NANOMATERIALS
AND ENVIRONMENT

Phase Transformations in Rapidly Quenched Al−Cr−Zr Alloys during Heat Treatment

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Abstract—Results from studying the effect zirconium has on solid-phase processes in aluminum−chromium alloys are presented. Rapidly quenched alloys are prepared via melt spinning. The quenching rate is ~10^6 K/s. By means of physicochemical analysis, it is shown that doping Al−Cr alloys with zirconium improves the thermal stability of supersaturated solid solutions and stabilizes their microcrystalline structure; this hinders the coagulation of intermetallic phases and thus improves the hardness of the alloys. It is found that supersaturated solid solutions of Cr and Zr in aluminum undergo stepwise decomposition; the temperature and time parameters of each step are shown in TTT diagrams.

INTRODUCTION

Fairly extensive regions of aluminum-based supersaturated solid solutions (SSSes) form in Al−Cr alloys [1, 2]. However, the dispersion hardening of these systems leads to the formation of coarse inclusions of intermetallic phases prone to coagulation; this substantially degrades the strength properties of aluminum alloys. We therefore used zirconium, a well-known modifier, as a third component in this work [2].

The aim of this work was to determine the effect Zr has on solid-state processes that occur in aluminum−chromium alloys.

Analysis of the literature data showed that crystallization processes in such alloys quenched at a rate of 10^6 K/s are poorly understood. The interaction between elements in the respective binary systems under equilibrium conditions was studied in considerable detail in [3]. Phase equilibria in a ternary system were studied in an aluminum-rich region in [3, 4].

EXPERIMENTAL

Rapidly quenched alloys (RQAs) were prepared via melt spinning in the form of tapes with widths of 2−5 mm and thicknesses of 0.01−0.02 mm by rapidly cooling a melt jet on the outer surface of a copper cylinder rotating at high speed. The quenching rate was ~10^6 K/s, as was determined from a calibration graph constructed in sample thickness (mm)−quenching rate (K/s) coordinates [3]. Powder X-ray diffraction analysis was performed on a DRON-4 instrument with monochromatized CrK_α and FeK_α radiation. Interplanar distances were determined using the EXPRESS software. Phases were identified using the JCPDS−ICDD database. The quantitative composition of the alloy samples was determined via local X-ray diffraction analysis on a JXA-840 instrument using a set of 10-s pulses at seven or eight phase points. Our studies were conducted using characteristic K_α radiation at an accelerating voltage of 20 kV. Corrections for the conversion of relative intensities to relative concentrations were introduced by means of ZAF correction in accordance with the standard procedure. Hardness was measured on a TP-7P-1 instrument at a load of 50 N (the Vickers method). Chemical analysis was performed via inductively coupled plasma atomic emission spectrometry (argon plasma) on a Thermo Jarrel Ash ICAP-61 instrument.

RESULTS AND DISCUSSION

The compositions of the studied alloys, the X-ray diffraction and hardness data for Al−Cr−Zr RQAs are presented in the table and Figs. 1−5.

RQAs with chromium contents of 0.1−5.0 at % can be characterized as SSSes of chromium in aluminum. In our alloy with a terminal composition of 95 at % Al and 5 at % Cr and subjected to heat treatment at 620 K for 48 h, CrAl$_7$ intermetallic compound was detected in addition to the SSS (Fig. 1).

If we assume that the temperature of the onset of decomposition is the one at which hardness begins to vary at a fixed heating time, it follows from Fig. 2 that

Chemical and phase composition of Al–Zr–Cr alloys (annealing times, 48 and 72 h)

Composition, at %			RQA	Phase composition, at %			
				$T = 520$ K		$T = 620$ K	
Al	Zr	Cr		48 h	72 h	48 h	72 h
99.9	–	0.1	Al	Al	Al	Al	Al
99.3	–	0.7	Al	Al	Al	Al	Al
99.0	–	1.0	Al	Al	Al	Al	Al
98.8	–	1.2	Al	Al	Al	Al	Al + CrAl$_7$
95.0	–	5.0	Al	Al	Al	Al + CrAl$_7$	Al + CrAl$_7$
99.9	0.1	–	Al	Al	Al	Al	Al
99.6	0.4	–	Al	Al	Al	Al	Al
99.3	0.7	–	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$	Al + ZrAl$_3$	Al	Al	Al
99.0	1.0	–	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$
98.8	1.2	–	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$	Al + ZrAl$_{3(c)}$ + ZrAl$_{3(t)}$
99.8	0.1	0.1	Al	Al	Al	Al + CrAl$_7$	Al + CrAl$_7$
98.8	0.5	0.7	Al	Al	Al	Al + CrAl$_7$	Al + CrAl$_7$
97.8	1.0	1.2	Al	Al + ZrAl$_3$	Al + ZrAl$_3$	Al + CrAl$_7$	Al + CrAl$_7$
96.4	1.6	2.0	Al + ZrAl$_{3(t)}$	Al + ZrAl$_{3(t)}$	Al + ZrAl$_{3(t)}$	Al + ZrAl$_{3(t)}$	Al + ZrAl$_{3(t)}$

for alloys with chromium contents of 0.1–1.0 and 1.2–5.0 at %, this temperature is 670 (48 h) and 523 K (48 h), respectively (Fig. 2).

