

Synthesis of a Decagonal Phase in the Al–Cu–Fe–Cr System by Mechanical Alloying

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Received July 2, 2015

Abstract—Quasicrystalline Al–Cu–Fe–Cr alloys have been prepared by mechanical activation. The morphology of powder particles has been investigated after thermomechanical processing under various conditions. We have identified the sequence of phase transformations in the quaternary alloys in the stability region of quasicrystalline phases and optimized conditions for obtaining a maximum fraction of a decagonal state in powder materials.

Keywords: mechanical activation, quasicrystalline decagonal and icosahedral phases, heat treatment

DOI: 10.1134/S0020168516020023

INTRODUCTION

The icosahedral and decagonal phases in the Al–Cu–Fe and Al–Cu–Cr systems have been the subject of extensive studies [1–3]. The Al–Cu–Fe system has been shown to contain a stable icosahedral phase [4, 5], whereas the chromium system contains both icosahedral and decagonal phases [6, 7]. At the same time, there is insufficient consistent data on phase equilibria and transformations in the Al–Cu–Fe–Cr system. Daniels et al. [8] and Dong et al. [9] investigated cast alloys of the quaternary system. In fact, processes in mechanically activated multicomponent materials have not yet been studied in detail. Research interest in such materials is aroused by the fact that the composition Al₆₅Cu₂₅Fe₅Cr₅ is close to the thermodynamically stable composition Al₆₄Cu₂₄Fe₁₂, which has been studied in detail [10–12]. Undoubtedly, doping of the ico-phase with chromium may lead to the formation of various quasicrystalline (QC) states in the material. As pointed out by Kim et al. [13], mechanical activation and short-term heat treatments in an aluminum-rich region (70–75 at % Al) may yield an *i* + *d* QC phase mixture. The second composition chosen, Al₇₀Cu₂₀Fe₅Cr₅, is close to Al₇₀Cu₂₀Cr₁₀, a composition from which an impurity-free *d*-phase was obtained [14].

In this paper, we describe a process for reproducible synthesis of powder materials based on Al–Cu–Fe–Cr alloys in a quasicrystalline state.

EXPERIMENTAL

The starting materials used in this study were 99.9%-pure aluminum (particle size from 10 to

20 μm), electrolytic copper (10 to 20 μm), Armco iron (40 to 60 μm), and electrolytic refined chromium (20–40 μm). Powder mixtures were activated by grinding in a laboratory-size vibratory ball mill at a power of 5 W per grinding vial. The ball-to-powder weight ratio was 10 : 1. We used ShKh-15 steel balls 6.5 mm in diameter. The weight of the starting mixture for the mechanical activation (MA) was 3 g, and the total milling time was 15 h. The process was run in an argon atmosphere. In intermediate steps, we took samples of the mixtures after 5, 7, 10, and 12 h of milling [15].

The powder samples were characterized by scanning electron microscopy on a Carl Zeiss LEO EVO-50 XVP equipped with an Oxford Instruments INCA Energy 450 energy dispersive X-ray spectrometer and operated at an accelerating voltage of 15 kV [16].

To determine the initial particle size, the powder samples were applied to adhesive tape in a single layer after mechanical activation.

The phase composition of the powders was determined by X-ray diffraction on a DRON-3 diffractometer using a graphite monochromator (CuK_α radiation, angular range 20° ≤ 2θ ≤ 95°, scan step of 0.1°, counting time of 3 s per data point). The diffraction patterns were analyzed using an X-ray software package [17].

Thermal transformations of the samples after milling for 5–12 h were followed using thermal analysis with a Netzsch STA 449 F1 Jupiter system in the temperature range 25–920°C. The heating rate was 20°C/min. Heat treatment temperatures were chosen using calorimetry data.

