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Experimental identification of the degenerated equilibrium in extreme Al end of the Al–Cr system

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The invariant equilibrium in extreme Al side of the Al–Cr system has been the subject of several investigations [1–7]. Due to its degenerated nature, which means that the invariant reaction temperature is very close to the melting point of Al, the temperatures reported in these studies [1–7] show noticeable discrepancies. Table I summarizes the experimentally observed invariant reaction temperature among (Al), liquid and $Al_{45}Cr_7$. All of the temperatures quoted in the present work have been converted into international temperature scale of 1990 [8]. The formula $Al_{45}Cr_7$ is based on crystal structure data [9, 10]. As shown in Table I, in the literature five groups of authors [1, 2, 4, 6, 7] reported an eutectic reaction type ($L \leftrightarrow (Al) + Al_{45}Cr_7$), whereas the remaining two groups [3, 5] suggested a peritectic one, $L + Al_{45}Cr_7 \leftrightarrow (Al)$. In the phase diagram assessed by Murray [11, 12], the peritectic reaction type is adopted. The purpose of the present work is to identify the degenerated nature for the invariant reaction among (Al), liquid, and $Al_{45}Cr_7$ by means of differential scanning calorimetry (DSC), X-ray diffraction (XRD) and electron probe microanalysis (EPMA) methods.

Three samples (pure Al, 1 at.% Cr, and 8 at.% Cr) were prepared by using 99.999% purity Al rod and 99.999% purity Cr piece (both from Johnson Matthey Company, MA 01835, USA). Samples with the weight of about 2 g were prepared by arc melting of Al rods and Cr pieces in an ambient atmosphere of 99.998% purity Ar. The as-cast samples were sealed in evacuated quartz tubes under vacuum of 10^{-4} bar, annealed at 630 °C for 31 days, and then water-quenched. No chemical analysis for the alloys was conducted since the weight losses during arc-melting were less than 0.5 mass%. The phase identification was performed by means of XRD (PW 1729, X-ray generator, Philips) using Cu $K\alpha_1$ radiation with Si as an internal standard, and the phase composition was determined by using EPMA (CAMECA SX 50, France). Pure Al and Cr, which were subjected to the same treatment at that employed for the alloys, were used as standards. Conventional matrix correction, which deals with the deviation from linearity by including the effects of atomic number (Z), absorption (A) and fluorescence (F), was employed to calculate the compositions from the measured X-ray intensities with an accelerating voltage of 20 kV and a beam current of 20 nA.

DSC (Perkin-Elmer model II, Norwalk, Connecticut, USA) measurements were carried out in Cu pans under a flow of 99.998% purity Ar. In order to avoid the reaction between the samples and Cu pans, the sample wrapped with Ta foil is put into Cu pan sample holder. Another Ta foil with the same weight as that in the sample holder is inserted into Cu pan reference holder. Three heating rates of 2, 5, and 10 K/min were conducted between room temperature and 800 °C. The temperature and enthalpy of transformation in DSC measurement were calibrated to pure elements In, Pb, and Zn. Phase transformation temperatures above 800 °C were measured with DTA (DTA 701L, Bahr Thermoanalyse GmbH, Germany) and were calibrated against the melting temperatures of Al, Ag and Au.

Table II presents the phases identified by XRD, phase compositions measured with EPMA as well as phase transition temperatures obtained from DSC and DTA measurements. XRD data confirmed the compound $Al_{45}Cr_7$ and its crystal structure. The observed lattice parameters match closely with those compiled by Villars and Calvert [13] and are thus not presented here. According to EPMA measurement, the composition of $Al_{45}Cr_7$ is 13.05 ± 0.5 at.% Cr, which agrees well with the phase composition (13.5 at.% Cr) deduced from the crystal structure data [9, 10]. In Fig. 1, the measured enthalpy of melting below 800 °C by using DSC is plotted for pure Al, $Al_{0.99}Cr_{0.1}$, and $Al_{0.92}Cr_{0.08}$. These data are the average value resulting from three different heating rates, i.e., 2, 5, and 10 K/min. For pure Al, the presently obtained enthalpy of melting is 10.577 ± 0.15 kJ/(mol-atoms), which is in excellent agreement with the literature value 10.711 kJ/(mol-atoms) [14]. It is expected that for $Al_{45}Cr_7$ the enthalpy of melting is zero below 835 °C,

