PHASE TRANSFORMATIONS IN MECHANICALLY ALLOYED Al-Cu-Cr POWDERS

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Abstract

Mechanical alloying was used to form a decagonal phase in the Al-Cu-Cr system. Elemental powders of Al$_6_5$Cu$_2_4$Cr$_1_1$, Al$_6_7$Cu$_2_0$Cr$_1_3$, Al$_6_5$Cu$_2_4$Cr$_1_1$, Al$_6_9$Cu$_2_1$Cr$_1_0$ and Al$_7_8$Cu$_1_0$Cr$_1_2$ compositions (in at. %) were mechanically alloyed in a planetary ball mill. Annealing 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 and was present in various amounts in all investigated alloys. No icosahedral quasicrystalline phase was found in the samples. The maximum content (95 vol. %) of decagonal quasicrystalline phase was observed for Al$_6_9$Cu$_2_1$Cr$_1_0$ compound annealed at 635 °C. Further increase in the annealing temperature results in the quasicrystalline phase transformation into ψ-Al$_6_5$Cu$_2_4$Cr$_1_0$ phase, which is an approximant phase to icosahedral quasicrystal.

Introduction

Due to the particularities of crystallographic and electronic structure, the properties of quasicrystalline (QC) phases are similar to those of ceramics: they are brittle, hard, and have a low friction coefficient [1-3]. Powdered QC may be applied as fillers in different types of metal-matrix [4-6] or polymer-matrix [7,8] materials. It has been widely reported [9-14] that QC phases can be obtained by means of mechanical alloying in different systems. For instance, the Al-Cu-Fe system has attracted particular attention, because a thermodynamically stable QC phase can form in this system [14-19]. Al-Cu-Fe quasicrystalline phase was widely applied as the reinforcement [7-9,20,21] to obtain the composites that combine high mechanical and tribological properties; however, the corrosion resistance of QC in Al-Cu-Fe system is not high [22]. This is a reason to search for the QC phases in a close system, for example, in the Al-Cu-Cr one.

The quasicrystalline phases in this system can be formed by melt quenching; in some cases, quasicrystals are formed by annealing of quenched alloys [23-27]. No data about the thermodynamic stability of the QC phases in this system are available. It is known that both icosahedral [23-26] and decagonal [26-27] crystalline phases can be obtained in the Al-Cu-Cr system. As was found in [26], the decagonal phase is formed in the alloys, which are close to Al$_{7_5}$Cu$_{1_0}$Cr$_{1_3}$ in the chemical composition, whereas the icosahedral phase is formed in the Al$_{6_9}$Cu$_{2_1}$Cr$_{1_0}$ alloy, i.e., at the Al and Cu concentrations typical of the icosahedral phase in the Al-Cu-Fe system [15-19]. On the other hand, the formation of an icosahedral phase was observed in [27] for the Al$_{7_5}$Cu$_{1_6}$Cr$_{1_2}$ composition, i.e., the phase formation in this system depends not only on the chemical composition, but also on the method of alloy preparation. The phase formation in the Al-Cu-Cr system by mechanical alloying was studied for the Al$_{6_5}$Cu$_{2_4}$Cr$_{1_1}$ [13] and Al$_{6_9}$Cu$_{2_1}$Cr$_{1_0}$ [28] compositions. It was found that the mechanical alloying did not lead to the formation of any quasicrystalline phase, whereas the annealing of the mechanically alloyed composition resulted in the formation of a single-phase alloy with icosahedral [13] or decagonal [28] quasicrystalline structure. Here we use a combination of mechanical alloying and subsequent annealing to obtain the quasicrystalline phases in the Al-Cu-Cr powders of various element contents.

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 under argon atmosphere, and the flask was loaded into the furnace.

The structure of specimens was examined using the X-ray diffraction analysis. The tracing of diffraction spectra was carried out using a DRON-4-07 X-ray diffractometer with monochromatized CoK$_\alpha$ emission. To calculate the obtained spectra, a special pocket of programs was used. The phase composition of samples and the lattice parameter were determined. The lattice parameters were calculated to the accuracy of $aa/\alpha = 0.0015$. For the multiphase samples, because of complexity of crystal structures of compounds of Al-Cu-Cr system, the data of quantitative analysis can be considered only as semiquantitative. 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. For the calculations, the corundum number was taken as the equal to one; this can differ by several 10 times from the true value. Therefore, the true amount of decagonal quasicrystalline phase can differ significantly from the calculated one. However, the comparison of the samples with each other using this calculation will be correct.