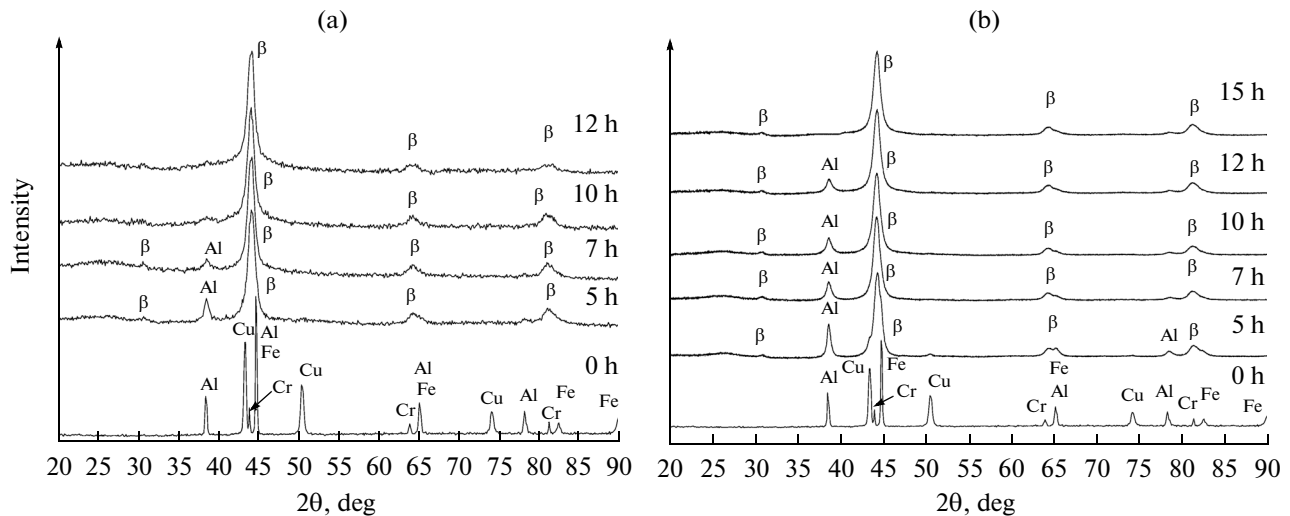


Fig. 1. X-ray diffraction patterns of the (a) $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ and (b) $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ samples after 15 h of milling.

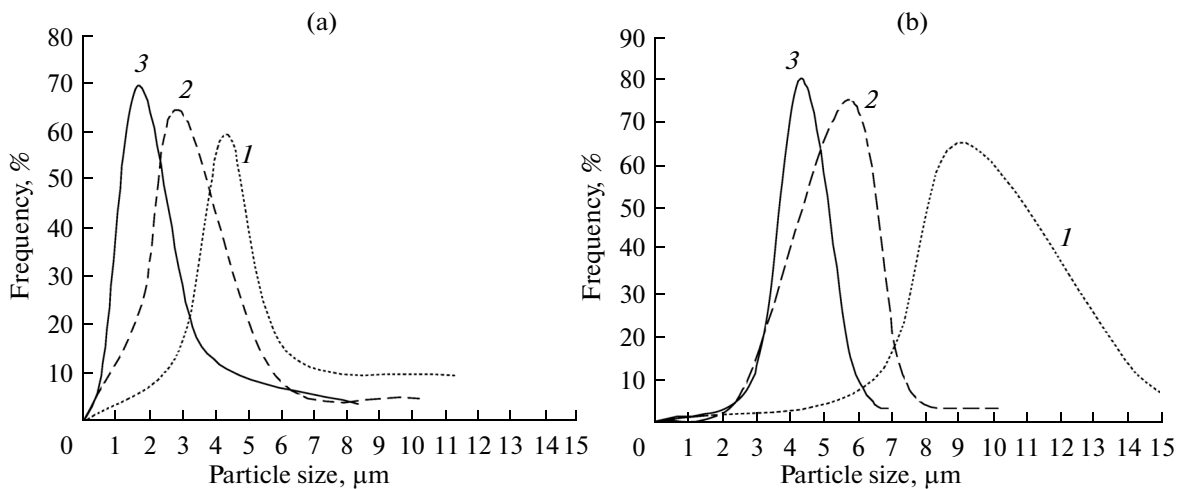


Fig. 2. Particle size distributions in the (a) $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ and (b) $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ samples after milling for (1) 7, (2) 10, and (3) 12 h.

RESULTS AND DISCUSSION

The onset of phase transitions in mechanically activated materials is known to depend on the particle size and morphology in the milled powder mixtures and the energy accumulated on the particle surface [1, 4, 18]. The most favorable conditions for the formation of a QC structure are created at a certain particle size of the milled powder. In view of this, we took samples after 7, 10, and 12 h of milling in order to determine the particle size of the powder and characterize it by X-ray diffraction.

