Mechanical Alloying of $\text{Al}_{73}\text{Cu}_{11}\text{Cr}_{16}$ Alloy from Ion Irradiated Powders

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$\text{Al}_{73}\text{Cu}_{11}\text{Cr}_{16}$ alloys were prepared by mechanical alloying of the irradiated by Ar^+ ions elemental powders. Evolution of alloy structure at ball milling, as well as during the further annealing, was investigated using X-ray diffraction and differential scanning calorimetry. It was shown that ball milling leads to the Cu dissolution in Al and Cr and to the formation of Al_2Cu intermetallic phase. An increase of the milling duration leads to an increase of the Al_2Cu phase content in the samples. Ion irradiation of initial elemental powders results in an increase of their interaction rate at milling. In the case of irradiated powders using as initial materials, a content of Al_2Cu phase after milling is higher than in the case of using non-irradiated elemental powders. No effect of irradiation of initial elemental powders on the phase transformation at heating was observed. The annealing results in the decomposition of Al- and Cr-based supersaturated solid solutions. An increase in the Al_2Cu phase content at heating was observed only in the samples, which were milled for 4 h. In the samples milled for 14 h, nearly no increase in Al_2Cu phase content at heating was observed. Heating up to 500–600 °C results in the single-phase decagonal quasicrystalline phase formation for all of the studied samples.

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1. Introduction

The peculiarities of quasicrystals, such as a combination of high hardness with high antifriction properties, allow us to consider them as promising materials for industrial application [1–3]. However, there are some obstacles to the widespread use of quasicrystals as the structural materials. Quasicrystals usually have a narrow (no more than 1–2 at.% for each component) concentration range of existence, and complex process of crystallization from the melt, which hampers the use of classic metallurgical techniques for quasicrystal formation. To overcome the above-mentioned difficulties, alternative methods of alloys preparation, such as mechanical alloying, can be used. It is known that mechanical alloying allows one to extend the concentration range of existence of phases [4, 5]. This is of particular importance in the case of intermetallic compounds, including quasicrystals. Moreover, at mechanical alloying, all reactions proceed in the solid state. This helps to overcome the problems, which are associated with complex behavior of solidification during conventional casting.

The formation of quasicrystals both directly by mechanical alloying and by heating of mechanically alloyed powders has been widely reported [6–16]. The quasicrystals are considered as promising fillers for polymer [17–19] and metal [19–22] matrixes to design wear-resistive antifriction composites. The quasicrystals of most studied Al-Cu-Fe system, however, possess some drawbacks, such as a high chemical activity, and, correspondingly, a low corrosion resistance [23, 24]. That is why the investigation of the quasicrystals of the relative systems, such as Al-Cu-Cr, may be of particular interest.

In our previous papers, the phase transformations in Al-Cu-Cr system at mechanical alloying and subsequent heating were studied. A possibility of decagonal quasicrystalline phase formation by mechanical alloying and subsequent heating was shown [25, 26]. The phase transformations at heating of mechanically alloyed powders were studied in detail in [27, 28]. Here, we investigate an effect of ion irradiation of initial elemental powders on the mechanical alloying of $\text{Al}_{73}\text{Cu}_{11}\text{Cr}_{16}$ powder.

2. Experimental details

The elemental powders of Al (98.0%, powder size $\approx 250 \mu\text{m}$), Cu (99.5%, $\approx 30\text{--}50 \mu\text{m}$) and Cr (98.5%, $\approx 30\text{--}50 \mu\text{m}$) were used as the start materials. The ion irradiation of elemental powders was carried out by continuous Ar^+ gas ion beams according to technique described in [29]. The tape ion beam (20 by 100 mm² in cross-section) was cut from Ar^+ gas ion beams of round cross-section using a collimator. Stainless steel tray with the powder was moved under the ion beam with a velocity of 1 cm/s. The thickness of the irradiated powder was close to an average size of its particles. The irradiation parameters were as follows: the ion energy was 20 keV, the ion current density was 150 $\mu\text{A}/\text{cm}^2$; the number of passes under the beam was 50 times, which corresponded to the irradiation dose of $6 \times 10^{16} \text{ cm}^{-2}$; and the maximum temperature of heating by ion beam was no more than 100 °C.

