON-4-07 X-ray diffractometer on monochromatized CoKα radiation. The measured spectra was processed using a special pocket of programs. The phase composition of samples and the lattice parameter were determined. The lattice parameters were calculated to the accuracy of Δa/a = 0.0015. For the multiphase samples, because of complexity of crystal structures of compounds of Al-Cu-Cr system, the results of phase analysis can be considered only as semiquantitative data. Structural data for the phase analysis was taken from papers [15 - 19]; it should be noted that for almost a half of ternary phases of this system the crystalline structure is not determined. The fraction of decagonal quasicrystalline phase was determined in the relative units, because the corundum number, which is the measure of absolute intensity of phases, is unknown for this phase. However, the comparison of the samples with each other using this calculation will be correct.

3. Results
The elemental mixtures of Al_{67}Cu_{20}Cr_{13} and Al_{75}Cu_{10}Cr_{15} compositions were milled for 0.5, 1 and 2 h. The granulometric analysis of as-milled powders showed a wide spread of the particle size: the size of small fractions was from 200 to 400 µm, whereas the size of coarse fraction particles exceeds 1000 µm. The phase composition of all as-milled mixtures is identical and represents the mixture of initial components. Figure 1 gives spectra, which are typical for these mixtures. The lattice parameters of phases did not change with the milling time and corresponded to the parameters of pure elements, i.e. no solid solutions formed.

The data of quantitative phase analysis show that different fractions of powders have nearly similar chemical and phase composition; moreover, the maximum deviations from the initial compositions do not exceed 2 at. %. Chemical analysis provided using the analytical setup of scanning electron microscope gives for the Al_{67}Cu_{20}Cr_{13} sample the composition of Al_{71}Cu_{18}Cr_{11}, no traces of other elements were observed, i.e. amount of impurities, which can be provided by the milling process (mainly iron), is less than 0.1 at. %. Such good agreement between the chemical composition of the initial and as milled powders, as well as between the phase and chemical composition of different-size fractions of as-milled powders, seems unexpected, because significant adhesion of material to the walls of vials occurs in the course of milling. The mass of the produced powder was smaller for the composition enriched in aluminum and decreased with increasing milling time.

A tendency to adhesion of powder to the wall of vial in the milling can be associated with rather high temperature in the vials. As it was mentioned above, the average temperature in this type of mill can be about 200°C and more [20]. Since the melting point of aluminum is not high (660°C), apparently, the significant adhesion of aluminum is a result of local melting and/or an increase in the plasticity with increasing temperature. The predominance of coarse particles in the as-milled mixture with high content of aluminum indicates that the weldability between the particles increases with increasing amount of aluminum. The thermal analysis of Al_{67}Cu_{20}Cr_{13} and Al_{75}Cu_{10}Cr_{15} mixtures, which had been milled for various times, was performed. The DSC curves showed no differences between the samples milled for 1 and 2 hours. This allowed us to select 1 hour of treatment as the optimal time, which is sufficient for the formation of dispersed laminar structure; the heating of the latter will lead to the required phase transformations. Samples milled for 1 h were selected for the further study. Figure 2 shows the DSC curves for these samples, temperatures of annealing for the phase analysis are indicated by arrows on this figure. Changes in the phase composition, which are calculated from the spectra, are schematically given in Fig. 2.
The chemical composition of alloys was calculated from the results of quantitative phase analysis of samples annealed at 800°C. For initial “Al₆₇Cu₂₀Cr¹₃” alloy, the final composition appeared to be Al₆₉Cu₁₇Cr₁₄, and for the “Al₇₅Cu₁₀Cr¹₅” alloy, Al₇₅Cu₉Cr₁₆. So, after the annealing, as well as after the mechanical alloying, there are no foundations to propose any noticeable deviation of the composition from the initial mixture, we can consider the samples as true ternary alloys.

Figure 2 shows that, in spite of the absence of noticeable thermal effects up to the temperature of 530°C, even at this temperature, several intermetallic compounds form in the alloys. These are binary and ternary phases. Furthermore, unreacted aluminum and, in the case of Al₆₇Cu₂₀Cr¹₃ composition, chromium remain in the sample.

The φ-Al₇₁Cu₁₈Cr₁₂ phase was identified using the experimental spectrum given in [19], where neither homogeneity range of the phase nor the crystallographic data were reported. On the other hand, in our previous work [14], based on the data obtained in [21], we constructed a bar diagram for a decagonal quasicrystalline phase of Al-Cu-Cr system, and its comparison with the experimental spectrum shows a good agreement between not only the most intense reflections, but also between the majority of weak reflections. Comparing the results of previous study with the peaks corresponding to the φ-Al₇₁Cu₁₈Cr₁₂ phase, we conclude that it is a quasicrystal with the decagonal symmetry.

Decagonal quasicrystalline phase, as it follows from Figure 2, was obtained both in Al₇₅Cu₁₀Cr₁₅ and
Al$_{67}$Cu$_{20}$Cr$_{13}$ alloys. In both cases, its fraction was maximum after the annealing at 550 – 570 °C; with further increase in the temperature, its amount decreased. In the Al$_{67}$Cu$_{14}$Cr$_{13}$ alloy, the disintegration of quasicrystal led to an increase in the fraction of nearly hexagonal $\zeta$-Al$_{72}$Cr$_{17}$Cu$_{11}$ phase. In the Al$_{67}$Cu$_{20}$Cr$_{13}$ alloy, a decrease in the fraction of quasicrystal was accompanied by an increase in the fraction of $\kappa$-Al$_{67}$Cu$_{14}$Cr$_{19}$. Thus, decagonal quasicrystal was obtained by annealing of as-milled powder for 1 hour, and its fraction was maximum for the Al$_{67}$Cu$_{20}$Cr$_{13}$ composition after the annealing at 570°C.

4. Conclusions

Alloys of the Al-Cu-Cr system were prepared by ball milling from the elemental powders. All as-milled compositions represent a mixture of pure elemental phases. The phase transformations at annealing for 1 h in the temperature range of 500 to 800 °C were investigated. It was found that the heating results in the formation of binary phases, which subsequently transform into the ternary phases. The identification of phases was performed using the stable phase diagram data given in [19]; the $\phi$-phase, whose structure was not determined in [19], was observed. Comparing the X-ray patterns of this phase with the results of earlier study [14], we conclude that it is a quasicrystal with the decagonal symmetry. Results of our study and the comparison with the equilibrium phase diagram [21] show that, in contrast to our previous knowledge, decagonal quasicrystalline phase can be stable in the Al-Cu-Cr ternary system at least at 700 °C. Further precision investigation of the $\phi$ phase and its thermodynamical stability is required to declare this fact as completely established.

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