According to microstructural analysis and X-ray diffraction data, the starting powder mixtures with the compositions $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ and $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ consisted of particles whose structure corresponded to crystals of pure Al, Cu, Fe, and Cr metals (Fig. 1). The

X-ray diffraction patterns of the $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ and $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ samples after 5 h of milling showed no reflections from pure Cu, Fe, or Cr metal and indicated the formation of a β -phase ($B2$ structure). Milling for 7 h reduced the average particle size of $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ by almost a factor of 2. In this sample, 60% of the particles were 4–5 μm in size. In $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$, more than 60% of the particles were on the order of 10 μm in size. X-ray diffraction characterization of the two samples showed that increasing the milling time by 2 h reduced the intensity of the reflections from aluminum. The particles with the lower aluminum content (65 at %) were chemically homogeneous (Fig. 2).

Further increasing the milling time to 10 h was accompanied not only by a reduction in particle size but also an increase in defect density in the particles.

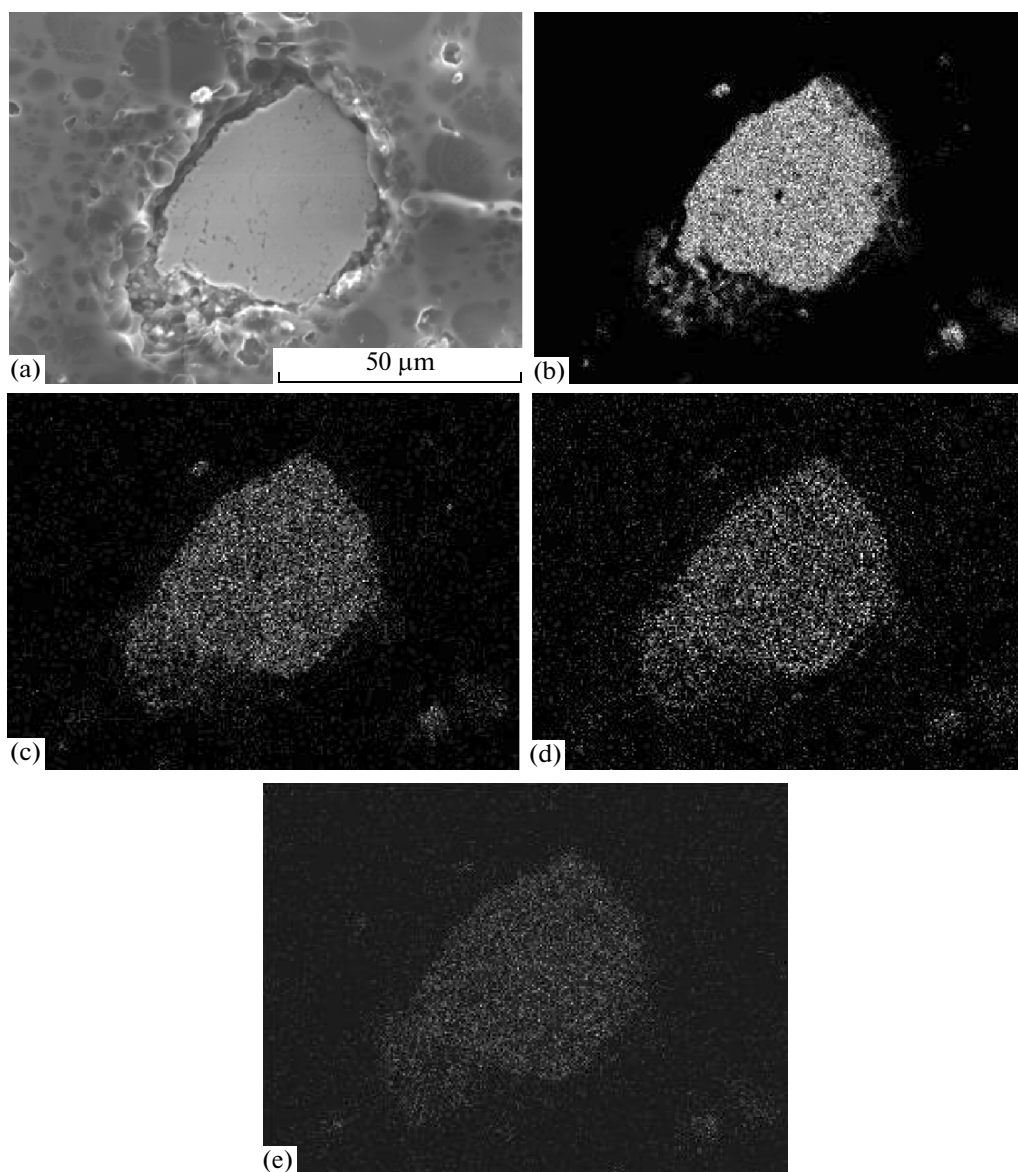


Fig. 3. (a) Electron micrograph of a polished section of an $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ particle after milling for 10 h and the corresponding (b) Al, (c) Cu, (d) Fe, and (e) Cr X-ray maps.