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Results and Discussion

Investigation was carried out for five alloys: Al_{67}Cu_{20}Cr_{13}, Al_{75}Cu_{10}Cr_{15}, Al_{65}Cu_{24}Cr_{11}, Al_{69}Cu_{21}Cr_{10}, Al_{78}Cu_{10}Cr_{12}; the chemical composition is given in at. %. To choose the compositions we based either on the data on the composition of quasicrystalline phases in the related systems (for example, in the system Al-Cu-Fe, the icosahedral quasicrystalline phase forms at the composition of Al_{65}Cu_{23}Fe_{12}), or on the works, devoted to the system under investigation [26]. The mechanical alloying of Al_{67}Cu_{20}Cr_{13} and Al_{75}Cu_{10}Cr_{15} elemental mixtures was performed for 1 h. It should be noted that due to the adhesion of milled powder to balls and the wall of vial of planetary ball mill, the produced amount of powder was of from 20 to 80 % of the loading powder amount, depending on the sample composition. To enhance the yield of mechanical alloying, the Al_{65}Cu_{24}Cr_{11}, Al_{69}Cu_{21}Cr_{10} and Al_{78}Cu_{10}Cr_{12} mixtures were treated with the additions of surfactant (ethyl alcohol), similarly to [29-31]. These three compositions underwent 1 hour of working in the ball mill with the addition 0.2 ml of ethyl alcohol. The phase composition of all as-milled mixtures was identical and represents the mixture of initial components only, the lattice parameters of these phases did not change with milling time and were equal to the parameters of pure elements.

Figure 1 gives the differential scanning calorimetry (DSC) curves of the as-milled samples.

![DSC curves of the as-milled Al-Cu-Fe powders](image)

As shown in Fig. 1, no significant effects were observed at the temperatures below 500 °C. In the temperature range of 530 to 600 °C, a broad exothermal effect was observed. Based on the DSC curve shapes, the presence of the endothermal effects in the same temperature range for some samples may be supposed. Comparing these DSC curves with those obtained earlier for the as-milled Al_{67}Cu_{22}Cr_{11} powder [19], we can see that the temperature range of the most intensive thermal effects for the Al-Cu-Cr system lies by 100-150 °C higher than that for Al-Cu-Fe system. The shape of the peaks was found to be broad for both systems. As it was indicated in [19], such broad peak corresponds to the simultaneous occurrence of more than one phase transformation, that is why it is difficult to relate this peak to a specific phase transformation. In [28], the Al_{69}Cu_{22}Cr_{11} decagonal quasicrystalline phase was formed by annealing of together milled Al and Cu_{67}Cr_{33} powder, which has been previously mechanically. The shape of DSC curve after the short-time milling (10 min) [28] was similar to that described in [19] for Al-Cu-Fe system, whereas an increase in the milling time to 30 min resulted in the appearance of the noticeable exothermal peak at 570-600 °C, which was related to the formation of the single-phase decagonal quasicrystalline structure [28]. In our experiments, the most marked pronounced exothermal maximum in this temperature range was found for the Al_{67}Cu_{22}Cr_{11} composition. The presence of the exothermal maximum at 570-600 °C was observed also for two samples, which are close to this in chemical composition; whereas for the samples enriched in Al and, correspondingly, depleted of Cu, no effects were observed in this temperature range (Fig. 1).

Based on the shape of the DSC curves, the X-ray analysis of phase evolution at heating was performed in the annealing temperatures range of 500 to 800 °C. Figure 2 shows the evolution of X-ray peaks with increasing temperature for Al_{67}Cu_{22}Cr_{11} sample. It is seen that, after heating to 530 °C, the alloy consists of two ternary phases and one binary phase, no pure elemental phases were observed in the sample.

Figure 2. X-ray diffraction patterns of the Al_{69}Cu_{21}Cr_{10} powders annealed at indicated temperatures for 1 h

Figure 3 shows the evolution of phase composition, which was calculated from the X-ray data, in the above-mentioned temperature range for all samples studied. Structural data for the ζ-Al_{72}Cr_{17}Cu_{11} and κ-Al_{67}Cu_{22}Cr_{11} phases are borrowed from the paper [32]. The chemical composition and the lattice parameter for the κ-Al_{67}Cu_{22}Cr_{11} phase are taken from [33].
Figure 3. Phase composition evolution of Al$_{75}$Cu$_{10}$Cr$_{15}$ (a) Al$_{67}$Cu$_{20}$Cr$_{13}$ (b), Al$_{65}$Cu$_{24}$Cr$_{11}$ (c), Al$_{69}$Cu$_{21}$Cr$_{10}$ (d) and Al$_{78}$Cu$_{10}$Cr$_{12}$ (e) mixtures with increase in the annealing temperature. DQC - decagonal quasicrystalline phase.