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TABLE I Summary of the experimental data on the invariant equilibrium in extreme Al side of the Al–Cr system

Source	Starting materials	Method	Claimed invariant equilibrium
[1]	Purity unknown	TA on cooling	$L \leftrightarrow (Al) + Al_{45}Cr_7$ at 646.3 °C
[2]	Purity unknown	TA on cooling	$L \leftrightarrow (Al) + Al_{45}Cr_7$ at 655.3 °C
[3]	99.97%Al, Cr (unknown)	TA on cooling	$L + Al_{45}Cr_7 \leftrightarrow (Al)$ at 661 °C
[4]	99.92%Al, Cr (unknown)	TA on heating	$L \leftrightarrow (Al) + Al_{45}Cr_7$ at 658.3 °C
[5]	99.998%Al, 99.99%Cr	TA on heating	$L + Al_{45}Cr_7 \leftrightarrow (Al)$ at 661.5 °C
[6]	99.9%Al, 99,5%Cr	DTA on heating	$L \leftrightarrow Al_{45}Cr_7 + (Al)$ at 657 °C
[7]	99.5%Al, 99.5%Cr	DSC on heating	$L \leftrightarrow Al_{45}Cr_7 + (Al)$ at 656 °C
This work	99.999%Al, 99.999%Cr	DSC on heating	$L \leftrightarrow Al_{45}Cr_7 + (Al)$ at 659.7 °C

TA means thermal analysis.

TABLE II Summary of the phases, their compositions as well as phase transition temperatures for the samples in the Al–Cr system annealed at 630 °C for 31 days

No	at.%Cr	Phase, phase composition (at.%Cr)	Transition temperature (°C)
1	0	Al	660.3
2	1	(Al): 0.32; $Al_{45}Cr_7$: 13.03	659.8, 755
3	8	(Al): 0.38: $Al_{45}Cr_7$: 13.07	659.6
3a	8	(Al): 0.38: $Al_{45}Cr_7$: 13.07	660.4, 835, 944

The phase transition temperatures for samples 1, 2 and 3 are obtained by extrapolating DSC onsets with the heating rates of 2, 5, and 10 °C/min to 0 °C/min, and those for sample 3a are from DTA measurement. All the temperatures have been converted into the international temperature scale of 1990 [8].

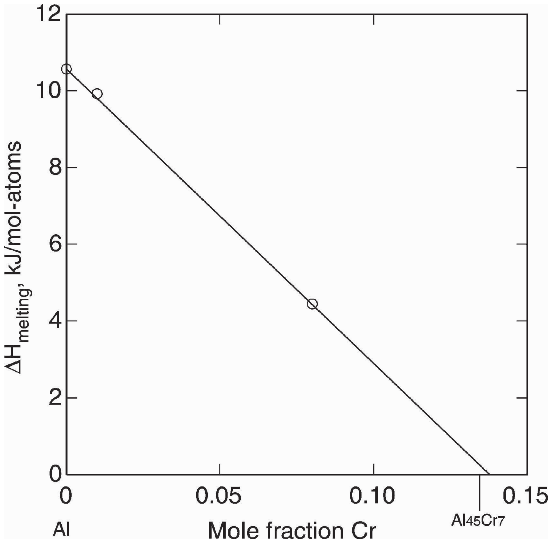

Figure 1 Measured enthalpy of melting below 700 °C by means of DSC for the samples annealed at 630 °C for 31 days.

at which it decomposes to liquid and $Al_{11}Cr_2$ [6]. The extrapolation to the enthalpy of melting of zero gives rise to the composition 13.7 at.% Cr for $Al_{45}Cr_7$. This extrapolated composition agrees well with the ideal composition (13.5 at.% Cr) and EPMA measurement (13.05 at.% Cr). Also the presently measured solubility for Cr in Al (0.35 at.% Cr at 630 °C) is in good agreement with those from the literature [3, 15].