Mechanical alloying was carried out in the Ar atmosphere using an AGO-2M ball mill at a rotational frequency of 620 rpm and centrifugal acceleration of

210 m/s². The duration of milling was 4, 8, and 14 h. The powder-to-ball ratio was 1:10; 200 g of balls (ball bearing steel) were charged in each vial (hardened steel) with a filling ratio of 35–40%. The 0.2 ml of ethyl alcohol served as a process control agent preventing adhesion of mixtures on the work surfaces.

The differential scanning calorimetry (DSC) curves were measured using a SETARAM LABSYS by heating of the powder samples in Al containers with a rate of 20 K/min in argon atmosphere; the same setup was used for annealing of samples. The X-ray diffraction (XRD) data were obtained with Co K_α radiation and treated using the Rietveld algorithm [30]. Error in lattice constant estimation was of ± 0.0001 nm. The QC volume fraction was evaluated by measuring the absolute intensity of almost single-phase quasicrystal obtained in [28] against the corundum reference.

3. Results and discussion

Figure 1 shows the X-ray diffractograms of powders, which were obtained by mechanical alloying from the irradiated elemental powders. It is seen that the interaction between aluminum and copper with Al₂Cu phase formation proceeds at mechanical alloying, as well as it was observed at mechanical alloying of the same composition from non-irradiated elemental powders [28]. No XRD patterns related to pure Cu phase were observed after the milling.

Fig. 1. X-ray diffraction patterns of samples prepared from irradiated powders by milling for 4 (a), 8 (b) and 14 (c) h.

Figure 2 shows the dependences of Al₂Cu phase content on the milling time for the samples, which were obtained from the irradiated and non-irradiated elemental powders. An increase in the milling time leads to an increase in the Al₂Cu phase content; for samples, which were mechanically alloyed from irradiated powders, the Al₂Cu phase content was higher than for those mechanically alloyed from the non-irradiated powders.

Figure 3 shows the DSC curves for the mechanically alloyed samples. The curves are close in the shape to those obtained in [28] for the samples, which were mechanically

Fig. 2. Dependences of Al₂Cu phase content on milling time for samples prepared from non-irradiated (1) and irradiated (2) elemental powders.

alloyed under similar conditions from the non-irradiated elemental powders. Large exothermal peak was observed in the temperature range of 370–430 °C. This peak corresponds to the solid state phase transformation in samples. Increase in milling time results in the decrease in the temperature of this peak, it means that for long-time milled samples phase transformations at heating proceeds at lower temperatures. Besides of this large peak, some small exothermal effects also occur in the DSC curves, nature of these small peaks is not clear.

Fig. 3. DSC curves for prepared from irradiated powders by milling for 4 (a), 8 (b) and 14 (c) h.

The endothermal effects at the temperatures above 800 °C correspond to the decomposition of decagonal quasicrystalline phase. The most intensive transformation at heating started at 900 °C (for the samples milled for 8 h) and at 920 °C (for the samples milled for 14 h); probably, these effects are associated with the peritectic transformation.

Figure 4 shows the typical evolution of XRD patterns of the samples, which were mechanically alloyed from the irradiated powders, after annealing for 1 h at various temperatures. It is seen that the phase transformation proceeds intensively up to a temperature of 550 °C, whereas in the temperature range of 550–900 °C, no noticeable changes in the XRD pattern shape were observed.

Fig. 4. Temperature evolution of X-ray diffraction patterns of samples prepared from irradiated powders by milling for 14 h. Peaks related to the decagonal quasicrystalline phase are indicated by arrows.

Fig. 5. Dependences of Al phase content on annealing temperature for samples prepared from non-irradiated (1 and 3) and irradiated (2 and 4) elemental powders by milling for 4 (1 and 2) and 14 (3 and 4) h.

Figure 5 shows the dependences of the content of the phase with fcc lattice (as it is shown below, it is the Al-based solid solution) on the annealing temperature. The annealing leads to a decrease in the Al-based phase content; for the samples, which were milled for a longer time, an amount of this phase decreases more intensive, and for such samples this phase disappears at lower temperatures than for the samples with lower milling duration.

Fig. 6. Dependences of Cr phase content on annealing temperature for samples prepared from non-irradiated (1 and 3) and irradiated (2 and 4) elemental powders by milling for 4 (1 and 2) and 14 (3 and 4) h.

Similar dependences (Fig. 6) were observed for the phase with bcc lattice, which is a Cr-based solid solution. It should be noted that the Cr-based phase is more stable than the Al-based phase: a certain amount of Cr-based phase was kept up to rather high temperature.