More than 65% of the particles in the $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ mixture were 2–3 μm in size. In the $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ sample after such treatment, the particles were predominantly 5–6 μm in size. In this milling stage, the reaction between the residual aluminum and the β -phase, $\text{Al}(\text{CuFe})$, which increased the percentage of the disordered β -phase, reached completion. The diffraction peak in the angular range 42° – 45° became stronger and sharper (Fig. 1a). The Al, Cu, Fe, and Cr X-ray maps of the particles in the milled $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ powder (Fig. 3) demonstrate that their components are uniformly distributed throughout the particles. In the case of the mixture with the composition $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$, the reflections from Al persisted up to 12 h of milling (Fig. 1b).

Milling for 12 h leads to further decrease in the particle size of the activated powders: 1–2 μm in $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ and 3–5 μm in the $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ mixture. The X-ray diffraction data obtained in this stage are similar to those obtained after 10 and 12 h of milling, except for the slight broadening of the peak corresponding to an ordered solid solution with a cubic structure (CsCl type) and a lattice parameter $a = 2.911 \text{ \AA}$. The state of the powder mixture containing 70 at % Al is characterized by the Al, Cu, Fe, and Cr X-ray maps of a polished section of a particle, which demonstrate that its components are uniformly distributed throughout the particle (Fig. 4).

According to the present results, mechanical activation leads to sequential formation of a homogeneous