Fig. 2 presents the invariant reaction temperatures measured with DSC against the heating rate. It clearly indicates the degenerated feature for the invariant equilibrium among liquid, (Al), and $Al_{45}Cr_7$: the eutectic reaction temperature is only lower by 0.6 °C than the melting point of Al. Such a small temperature difference cannot be resolved by means of DTA technique, as shown in the present work. The DTA measurement indicates the initial melting temperature of 660.4 ± 2 °C for $Al_{0.92}Cr_{0.08}$. This temperature is slightly higher than the melting point of Al. The degenerated nature of the invariant equilibrium cannot also be resolved with microstructure observation because the eutectic composition is very close to the composition of (Al) phase.

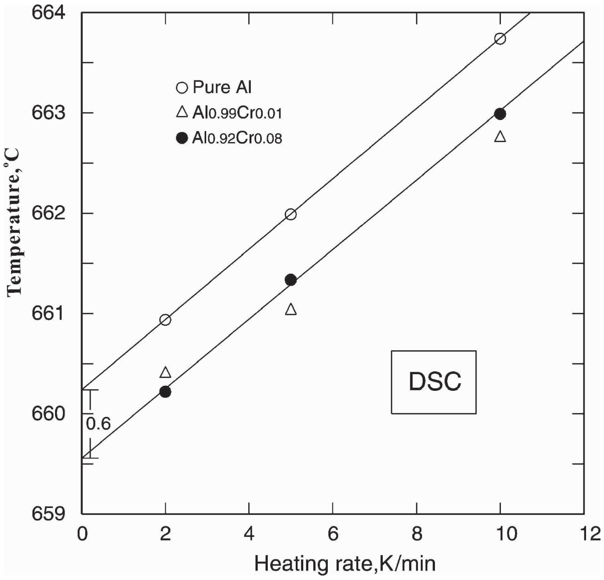

Figure 2 Measured invariant reaction temperature as a function of heating rate for the samples annealed at 630 °C for 31 days.

It has been observed that for the systems formed by elements in the same row of the periodic table (such as transition elements Ti, V, Cr, Mn, Fe, etc.) with another common element (such as Al) several constitutional properties (phase diagrams, phase structures, and thermodynamics) change according to a simple and systematic pattern [16]. The critically selected invariant reaction temperatures in Al-rich side of several transition metal–Al binary systems are shown in Fig. 3. By means of the same experimental procedure as that applied to $Al_{0.92}Cr_{0.08}$, the peritectic reaction temperature for $L + Al_{21}V_2 \leftrightarrow (Al)$ is determined to be 662.3 °C by using $Al_{0.95}V_{0.05}$ alloy prepared from 99.999% purity Al rod and 99.8% purity V slug. This temperature is higher by 2.7 °C than that from a recent measurement of Richter and Ipser [17], who used DTA to measure phase transformation temperatures. In order to reach equilibrium, $Al_{0.95}V_{0.05}$ alloy is annealed at 630 °C for two months in the present work. The invariant reaction