Figure 7 shows the dependences of the content of Al_2Cu phase on the annealing temperature. For the samples, which were mechanically alloyed for 4 h, a significant increase in the Al_2Cu phase content on the initial stage of annealing was observed. For the samples, which were milled for 14 h, no significant increase in this phase content at annealing was observed, which can be associated with a high-rate formation of decagonal quasicrystalline phase at annealing of the samples, which were milled for a longer time.

Fig. 7. Dependences of Al_2Cu phase content on annealing temperature for samples prepared from non-irradiated (1 and 3) and irradiated (2 and 4) elemental powders by milling for 4 (1 and 2) and 14 (3 and 4) h.

A significant (more than twice) increase in the Al_2Cu phase content at annealing, which was observed for the samples milled for 4 h, was unexpected, because no residual copper was found in the mechanically alloyed samples by XRD. According to the equilibrium phase diagram [31], the Al_2Cu phase has a narrow concentration range of existence; an addition of chromium to the Al-Cu system did not noticeably extend this range [32]. According to [33], the lattice constants of Al_2Cu phase increase with increasing aluminium content in the phase from $a = 0.60613$ nm and $c = 0.48724$ nm at the aluminium content of 66.4 at.% to $a = 0.60718$ nm and $c = 0.48802$ nm at the aluminium content of 68.0 at.%. In our case, Al_2Cu phase lattice constants for as-milled samples are $a = 0.6067$ nm and $c = 0.4886$ nm; these values were equal for samples, which were prepared from irradiated and non-irradiated elemental powders. After annealing at 430 °C, the lattice constants were $a = 0.6061$ nm and $c = 0.4879$ nm both for samples, which were prepared from irradiated and non-irradiated elemental powders. It is seen that the Al_2Cu phase lattice constants decrease at annealing. According to [33], this corresponds to a decrease of the aluminium content in the phase. Moreover, the changes in the lattice constants at annealing correspond to the deviation of chemical composition of Al_2Cu

phase within the concentration range of their existence according to the equilibrium phase diagram [31, 33]. The results of lattice constant values analysis exclude a possibility to increase the Al_2Cu phase content at heating by the dissolution of aluminium in this phase.

An increase in the Al_2Cu phase content at the annealing can be explained by the dissolution of copper in chromium and aluminium at mechanical alloying. The equilibrium solubility of copper in chromium and aluminium is insignificant; however, it is known that mechanical alloying can result in the formation of significantly supersaturated solid solutions [34]. The highest solubility of copper in aluminium at mechanical alloying is of 5.6 at.% [34]; and the highest solubility of copper in chromium at mechanical alloying is up to 30 at.% [35].

Figure 8 shows the dependences of lattice constants of Al- and Cr-based phases for as-milled samples on the milling time. These values were nearly the same for the samples, which were obtained from the irradiated and non-irradiated elemental powders. The lattice constant of Al-based phase decreased with increasing milling time, whereas the lattice constant of Cr-based phase increased with increasing milling time. According to [35, 36], such changes in the lattice constants correspond to an increase in copper content of Al and Cr.

Fig. 8. Dependences of Al (1) and Cr (2) phases lattice constant for samples prepared from irradiated elemental powders, on milling time.

The solubility of copper in Al and Cr can be estimated from the lattice constant. For the samples milled for 4 h, the lattice constant of Al-based phase is 0.4029 nm and the lattice constant of Cr-based phase is 0.2888 nm. These values are the same for the samples obtained from the irradiated and non-irradiated elemental powders. Using the linear dependence of lattice constant of Al-based solid solution on the copper content [36], (assuming that no other impurities are present in the solution), in our case the solubility of copper in Al was estimated at 2.5 at.%. Similarly, comparing the Cr-based phase lattice constant with the data obtained in [35], we can propose that the Cr-based phase contains up to 25 at.% copper. Comparing these data with the results of quantitative phase analysis, we calculate that the Al-based solid

solution contains about 15 at.% of the total amount of copper in the sample. Similarly, Cr-based solid solution contains of about 40 at.% of the total amount of copper in the sample. Thus, about 55% of copper atoms can locate in the Al- and Cr-based solid solutions in the samples milled for 4 h. Such amount is enough to provide a significant increase in Al_2Cu phase content at annealing (Fig. 7a).