Aluminum–zirconium RQAs with zirconium contents of up to 0.4 at % can be characterized as aluminum-based SSSes that are stable up to 620 K (48 h). Annealing at higher temperatures for 48 h leads to the formation of an equilibrium ZrAl$_3$ phase. In a terminal alloy containing 99.6 at % Al and 0.4 at % Zr, the SSS decomposes to form an equilibrium ZrAl$_3$ phase after annealing at 720 K for 60 h and at 620 K for 96 h.

Three phases were identified in the X-ray diffraction patterns of RQAs with zirconium contents of 0.7–1.2 at %: an aluminum-based SSS, an equilibrium tetragonal ZrAl$_3$ phase, and a metastable cubic ZrAl$_3$ phase with a Cu$_3$Au-type lattice (Fig. 2). Annealing at temperatures of 520–720 K increased the volume
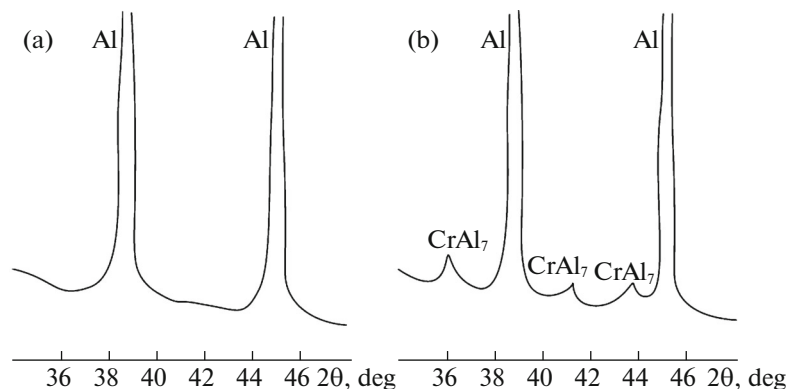

Fig. 1. Fragments of the X-ray diffraction pattern of an RQA containing 95.0 at % Al and 5.0 at % Cr (a) before and (b) after annealing at 620 K (48 h).
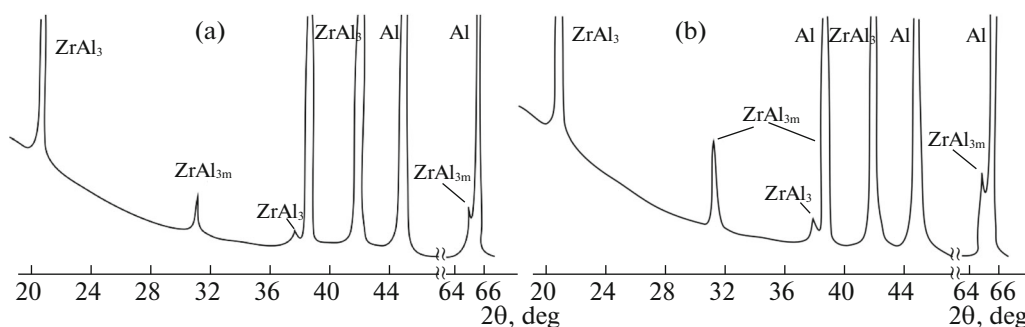
Fig. 2. Fragments of the X-ray diffraction pattern of an RQA containing 99.0 at % Al and 1.0 at % Zr after annealing at (a) 523 K (48 h) and (b) 723 K (48 h).
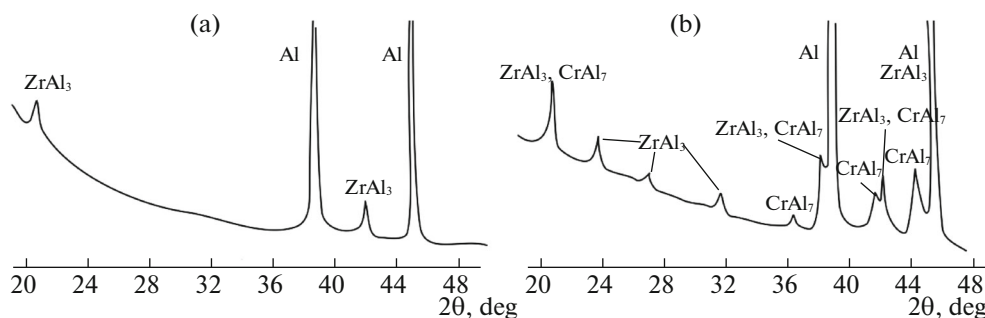

Fig. 3. Fragments of the X-ray diffraction pattern of an RQA containing 96.4 at % Al, 1.6 at % Zr, and 2.0 at % Cr (a) before and (b) after annealing at 770 K (24 h).

fraction of the tetragonal $ZrAl_3$ phase (equilibrium) and the coagulation of the metastable $ZrAl_3$ phase.