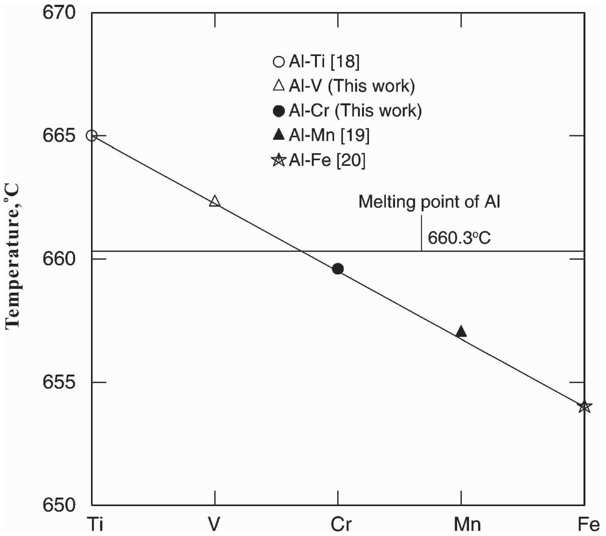

Figure 3 Invariant reaction temperatures in Al-rich side of several transition metal–Al binary systems plotted against the atomic number of the transition metal.

temperatures in the Ti–Al and Al–Mn systems are taken from recent measurements by Schuster *et al.* [18, 19], and that for the Al–Fe system from the COST compilation [20]. As shown in Fig. 3, a systematic correlation between the invariant reaction temperature and the position of the elements in the periodic table is observed. The eutectic reaction type in the Al–Cr system fits into the general pattern of the selected binary systems better than the peritectic one. This is an additional check on the reliability of the presently obtained results on the degenerated equilibrium of the Al–Cr system.

By considering the present experimental results and other observations critically selected from the literature [3, 4, 6, 15, 21–23], the phase relationship below 10 at.% Cr is presented in Fig. 4. Our further measurements [24] on several alloys $Al_{0.73}Cr_{0.27}$, $Al_{0.71}Cr_{0.29}$, $Al_{0.69}Cr_{0.31}$, $Al_{0.63}Cr_{0.37}$, and $Al_{0.55}Cr_{0.45}$ verified the general feature of the Al–Cr phase diagram constructed by Costa Neto *et al.* [6] instead of the one published by Mahdouk and Gachon [7]. The discrepancy could be attributed to the use of the less purity powders (99.5% Al and 99.5% Cr) as the starting materials in the work due to Mahdouk and Gachon. The Al-rich phase relationship obtained in the present work is expected to substitute for the currently accepted version [11, 12].

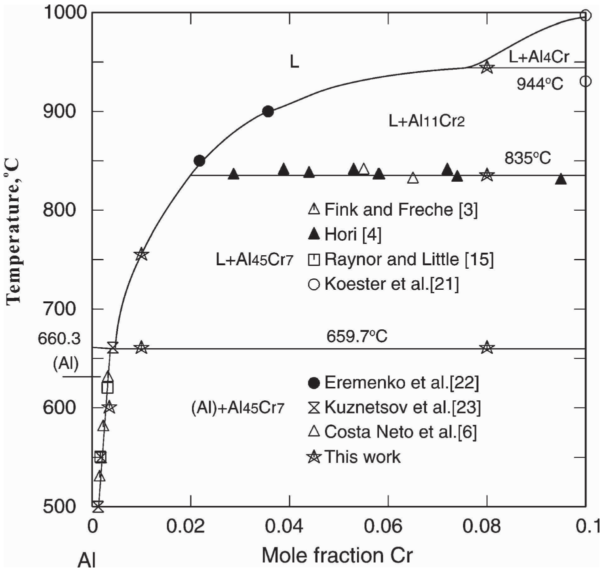

Figure 4 Revised Al-rich part the Al–Cr phase diagram.

The degenerated feature associated with the eutectic reaction $L \leftrightarrow Al_{45}Cr_7 + (Al)$ is unambiguously clarified by means of DSC measurements with a few different heating rates, supplemented by XRD and EPMA techniques. The successful application of the present approach to the identification of the degenerated equilibrium in the Al–Cr system indicates that the approach is equally valid for other binary systems and probably for multi-component systems also.

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