DQC - decagonal quasicrystalline phase, see text
The \( \varphi \)-Al\(_{71}\)Cu\(_{18}\)Cr\(_{12} \) phase was identified using the experimental spectrum, given in the [33], where neither homogeneity range of the phase nor the crystallographic data were reported. On the other hand, in our previous work [28], based on the data obtained in [34], we constructed a bar diagram for a decagonal quasicrystalline phase of this system, and its comparison with the experimental spectrum shows good agreement between not only the most intense reflections, but also between the majority of weak reflections. Comparing the results of the previous study with the peaks corresponding to the \( \varphi \)-Al\(_{71}\)Cu\(_{18}\)Cr\(_{12} \) phase, we conclude that it is a quasicrystal with the decagonal symmetry.

Figure 3 shows that, in spite of the absence of noticeable thermal effects up to temperature of 530 °C, even at this temperature several intermetallic compounds forms in the alloys. This is a number of the binary (CuAl\(_2\), CuAl, Cr\(_7\)Al\(_{45}\)) and ternary (decagonal quasicrystal, hexagonal \( \zeta \)-Al\(_{2}\)Cr\(_{15}\)-Cu\(_{11}\) and cubic \( \lambda \)-Al\(_{64}\)Cu\(_{5}\)(Cr\(_3\)) phases. In addition, unreacting aluminum and, in the case of Al\(_{64}\)Cu\(_{32}\)Cr\(_{15}\) composition, chromium remain in the sample. Decagonal quasicrystalline phase, as it follows from Fig. 3, was obtained in all investigated samples. For Al\(_{65}\)Cu\(_{25}\)Cr\(_{15}\) and Al\(_{64}\)Cu\(_{32}\)Cr\(_{15}\) alloys its fraction was maximum after the annealing at 550 - 570 °C, at higher temperatures its quantity decreased. In the Al\(_{72}\)Cu\(_{32}\)Cr\(_{15}\) alloy, a decrease in the fraction of quasicrystalline phase led to an increase in the fraction of hexagonal \( \zeta \)-Al\(_{2}\)Cr\(_{15}\)-Cu\(_{11}\) phase. In the Al\(_{64}\)Cu\(_{32}\)Cr\(_{15}\) alloy, a decrease of the fraction of quasicrystalline phase was accompanied by an increase in the portion of the \( \kappa \)-Al\(_{64}\)Cu\(_{32}\)Cr\(_{19}\) phase, which has complex cubic cell with 412 atoms.

Examining the phase transformations in the Al\(_{66}\)Cu\(_{25}\)Cr\(_{10}\) alloy, we notice that, as well as for two above alloys, ternary decagonal quasicrystalline phase forms, and its amount grows up to the temperature of 635 °C, at this temperature alloy is nearly single-phase. A fraction of decagonal quasi-crystalline phase slightly decrease at higher temperatures due to the formation of the phase, named as \( \varphi \) in [33], whose structure in this work was not indicated. However, the authors of [33] assume that this phase has cubic structure and they give its lattice parameter. The comparison of spectrum [33] with the spectrum of known Al\(_{5}\)Mn\(_4\) (cP138) phase, which is an approximant phase to icosahedral quasicrystal, allows to propose that the \( \psi \)-Al\(_{65}\)Cu\(_{25}\)Cr\(_{10}\) phase relates precisely to this structural type. However, it was impossible to describe its structure accurately (i.e. to indicate the coordinates of atoms and probability of filling of the regular systems of points) because of small content of this phase in the alloy. Thus, in the Al\(_{68}\)Cu\(_{25}\)Cr\(_{10}\) alloy by annealing at 635 °C nearly single-phase decagonal quasicrystal structure was obtained, which partially passed into the approximant of icosahedral quasicrystal, namely \( \psi \)-Al\(_{65}\)Cu\(_{25}\)Cr\(_{10}\) phase at higher temperatures.

