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NEW RESULTS ABOUT THE Al-Cr BINARY PHASE DIAGRAM

NOWE WYNIKI DLA DWUSKŁADNIKOWEGO UKŁADU Al-Cr

The Al-Cr phase diagram has been revisited, in the composition range from 6 to 46 at.% Al, by means of differential thermal analysis (DTA), X-ray diffraction (XRD) and electron probe microanalysis (EPMA). The intermetallic compounds of this system and the Cr solid solution were investigated by direct reaction calorimetry at high temperatures. The experimental enthalpies of formation were compared with available literature data. Partial enthalpies of dissolution of Cr in liquid Al were determined at 1001 and 1106°C.

Metodami różnicowej analizy termicznej (DTA), dyfrakcji rentgenowskiej (XRD) oraz mikroanalizy elektronowej (EPMA) poddano weryfikacji układ Al-Cr w zakresie stężeń pomiędzy 6 a 46% atomowych Al. Za pomocą kalorymetru przebadano w wysokich temperaturach fazy międzymetaliczne tego układu oraz roztwór stały (Cr). Uzyskane doświadczalne wartości ciepła tworzenia porównano z dostępnymi danymi z literatury. Określono cząstkowe ciepła rozpuszczania Cr w ciekłym Al w przedziale temperatur 1001 do 1106°C.

1. Introduction

The first complete equilibrium phase diagram of the aluminum-chromium system was published by K ö s t e r et al. [3]. The version selected by M a s s a l s k i et al. [10] reproduced mainly this work with some alteration in the Cr-rich part. In a previous paper, [14], we published a new version of Al-Cr phase diagram with our results in the Al-rich region.

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The main changes were the eutectic reaction at 656°C between Al primary solid solution and Al_7Cr, a eutectoid decomposition of $Al_{11}Cr_2$ ($Al_{11}Cr_2 = Al_7Cr + Al_4Cr$) at 785°C and the question of a unique phase in the 30 to 40 at.% Cr range instead of two: Al_9Cr_4 and Al_8Cr_5. In this paper we present the results of X-ray powder diffraction (XRD), electron probe microanalysis (EPMA) and differential thermal analysis (DTA) carried out in the vicinity of this ambiguous range of composition 30 to 40 at.% Cr. We give also a new set of enthalpies of formation versus composition of Cr primary solid solution, determined by direct reaction calorimetry at 1311°C and enthalpies of dissolution of solid chromium in liquid Al at 1001 and 1106°C. Results are compared with experimental data available in literature and with values from Miedema's empirical model [8].

2. Experimental procedures

2.1. Preparation of samples and determination of enthalpies of formation

All preparations were made under purified argon in a glove box at room temperature. Aluminum (−325 mesh, 99.5 wt.% pure) and chromium (2μm, 99.5 wt.% pure) powders were mixed in suitable proportions, then the mixture was compacted and the pellet was broken into pieces of about 50–100 mg. Samples, still at room temperature, were then dropped under argon into the calorimeter, at a temperature chosen in order to induce the mutual diffusion of the components. The global thermal effect measured by the calorimeter, Q, was the sum of the two pure metal heat contents, ($H_{T_0}^{T_1}$ (i) between room (T_0) and calorimeter (T_1) temperatures and of the enthalpy of formation, $\Delta_f H$, of the alloy at T_1. As enthalpy increments of elements, $H_{T_0}^{T_1}$ (i), are known [1995Bar], the enthalpy of formation $\Delta_f H$ of the alloy referred to the components at the reaction temperature is got. The calorimeter calibration was achieved by dropping cold alumina samples (50–100 mg) into the working crucible, the corresponding enthalpy increments being taken from the work of the NIST group [7].

2.2. Enthalpies of dissolution

Starting with an empty crucible (in an Ar atmosphere to prevent oxidation) at 1001 or 1106°C, small samples of Al at room temperature were dropped in order to constitute a bath of liquid Al (melting point, 660.323°C [9]). This series of samples allowed us to calibrate the calorimeter with the enthalpy change of aluminum given by B a r i n et al. [13] and to verify the response stability of the calorimeter. In a second step, pieces of Cr at room temperature were added. The heat effect of each addition was measured and corrected from Cr enthalpy increment taken in [13], in order to find the enthalpy of dissolution of chromium in the bath at the actual temperature and composition.