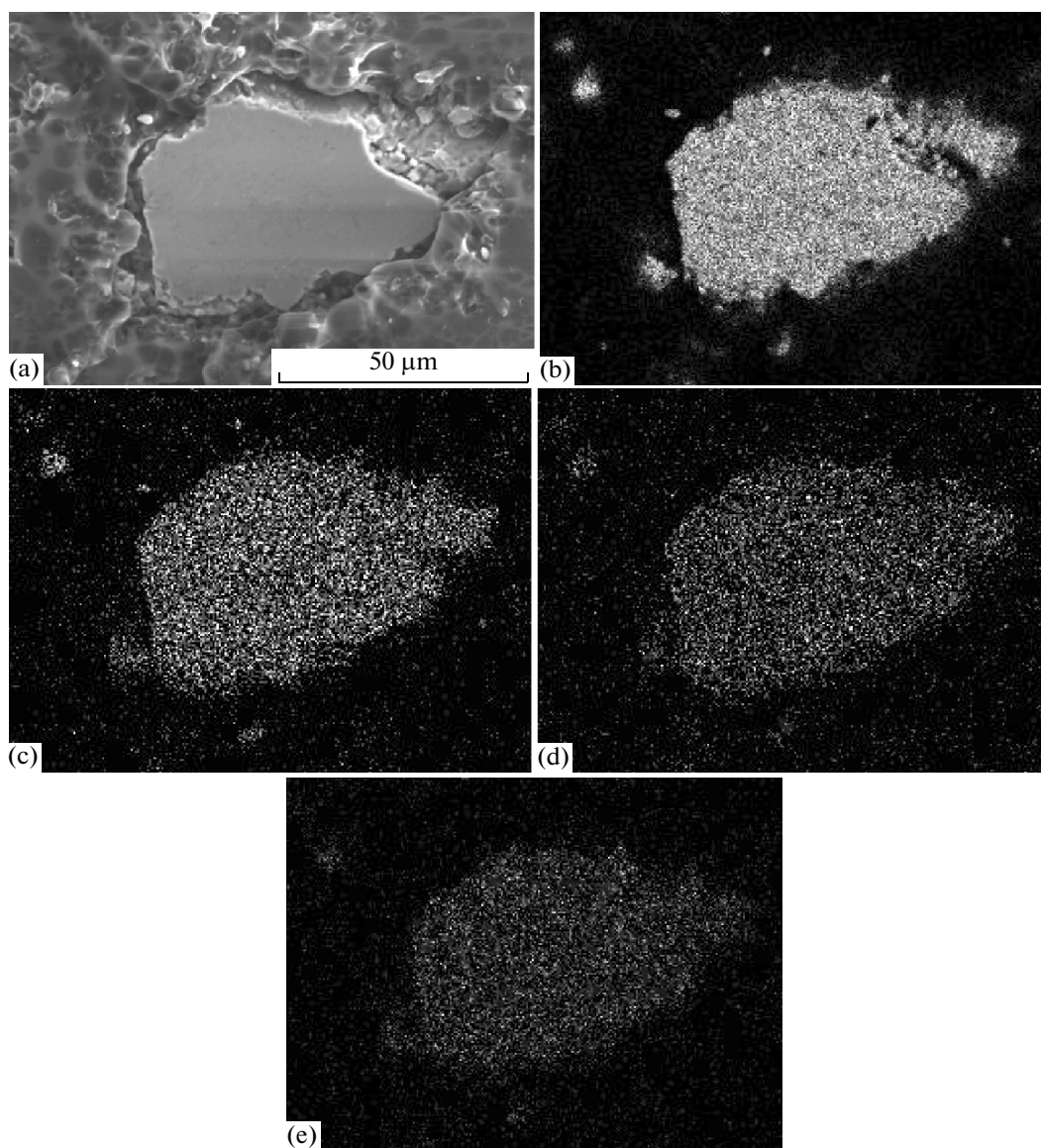


Fig. 4. (a) Electron micrograph of a polished section of an $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ particle after milling for 12 h and the corresponding (b) Al, (c) Cu, (d) Fe, and (e) Cr X-ray maps.

mixture of components. In all processing stages, the particle size of the $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ sample was greater by almost a factor of 2, which was undoubtedly related to the difference in the percentages of Al and Cu between the samples. Comparison of published data on the mechanical activation of an Al–Cu–Fe ternary alloy indicated analogy with the $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ sample according to X-ray analysis data, with the only difference that, because of the increase in the initial weight of the mixture, the milling time should be increased proportionally, by a factor of 1.5. It is worth noting that the Al crystals in the $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ sample persisted over the entire range of milling times studied. Similar results were reported by Shevchukov et al. [19]. Short-term milling leads to the formation of a quaternary β -solid solution: Al(CuFeCr).

The phase formation sequence and structural transitions in the milled samples were identified using differential scanning calorimetry (DSC). The calorimetric curve of the $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ sample in Fig. 5a shows two (successive) exothermic peaks. One of them, 16.5 J/g in area and on the order of 100°C in width, centered at 450°C, is due to the formation of the ternary ω -phase, $\text{Al}_7\text{Cu}_2\text{Fe}$, with lattice parameters $a = 6.35 \text{ \AA}$ and $c = 14.85 \text{ \AA}$, which is consistent with data in the literature [18, 20, 21]. The other, broad (double) peak corresponds to the formation of a QC d -phase. Note that, up to a temperature of 920°C, the reflections from β -Al(CuFeCr) also persist.

