A thermodynamic study of the Al–Cr–Nb ternary system

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Abstract

The Al–Cr–Nb isothermal section at 1000°C was studied by thermal analysis, X-ray diffraction and electron microprobe analysis. The enthalpies of formation of the different compounds were determined by direct reaction calorimetry. Results are presented and discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Al–Cr–Nb is one of the ternary systems of interest to understand the behavior of many industrial alloys. At the same time, the available literature about it is very poor and results about phase diagrams are not only scarce but also contradictory. This is the reason of this new study, which combines the classical techniques of X-ray diffraction (XRD) and electron probe microanalysis (EPMA) with direct reaction calorimetry (DRC). It will be shown that DRC, which uses fine powders of the elements to synthesize the different compounds in the solid state, finds an extension in the study of phase diagrams.

2. Experimental

2.1. Pure metals

Table 1 gives the characteristics of the pure metals, which have been used throughout this work.

2.2. Calorimetry

The determination of the compound enthalpies of forma-

tion were performed by DRC, which consists of synthesizing the compounds, starting from the pure elements, directly inside the crucible of a high temperature calorimeter. This method has already been described [3] and we will here just recall the principle. Powders of the two or three components of the alloy are mixed together, at room temperature, in the right proportions, inside a glove box under purified argon. The mixture is compressed in order to make small pellets of about 30–150 mg, which are loaded in an argon tight sample dispenser. Then, the dispenser is connected to the calorimeter and the samples are dropped, one after the other, still at room temperature, into the crucible of the calorimeter. The calorimeter temperature is high enough to ensure a quick diffusion of the elements into the others, but lower than the melting point or the peritectic temperature of decomposition of the compound. In the case of peritectic decomposition, care is taken to avoid a partial melting of the samples during highly exothermic reactions. The calorimeter measures a quantity of heat, which can be considered as the sum of two contributions:

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Table 1
Characteristics of pure metals

Metal	Purity (mass.%)	Size (μm)	Packaging atmosphere	Supplier
Al	99.5	<44	Argon	CERAC
Cr	99.5	2	Argon	Alpha Ventron
Nb	99.8	<5	Argon	CERAC

Table 2
Enthalpies of formation of the Al–Cr compounds

Compound	Calorimeter Temp. (°C)	Enthalpy of formation J/mole of atoms		
		Our measurements (standard deviation)		Ref. [1]
		a	b	
$Al_{0.61}Cr_{0.39}$ (Al_8Cr_5)	1203	−23 500 (500)	−17 700 (500)	−15 050
$Al_{0.61}Cr_{0.39}$ (Al_8Cr_5)	1010	−23 700 (400)	−17 650 (400)	−15 050
$Al_{0.69}Cr_{0.31}$ (Al_9Cr_4)	940	−24 800 (500)	−17 850 (500)	−15 880
$Al_{0.805}Cr_{0.195}$ (Al_4Cr)	921	−24 800 (800)	−16 700 (800)	−17 140
$Al_{0.84}Cr_{0.16}$ ($Al_{11}Cr_2$)	843	−20 050 (400)	−11 400 (400)	−15 050
$Al_{0.87}Cr_{0.13}$ (Al_7Cr)	710	−22 600	−13 400	−13 380

[a] References: liquid Al, bcc Cr.
[b] References: fcc Al, bcc Cr.

- The pure metal heat contents between room and calorimeter temperatures;
- The enthalpy of formation of the compound at the temperature of the calorimeter.