Our conclusions can be supported by the fact that annealing up to 430 °C results in an increase of Al-based phase lattice constant to 0.4053 nm, whereas Cr-based phase lattice constant decreases to 0.2882 nm. The lattice constants of Al- and Cr-based solid solutions for the annealed samples are close to the values for pure metals (0.4050 and 0.2885 nm, respectively [37]). This supports our conclusion that annealing leads to the decomposition of solid solutions with the transition of copper atoms to the Al_2Cu intermetallic phase.

From the temperature dependences of Al_2Cu phase content (Fig. 7), it is seen that the effect of ion irradiation is compensated by the heating of samples. A comparison of curves 1 and 2 (Fig. 7) shows that, for as-milled samples, an amount of Al_2Cu phase is higher for the samples, which were prepared from the irradiated elemental powders (see also Fig. 2), whereas, at heating, a difference in the Al_2Cu phase content between the samples obtained from irradiated and non-irradiated powders gradually decreases and, then, vanishes.

The absence of irradiation effect on the phase transformation at heating can be confirmed also by the temperature dependences of the decagonal quasicrystalline phase content in samples (Fig. 9). The dependences for the samples, which were prepared from the irradiated and non-irradiated powders, almost coincide. The rate of single-phase quasicrystalline structure formation depends only on the mechanical alloying duration; an increase in the milling time leads to a decrease in the temperatures of both quasicrystalline phase formation and completion of single-phase quasicrystalline structure formation.

Fig. 9. Dependences of QC phase content on annealing temperature for samples prepared from non-irradiated (2 and 4) elemental powders by milling for 4 (1 and 2) and 14 (3 and 4) h.

4. Conclusions

The formation of $\text{Al}_{73}\text{Cu}_{11}\text{Cr}_{16}$ single-phase decagonal quasicrystalline alloy by mechanical alloying with subsequent annealing was investigated. It was shown that both solution of copper in aluminium and chromium and Al_2Cu intermetallic phase formation proceed during ball milling. An increase in the milling time leads to an increase of Al_2Cu content in the as-milled samples. The ion irradiation of initial elemental leads to an increase in the component interaction rate at milling; the content of Al_2Cu is slightly higher in samples, which were obtained from the irradiated powders. No effect of the irradiation on the phase transformations at heating was observed. An increase in the milling time leads to a decrease in the temperatures of both quasicrystalline phase formation and completion of single-phase quasicrystalline structure formation. The annealing at the temperatures of 500–600 °C leads to the formation of completely single-phase quasicrystalline structure.