In Al\(_{66}\)Cu\(_{25}\)Cr\(_{11}\) alloy, the maximum quantity of decagonal quasicrystal was obtained after the annealing at 625 °C, although its fraction this case is lower than in the Al\(_{68}\)Cu\(_{25}\)Cr\(_{10}\) alloy. However, the heating up to 770 °C led to the formation of \( \psi \)-Al\(_{65}\)Cu\(_{25}\)Cr\(_{15}\) phase. The Al\(_{68}\)Cu\(_{25}\)Cr\(_{15}\) alloy contained the largest amount of aluminum. Possibly, therefore after low-temperature annealing at 525 °C a small quantity of unreacted aluminum was observed. The phase composition in this alloy almost did not change with annealing. The decagonal quasicrystalline phase, which composition in [33] was indicated as Al\(_{68}\)Cu\(_{25}\)Cr\(_{15}\), CuAl\(_2\) phase and a small amount of non-identified phase, which, judging from the phase diagram, must be the binary phase of Al-Cr system, were observed in the alloy. CuAl\(_2\) phase is equilibrium in this alloy. The fraction of decagonal quasicrystalline phase in the Al\(_{67}\)Cu\(_{21}\)Cr\(_{11}\) alloy virtually does not change with the temperature and is smaller than in the Al\(_{68}\)Cu\(_{25}\)Cr\(_{10}\) alloy after the annealing at 635 °C. However, since Al\(_{67}\)Cu\(_{21}\)Cr\(_{12}\) alloy contains very high amount of decagonal quasicrystalline phase, we can to propose that its homogeneity range is actually very wide.

We will explain the presence of a large number of phases, that were was observed for some samples at temperatures 500-550 °C. The homogenization of composition by diffusion cannot be completed in an hour of annealing of laminar composite, which forms by mechanical alloying of metals [35,36]; therefore we observe a several phases, which refer to different local compositions of laminar composite. After the milling, because of high content of Al, regions, in which aluminum are in contact with chromium or copper prevail. Furthermore, chromium - copper system has positive mixing energy and these elements can not form intermetallic compounds or solid solutions. Therefore, as the reaction proceeds at the interfaces, first the binary phases of Cu-Al and Cr-Al systems form; similar consequence of phase transformations at heating was earlier observed for the Al-Cu-Fe system [19]. In Al\(_{65}\)Cu\(_{25}\)Cr\(_{10}\) alloy with relatively high content of copper, in addition to the intermetallic compound CuAl\(_2\), CuAl phase forms as indication of the local composition of as-milled sample. Additionally, we have to note that eutectic transformation L → Al+CuAl\(_2\) exists in the aluminum side of Cu-Al system at 550 °C. Probably, the low-temperature endothermic peaks in DSC curves correspond to this transformation. Cubic \( \lambda \)-Al\(_{64}\)Cu\(_{5}\)(Cr\(_3\)) phase actually is nearly binary, since the chromium content in it is extremely small; therefore it is possible to explain its appearance at low annealing temperatures by the dissolution of small amount of chromium in the eutectic Cu-Al liquid. For other ternary phases, the situation is less clear. Formation of complex hexagonal \( \zeta \)-Al\(_{2}\)Cr\(_{15}\)-Cu\(_{11}\) phase at the low-temperature annealing of Al\(_{68}\)Cu\(_{25}\)Cr\(_{15}\) is possible, since composition of this phase is close to the total composition of the alloy, and some regions of the mixture can be close to this phase in composition even after 1 hour of ball-milling. An increase in the fraction of this phase with increasing temperature confirms this supposition. The formation of decagonal quasicrystalline phase can be explained by the same way. Furthermore, one additional possibility exist, namely, quasicrystal can easily form, if it has a wide homogeneity range. In this case, the gradual dissolution of chromium in the binary intermetallic compounds of Cu- Al system surely will lead to the formation of \( \zeta \)-Al\(_{2}\)Cr\(_{15}\)-Cu\(_{11}\) phase, which lies “on the way” to the total composition of alloy.

**Conclusions**

Alloys of the compositions Al\(_{66}\)Cu\(_{25}\)Cr\(_{13}\), Al\(_{68}\)Cu\(_{25}\)Cr\(_{15}\), Al\(_{68}\)Cu\(_{25}\)Cr\(_{17}\), Al\(_{68}\)Cu\(_{25}\)Cr\(_{19}\), and Al\(_{68}\)Cu\(_{25}\)Cr\(_{21}\) were prepared by ball milling from the elemental powders. All the as-milled compositions represent a mixture of pure elemental phases. The phase transformations at annealing for 1 h in the temperature range of 500-800 °C were investigated. It was observed that the heating results in the formation of binary phases, which subsequently transform into the ternary phases. Identification of phases was performed using the stable phase diagram data given in [33]; the \( \varphi \) phase, which structure was not determined in [33],
was observed. Comparing the X-ray patterns of this phase with the results of earlier study [28], we conclude that it is a quasicrystal with the decagonal symmetry. Results of our study and the comparison with the equilibrium phase diagram [33] show that, in contrast to our previous knowledge, decagonal quasicrystalline phase may be stable in the Al-Cu-Cr ternary system, at least at 700 °C. Further precision investigation both of this phase and its stability is required to declare this fact as completely established.

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References

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