As the heat contents of pure metals are tabulated [6], the enthalpy of formation at the calorimeter temperature is readily deduced. Dropping alumina cold samples inside the crucible, in turn with the metallic samples provides the calibration of the calorimeter. Alumina heat contents are taken from the work of Ref. [2]. The most often, during one experiment, six pieces of alumina and five metallic samples of one composition are used.
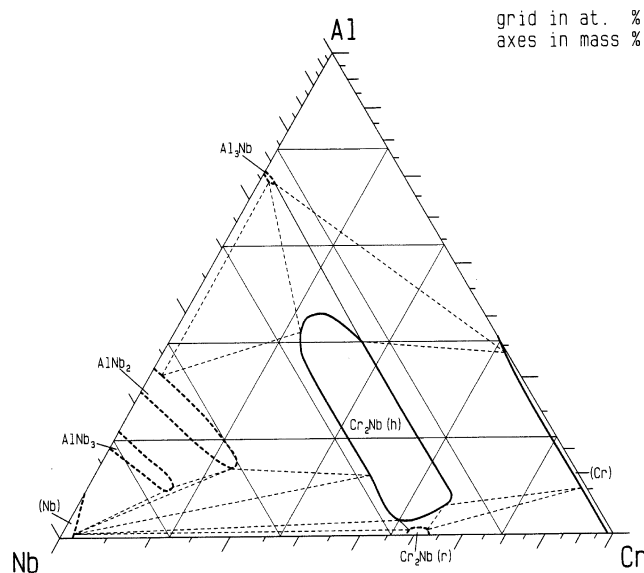

Fig. 1. Isothermal section at 1000°C from [5]. The Al–Cr compounds are not taken into account and the extend of the intermediate phases in the ternary field is ill defined.
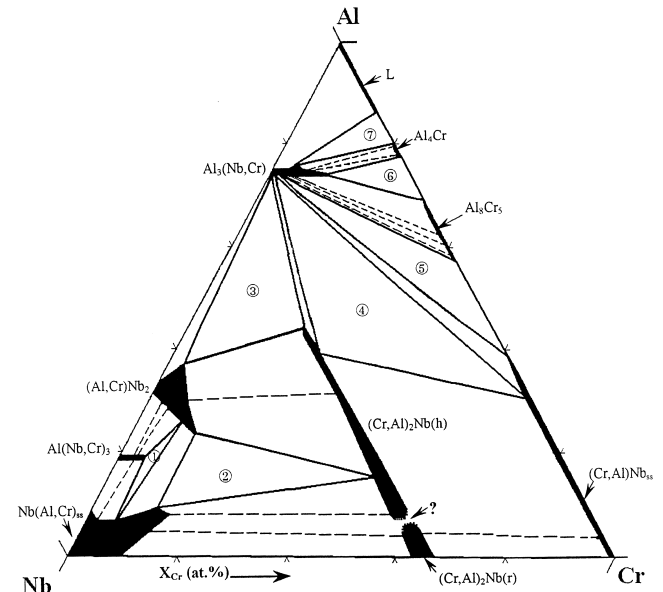

Fig. 2. Experimental isothermal section of the Al–Cr–Nb system at 1000°C. Numbers in the three phase-fields correspond to those of Table 3, which gives the limiting compositions of these domains. Tie lines are indicated by dashed lines. The question mark means that the limits of the two forms of $(Cr,Al)_2Nb$ are not determined accurately in the area between them, because of the difficulty of separation of the two varieties with such very close compositions.

2.3. Check of the products

After completion of an experiment, the calorimeter is cooled to room temperature and samples are examined. One is crushed into powder with a pestle in a mortar, the powder is X-rayed without any further heat treatment, and the diffraction pattern is compared to available literature data. Another sample is submitted to EPMA and its composition, its homogeneity and the presence of unwanted phases are checked. Standards for EPMA are the pure metals in bulk form.

2.4. Extension of the DRC to phase diagram determination

The DRC process involves fine powders that react together in the solid state, thus it avoids the problems associated with the classical preparation of alloys by melting and solidification. In particular, a compound with peritectic decomposition may be synthesized with nearly no trace of the neighboring phases. In addition, the segregations that may sometimes appear in the samples cannot be larger than the initial grains. It is possible to use our technique, not only to prepare single compounds, but also two or three phase-mixtures in the calorimeter. The enthalpy of reaction can be measured and compared to those of the single phases, as a check of consistency of the results. A difficulty is that, during the cooling of the calorimeter, phase equilibria may change. Once at room temperature the samples are sealed in evacuated silica tubes, heat treated for typically 1 week at the temperature of interest, and quenched in cold water. Then, they are subjected to XRD and EPMA. The main drawback of this method is the level of impurity of fine powders, which is higher than that of refined bulk materials. In addition, contamination during experiments may aggravate the situation. As said before, all samples are prepared inside a glove box under purified argon, and thorough checks are made by EPMA to look at the possible contaminants or impurities.