2.3. Phase characterization and DTA investigations

After each calorimetry experiment, XRD and EPMA were used to check both structure and composition of products. XRD were performed with copper $K\alpha_1$ radiation ($\lambda = 0.154056$ nm) on powdered samples. Pure silicon was added as an internal standard. Lattice parameters were determined with U-Fit [11]. We also used Lazy-Pulverix [6] to compute X-ray patterns on the basis of published crystallographic data. Chemical compositions were determined with a Cameca microprobe. DTA investigations were carried out with help of a SETARAM DTA 92. Samples were cycled at heating and cooling rates of 2°C, 5°C or 10°C per minute under argon in alumina crucibles.
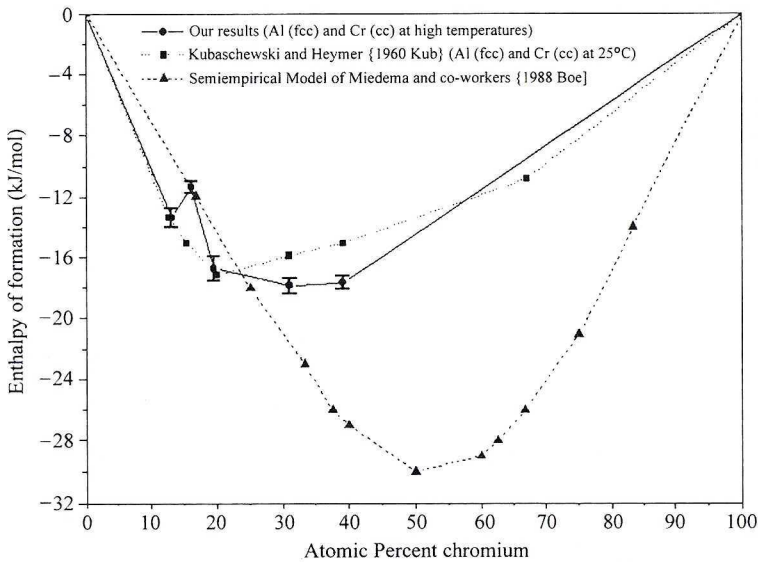

Fig. 1. Enthalpies of formation of Al-Cr intermetallics. Comparison between our results and experimental values from Kubaschewski and Heymer [2] and predicted values from Miedema's empirical model [8]

3. Results

3.1. Enthalpies of formation of intermetallic compounds

Fig. 1 shows our experimental values of enthalpies of formation of Al-Cr intermetallics determined by direct reaction at 710°C (Al_7Cr), 843°C ($Al_{11}Cr_2$), 921°C (Al_4Cr), 1010°C (Al_8Cr_5) and referred to fcc Al and cc Cr at the measurement temperatures. Our results fit those of Kubaschewski and Heymer [2] (cited in Hultgren [5]) except for $Al_{11}Cr_2$ for which we have observed an eutectoid decomposition at 785°C [14].

3.2. Enthalpies of formation of Cr solid solutions

Fig. 2 gives the enthalpies of formation of $Al_{0.20}Cr_{0.80}$, $Al_{0.30}Cr_{0.70}$ and $Al_{0.40}Cr_{0.60}$ determined by direct reaction calorimetry at 1311°C and referred to Al (liq.) and Cr (cc). Fig. 3 gives the parameter a of **Cr**Al centered cubic solid solutions obtained by X-ray diffraction. X-rayed alloys were synthesized at 1311°C, annealed in evacuated silica tubes during one week at 1000 %C, then water quenched. Our X-ray results fit those of literature.
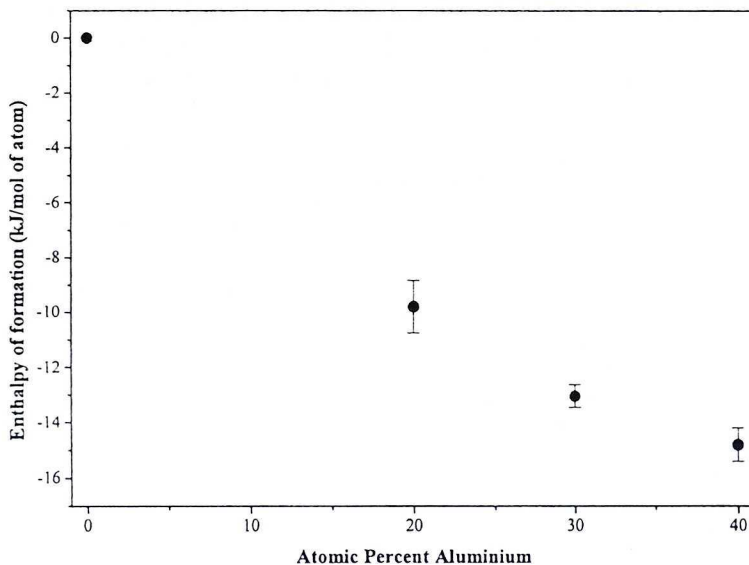

Fig. 2. Experimental enthalpies of formation of Al_xCr_{1-x} (x = 0.20, 0.30 and 0.40) alloys. With Al (liq) and Cr (bcc) reference states
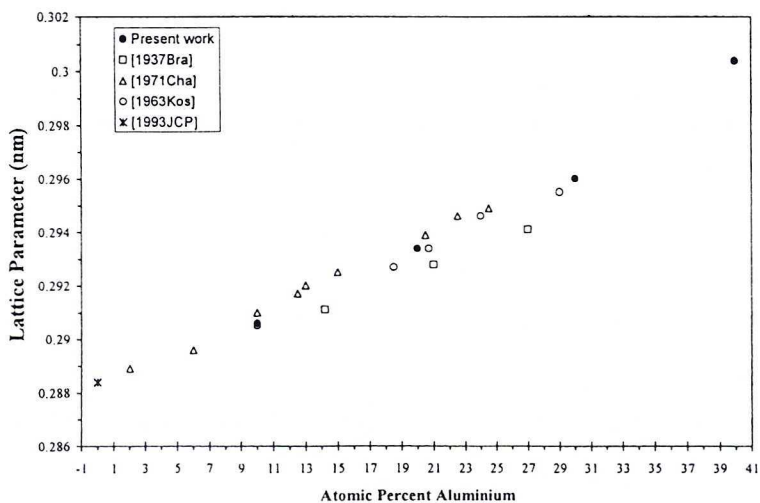