The DSC curve of the $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ sample contains both exothermic and endothermic peaks. The

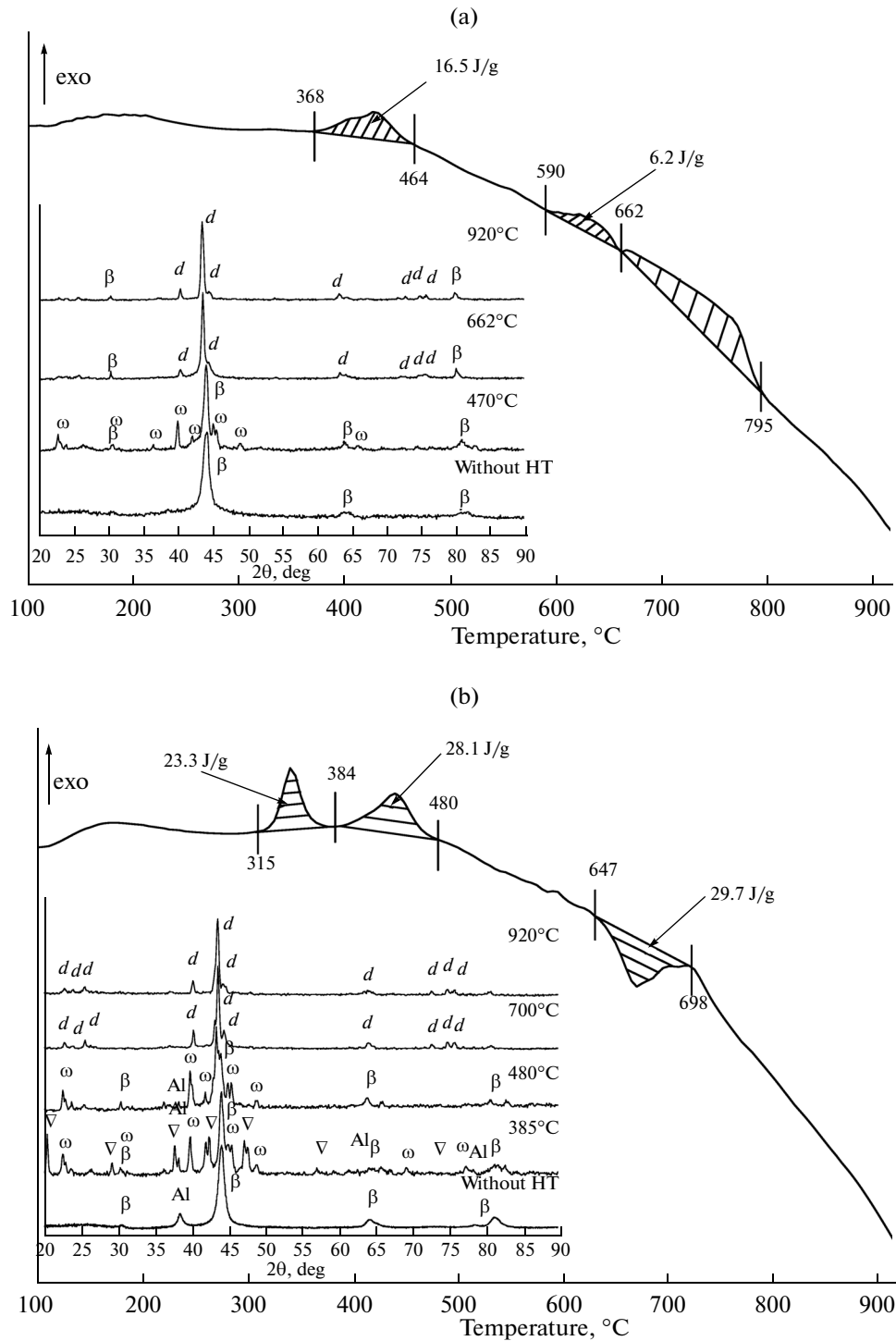


Fig. 5. Heat release (DSC) curves and X-ray diffraction patterns of the (a) $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ and (b) $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ samples: $\omega = \text{Al}_7\text{Cu}_2\text{Fe}$, $\beta = \beta$ -phase ($\text{Al}(\text{CuFeCr})$), $d = d$ -phase, $\nabla = \text{Al}_2\text{Cu}$, HT = heat treatment.

exothermic peak in the temperature range 315–384°C corresponds to the formation of a tetragonal θ -phase (Al_2Cu). Its content is 29.5% (table). The other exotherm, in the temperature range 385–484°C, is attributable to the formation of the ω -phase and is similar to that for the $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ sample. The endothermic

peak at 660°C corresponds to aluminum melting, as evidenced by the presence of reflections from unreacted Al in the milled sample (Fig. 1b). In contrast to the $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ sample, at heat-treatment temperatures above 700°C we observe only reflections from the d -phase (Fig. 5b, inset).