Table 3
Composition of the phases in equilibrium, at 1000°C, in the Al–Cr–Nb system

Domain number[a]	Phases involved in the equilibrium	Composition of phases by EPMA[b]		
		Al (at.%)	Cr (at.%)	Nb (at.%)
1	$(Al,Cr)Nb_2$	25.5	8	66.5
	$Al(Nb,Cr)_3$	19	4.4	76.6
	$Nb(Al,Cr)_{ss}$	7	5.2	87.8
2	$(Al,Cr)Nb_2$	24.4	10.7	64.9
	$Nb(Al,Cr)_{ss}$	9.7	11.5	78.8
	$(Cr,Al)_2Nb(h)$	14	49.7	36.3
3	$Al_3(Nb,Cr)$	73.8	0.2	26
	$(Al,Cr)Nb_2$	37.6	2.7	59.7
	$(Cr,Al)_2Nb(h)$	44.4	21.3	34.3
4	$Al_3(Nb,Cr)$	73.9	0.9	25.2
	$(Cr,Al)_2Nb(h)$	38.4	27.4	34.2
	$(Cr,Al)Nb_{ss}$	30	69.4	0.6
5	$Al_3(Nb,Cr)$	72.8	1.3	25.9
	Al_8Cr_5	57.4	42.4	0.2
	$(Cr,Al)Nb_{ss}$	39.3	60.6	0.1
6	$Al_3(Nb,Cr)$	74.3	10.8	14.9
	Al_4Cr	77.8	22.1	0.1
	Al_8Cr_5	69.9	29.9	0.2
7	$Al_3(Nb,Cr)$	75.5	3.7	20.8
	Al_4Cr	79.5	20.4	0.1
	Liquid	86.2	13.6	0.2

[a] These numbers correspond to those of Fig. 2.
[b] Uncertainties about compositions are less than 1 at.%.

3. Results

3.1. Al–Cr

This system is different from the two other binaries because its compounds do not dissolve noticeable quantities of niobium, while those of the two other systems accept some amounts of the third element. In addition, the

Table 4
Enthalpies of formation of the compound $Al(Nb,Cr)_3$ as a function of composition

Alloy composition	Calorimeter Temp. °C	Enthalpy of formation (J/mole)	
		$\Delta_f H$ [a] (standard deviation)	$\Delta_f H$ [b] (standard deviation)
$Al_{0.20}Nb_{0.80}$	1426	−19 700 (2300)	−17 900 (2300)
$Al_{0.19}Cr_{0.02}Nb_{0.79}$	1428	−17 200 (1000)	−15 500 (1000)
$Al_{0.19}Cr_{0.04}Nb_{0.77}$	1423	−12 300 (1800)	−10 600 (1800)

[a] Referred to: Al (liq), Cr (cc) and Nb (cc) at T.
[b] Referred to: Al (fcc), Cr (cc) and Nb (cc) at T.

binary phase diagram, which was selected by Massalski et al. [4], did not fit our first results. Consequently, we studied it in detail. Our findings have already been published [7]. We summarize the main points in the following. $Al_{11}Cr_2$ is not stable down to room temperature, but only from 895°C (peritectic decomposition) to 785°C (eutectoid decomposition). Al_9Cr_4 and Al_8Cr_5 are just the same compound with a domain of homogeneity from about 30 to 41 at.% of Cr. The enthalpies of formation of the different phases are given in Table 2.