Fig. 3. Lattice parameter of Cr primary solid solution. Comparison between our experimental results and the values available in the literature

3.3. Partial enthalpies of dissolution of Cr in AlCr alloys at 1001 and 1101°C

We tried to determine the partial enthalpy of Cr as a function of the composition in the liquid and liquid + solid domains at 1001 and 1106°C, as well as the compositions of the liquidus below and above the peritectic decomposition of Al$_4$Cr. Due to the absence of stirring in the crucible during the experiments no liquid homogeneity could be ensured and finally we could only check the positions of liquidus which corresponded to response change of the calorimeter and get indicative values of Cr solution enthalpies in liquid Al at infinite dilution:

$$H_{Cr}(x_{Cr} = 0) = -36000 \pm 1400 \text{ J/mol. at } 1001°C$$

$$H_{Cr}(x_{Cr} = 0) = -28000 \pm 1100 \text{ J/mol. at } 1106°C.$$

3.4. Al$_9$Cr$_4$ and Al$_8$Cr$_5$

Our first studies in the range 30 to 40 at.% Cr didnot confirm Massalski diagram [10]. There was no peritectic at 1170°C and an alloy with $x_{Cr} = 0.36$ annealed at 850°C during one week and water quenched was found homogeneous instead of being Al$_9$Cr$_4$+Al$_8$Cr$_5$. These observations were confirmed by results in the ternary system Al-Cr-Nb. So, we adopted the notation Al$_8$Cr$_5$ for all the compositions between 30 and
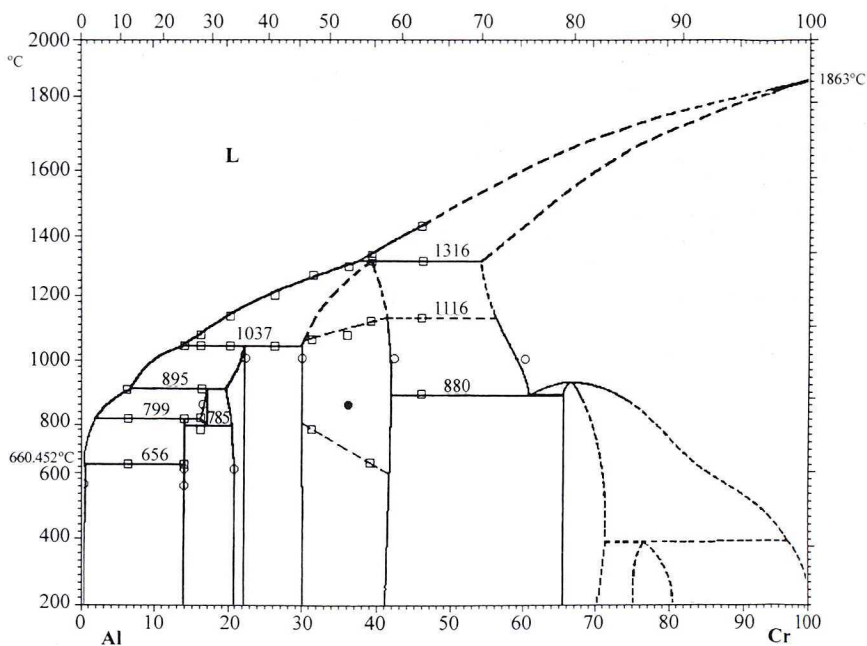

Fig. 4. The AlCr phase diagram after our results. ○EPMA, □ DTA, ● single phase

42 at.% Cr. DTA experiments on alloys with $x_{Cr} = 0.31$ and 0.39 gave comparable results with a first allotropic transformation: $\alpha Al_8Cr_5 \rightarrow \beta Al_8Cr_5$ at 780°C for $x_{Cr} = 0.31$, 680°C for $x_{Cr} = 0.39$, and another: $\beta Al_8Cr_5 \rightarrow \gamma Al_8Cr_5$ at 1055*C and 1112°C respectively. We concluded that there is only one broad phase in this domain of concentration.

4. The Al-Cr phase diagram

Fig. 4 gives the Al-Cr phase diagram redrawn in the composition range from 6 to 46 at.% Cr to take into account our results. The main changes are: a eutectic between Al and Al_7Cr, a eutectoid decomposition of $Al_{11}Cr_2$ and only one compound between 30 and 42 at.% Cr.

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