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References

- [1] D.J. Srodelet, J.M. Dubois, *MRS Bull.* **22**, 34 (1997).
- [2] J.E. Shield, M.J. Kramer, R.W. McCallum, *J. Mater. Res.* **8**, 1199 (1993).
- [3] A. Inoue, H. Kimura, *Nanostruct. Mater.* **11**, 221 (1999).
- [4] N.S. Cohen, O.A. Pankhurst, L.F. Barquin, *J. Phys. Condens. Matter.* **11**, 8839 (1999).
- [5] V.V. Tcherdyntsev, S.D. Kaloshkin, I.A. Tomilin, E.V. Shelekhov, Yu.V. Baldokhin, *Nanostruct. Mater.* **12**, 139 (1999).
- [6] E.Yu. Ivanov, I.G. Konstanchuk, B.D. Bokhonov, V.V. Boldyrev, *React. Solids* **7**, 167 (1989).
- [7] J. Eckert, L. Schultz, K. Urban, *Mater. Sci. Eng. A* **133**, 393 (1991).
- [8] J. Eckert, L. Schultz, K. Urban, *Acta Metall. Mater.* **39**, 1497 (1991).
- [9] N. Asahi, *Mater. Sci. Eng. A* **226–228**, 69 (1997).
- [10] F. Schurak, J. Eckert, L. Schultz, *Nanostruct. Mater.* **12**, 107 (1999).
- [11] V. Srivinas, P. Barua, B.S. Murty, *Mater. Sci. Eng. A* **294–296**, 65 (2000).
- [12] A.I. Salimon, A.M. Korsunsky, E.V. Shelekhov, T.A. Sviridova, *Mater. Sci. Forum* **294–296**, 676 (2000).
- [13] A.I. Salimon, A.M. Korsunsky, S.D. Kaloshkin, V.V. Tcherdyntsev, E.V. Shelekhov, T.A. Sviridova, *Mater. Sci. Forum* **321–324**, 137 (2000).
- [14] A.M. Korsunsky, E.V. Shelekhov, T.A. Sviridova, S.D. Kaloshkin, V.V. Tcherdyntsev, Yu.V. Baldokhin, *Acta Mater.* **49**, 1821 (2001).
- [15] S.D. Kaloshkin, V.V. Tcherdyntsev, A.I. Salimon, I.A. Tomilin, T. Spataru, G. Principi, *Hyperfine Interact.* **139/140**, 399 (2002).
- [16] V.V. Tcherdyntsev, S.D. Kaloshkin, A.I. Salimon, I.A. Tomilin, A.M. Korsunsky, *J. Non-Cryst. Solids* **312–314**, 399 (2002).
- [17] P.D. Bloom, K.G. Baikerikar, J.U. Otaigbe, V.V. Sheares, *Mater. Sci. Eng. A* **294–296**, 156 (1997).
- [18] B.C. Anderson, P.D. Bloom, K.G. Baikerikar, V.V. Sheares, S.K. Mallapragada, *Biomaterials* **23**, 1761 (2002).
- [19] S.D. Kaloshkin, V.V. Tcherdyntsev, V.D. Danilov, *Cryst. Rep.* **52**, 953 (2007).
- [20] F. Ali, S. Scudino, M.S. Anwar, R.N. Shahid, V.C. Srivastava, V. Uhlenwinkel, M. Stoica, G. Vaughan, J. Eckert, *J. Alloys Comp.* **607**, 274, (2014).
- [21] S.D. Kim, D.S. Ko, W.K. Jang, K.S. Shin, Y.W. Kim, *Mater. Sci. Eng. A* **528**, 4845 (2011).
- [22] S.D. Kaloshkin, V.V. Tcherdyntsev, A.I. Laptev, A.A. Stepashkin, E.A. Afonina, A.L. Pomadchik, V.I. Bugakov, *J. Mater. Sci.* **39**, 5399 (2004).
- [23] E. Huttunen-Saarivirta, *J. Alloys Comp.* **363**, 150 (2004).
- [24] A. Rüdiger, U. Köster, *Mater. Sci. Eng. A* **294–296**, 890 (2000).
- [25] V.V. Cherdyntsev, E.A. Leonova, S.D. Kaloshkin, *Phys. Met. Metallogr.* **95**, 478 (2003).
- [26] V.V. Tcherdyntsev, T.A. Sviridova, A.P. Shevchukov, S.D. Kaloshkin, *Z. Kristallogr.* **223**, 751 (2008).
- [27] T.A. Sviridova, A.P. Shevchukov, E.V. Shelekhov, D.L. Diakonov, V.V. Tcherdyntsev, S.D. Kaloshkin, *J. Alloys Comp.* **509**, S299 (2011).
- [28] A.P. Shevchukov, T.A. Sviridova, S.D. Kaloshkin, V.V. Tcherdyntsev, M.V. Gorshenkov, M.N. Churyukanova, D. Zhang, Z. Li, *J. Alloys Comp.* **586**, S391 (2014).
- [29] N.V. Gavrilov, S.P. Nikulin, G.V. Radkovskii, *Instrum. Exp. Tech.* **39**, 81 (1996).
- [30] E.V. Shelekhov, T.A. Sviridova, *Met. Sci. Heat Treatm.* **42**, 309 (2000).
- [31] *Binary Alloys Phase Diagrams*, Ed. T.B. Massalski, Am. Soc. Met., 1987.
- [32] R.Z. Chen, C.J. Lin, D.X. Li, J.X. Zheng, *Acta Phys. Sin.* **30**, 555 (1981).
- [33] N. Ponweiser, C.L. Lengauer, K.W. Richter, *Intermetallics* **19**, 1737 (2011).
- [34] C. Suryanarayana, *Prog. Mater. Sci.* **46**, 1 (2001).
- [35] V.V. Cherdyntsev, S.D. Kaloshkin, V.N. Serdyukov, I.A. Tomilin, E.V. Shelekhov, *Phys. Met. Metallogr.* **97**, 392 (2004).
- [36] I. Lichioiu, I. Peter, B. Varga, M. Rosso, *J. Mater. Sci. Tech.* **30**, 294 (2014).
- [37] L.I. Mirkin, *Handbook of X-ray Analysis of Polycrystalline Materials*, Consultants Bureau, New York 1964.