Table 5
Enthalpies of formation of the compound $(Al,Cr)Nb_2$ as a function of composition

Alloy composition	Calorimeter Temp. °C	Enthalpy of formation (J/mole)	
		$\Delta_f H$ [a] (standard deviation)	$\Delta_f H$ [b] (standard deviation)
$Al_{0.33}Nb_{0.67}$	1426	−29 800 (1000)	−26 800 (1000)
$Al_{0.28}Cr_{0.05}Nb_{0.67}$	1387	−27 700 (1000)	−25 200 (1000)
$Al_{0.33}Cr_{0.04}Nb_{0.63}$	1450	−30 200 (1200)	−27 200 (1200)

[a] Referred to: Al (liq), Cr (cc) and Nb (cc) at T.
[b] Referred to: Al (fcc), Cr (cc) and Nb (cc) at T.

Table 6
Enthalpies of formation of the compound $Al_3(Nb,Cr)$ as a function of composition

Alloy composition	Calorimeter Temp. °C	Enthalpy of formation (J/mole)	
		$\Delta_f H$ [a] (standard deviation)	$\Delta_f H$ [b] (standard deviation)
$Al_{0.74}Nb_{0.26}$	1001	−54 600 (900)	−47 200 (900)
$Al_{0.74}Cr_{0.02}Nb_{0.24}$	1000	−52 550 (1200)	−45 200 (1200)
$Al_{0.74}Cr_{0.04}Nb_{0.22}$	1001	−50 600 (1800)	−43 200 (1800)
$Al_{0.74}Cr_{0.06}Nb_{0.20}$	1001	−49 000 (800)	−41 600 (800)
$Al_{0.74}Cr_{0.08}Nb_{0.18}$	1000	−46 900 (950)	−39 500 (950)
$Al_{0.74}Cr_{0.10}Nb_{0.16}$	1001	−45 200 (800)	−37 800 (800)

[a] Referred to: Al (liq), Cr (cc) and Nb (cc) at T.
[b] Referred to: Al (fcc), Cr (cc) and Nb (cc) at T.

Table 7
Enthalpies of formation of the compound $(Cr,Al)_2Nb$ (h) as a function of composition

Alloy composition	Calorimeter Temp. °C	Enthalpy of formation (J/mole)	
		$\Delta_f H$ [a] (standard deviation)	$\Delta_f H$ [b] (standard deviation)
$Al_{0.10}Cr_{0.567}Nb_{0.333}$	1485	−11 600 (1400)	−10 700 (1400)
$Al_{0.20}Cr_{0.467}Nb_{0.333}$	1485	−20 300 (400)	−18 500 (400)
$Al_{0.30}Cr_{0.367}Nb_{0.333}$	1485	−26 500 (800)	−23 800 (800)
$Al_{0.40}Cr_{0.267}Nb_{0.333}$	1485	−34 900 (1400)	−31 400 (1300)

[a] Referred to: Al (liq), Cr (cc) and Nb (cc) at T.
[b] Referred to: Al (fcc), Cr (cc) and Nb (cc) at T.

3.2. Al–Cr–Nb

Fig. 1 gives the isothermal section at 1000°C, taken from Ref. [5]. The same section that we determined is given in Fig. 2. Table 3 gives the concentrations, determined by EPMA, of the phases involved in the three phase equilibria mentioned in Fig. 2. The following tables give the enthalpies of formation of the different compounds as functions of their compositions. Compound nomenclature is built on this model: $A_x(B,C)_y$ is based on the binary A_xB_y in which some C is substituted. The right stoichiometries are indicated in the tables (Tables 1–7).

4. Conclusion

In this paper we give the first exhaustive experimental thermodynamic study of the Al–Cr–Nb system at 1000°C. The isothermal section of the phase diagram was determined and it is different from what was already pub-

lished. The enthalpies of formation of the compounds were measured as functions of composition and they are, for the best of our knowledge, the first coherent set of data describing the Al–Cr–Nb system. An optimization of the phase diagram will be undertaken in the near future.

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