The X-ray diffraction patterns of RQAs of Al–Cr–Zr ternary systems with chromium contents of 0.1–0.7 at % and zirconium contents of 0.1–0.5 at % exhibit a single system of reflections corresponding to the fcc lattice of an SSS of zirconium and chromium in aluminum. The hardness of the alloys with these compositions begins to grow at 623 K (48 h) and reaches its maximum values at 700–773 K (650–700 MPa), owing to the decomposition of the SSS. $ZrAl_3$ phase precipitates are finely dispersed, as is apparent from the broadening of the diffraction peaks in the diffraction patterns and the presence of a halolike background at low angles.

Finely dispersed precipitates of the equilibrium $ZrAl_3$ phase were observed after annealing at 620 K for 96 h and at 520 K for 120 h. Extremely finely dispersed compound $CrAl_7$ was detected at 770 K (60 h). At the same time, reduced broadening of the lines corresponding to the $ZrAl_3$ phase was observed, due apparently to grain growth in this phase.

With an increase in the chromium and zirconium content in the alloys (from 1.2 to 2.0 at % and from 1.0 to 1.6 at %, respectively), ultrafast crystallization leads to the formation of two phases: an aluminum-based SSS and an equilibrium tetragonal $ZrAl_3$ phase

(Fig. 3a). Annealing at 770 K (48 h) leads to the formation of the $CrAl_7$ compound, owing to the decomposition of the aluminum-based SSS (Fig. 3b). In addition, the broadening of reflections of the crystal lattice of the $ZrAl_3$ phase is reduced, suggesting that this phase is subject to coagulation. At lower annealing temperatures (520, 620 K), crystallization of the $CrAl_7$ phase from the SSS takes much more time (Fig. 4).
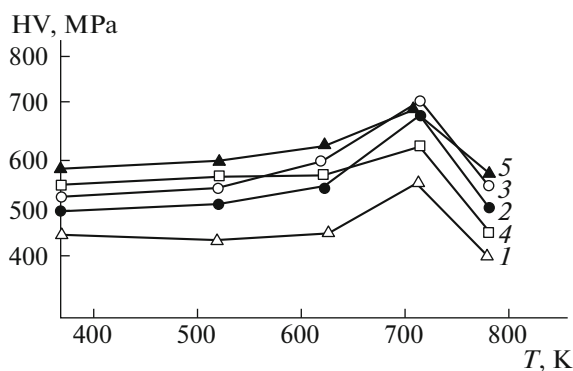

Fig. 4. Effect of annealing temperature (48 h) on the hardness of Al–Cr–Zr RQAs with Al contents of (*1*) 98.0, (*2*) 99.3, (*3*) 98.8, (*4*) 97.9, and (*5*) 96.4 at %; Cr contents of (*1*) 0.1, (*2*) 0.4, (*3*) 0.7, (*4*) 1.2, and (*5*) 2.0 at %; and Zr contents of (*1*) 0.1, (*2*) 0.3, (*3*) 0.5, (*4*) 0.9, and (*5*) 1.6 at %.
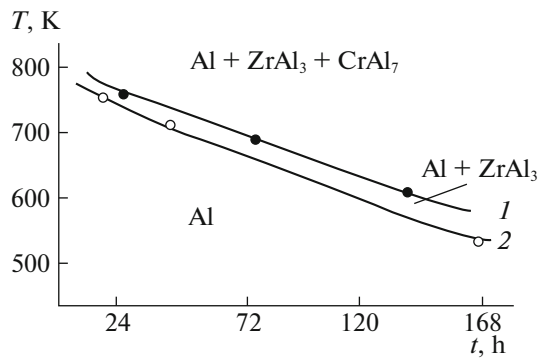
Fig. 5. TTT diagram of a RQA containing 98.8 at % Al, 0.5 at % Zr, and 0.7 at % Cr.

In ternary Al−Cr−Zr RQAs, the decomposition of the SSS is thus described by the scheme $Al(Zr, Cr)_{SSS} \rightarrow Al(Cr)_{SSS} + ZrAl_3 \rightarrow Al + ZrAl_3 + CrAl_7$.

Figure 5 shows the TTT diagram of an RQA containing 98.8 at % Al, 0.5 at % Zr, and 0.7 at % Cr. It confirms the scheme of SSS decomposition and shows the temperature and time parameters at each stage of the process.

CONCLUSIONS

The doping of Al−Cr alloys with zirconium improves the thermal stability of SSSes. Adding zirconium to aluminum−chromium alloys stabilizes their microcrystalline structure, hinders the coagulation of intermetallic phases, and thus improves the hardness of the alloys.

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