Phase composition (as determined by the Rietveld method with PHAN)

Composition	Heat-treatment temperature, °C	Phase	Percentage ($\pm 0.7\%$)	Lattice parameters, Å		
				<i>a</i>	<i>b</i>	<i>c</i>
Al ₆₅ Cu ₂₅ Fe ₅ Cr ₅	Without heat treatment	β -Al(CuFeCr)	100	2.90		
	470	β -Al(CuFeCr)	77.4	2.91		
		ω	22.6	6.35		14.85
	662	<i>d</i>	88.5	23.81	12.36	32.66
		β -Al(CuFeCr)	11.5	2.94		
	920	<i>d</i>	94.7	23.82	12.32	32.65
β -Al(CuFeCr)		5.3	2.94			
Al ₇₀ Cu ₂₀ Fe ₅ Cr ₅	Without heat treatment	Al	21.4	4.04		
		β -Al(CuFeCr)	78.6	2.90		
	385	Al	12.2	4.05		
		β -Al(CuFeCr)	37.2	2.89		
		ω	21.1	6.35		14.83
		Al ₂ Cu	29.5	6.07		4.89
	480	β -Al(CuFeCr)	59.8	2.93		
		ω	30.4	6.35		14.87
		Al	9.8	4.05		
		<i>d</i>	100	23.81	12.36	32.66
920	<i>d</i>	100	23.81	12.36	32.66	

The temperature at which the d -phase begins to grow depends on the particle size of the powder mixture. In the quaternary system, the initial stage of this process is diffusion-controlled. The energy released as a result of the formation of the QC phase also depends on the energy accumulated in the mixture as a result of mechanical activation.

X-ray diffraction characterization of the $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ mixture after milling for 12 h and heat treatment at a temperature of 470°C for 10 min indicated the presence of the ω -phase ($\text{Al}_7\text{Cu}_2\text{Fe}$) (23%) and β -phase (77%). Heat treatment at a temperature of 670°C for 10 min converted these phases into a powder mixture in a d -state with a small amount (on the order of 10%) of $\text{Al}(\text{CuFeCr})$. At a temperature of 700°C , an impurity-free d -phase was obtained from the $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ mixture.

The comparatively rapid transition of the system to a decagonal state can probably be accounted for by the fact that diffusionless mutual transformations of disordered solid solutions with a body-centered cubic structure into icosahedral and decagonal QC states are linked by similar orientation relationships between the lattice of the CsCl cubic phase and quasicrystals [13, 18].

CONCLUSIONS

A mechanically activated AlCuFeCr powder mixture has been studied for the first time by a variety of physicochemical characterization techniques (SEM, DSC, and X-ray analysis). Homogenization for 12 h is accompanied by a systematic decrease in particle size to $1\text{--}5\ \mu\text{m}$ and the formation of disordered $\text{Fe}(\text{AlCu})$ solid solutions with the $B2$ structure. Grinding for 15 h in a vibratory ball mill does not produce an icosahedral or decagonal QC state.

After annealing at a temperature of 470°C for 10 min, AlCuFeCr quaternary phases contain a crystalline ω -prephase with the composition $\text{Al}_7\text{Cu}_2\text{Fe}$. Milling the $\text{Al}_{65}\text{Cu}_{25}\text{Fe}_5\text{Cr}_5$ sample for 10 min at a temperature of 650°C leads to the formation of a mixture of a decagonal phase and $\beta\text{-Al}(\text{CuFeCr})$. Under similar conditions, the $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_5\text{Cr}_5$ mixture almost completely converts into a decagonal phase.

We have proposed a two-step mechanical activation process, which includes short-term annealing at a temperature of 650°C , for the synthesis of monodisperse QC d -phase powders on the order of $10\ \mu\text{m}$ in particle size, optimized the composition for the synthesis of QC powder materials, and determined the temperature stability range of the decagonal phase.

ACKNOWLEDGMENTS

This work was carried out using equipment at the Shared Characterization Facilities Center, Moscow

State University, and was supported by the RF Ministry of Education and Science (state contract no. 16.552.11.7081).

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Translated by O. Tsarev