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PHASE EQUILIBRIA IN THE Gd-Cr-Al SYSTEM AT 500°C

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ABSTRACT

The phase equilibria at 500°C of the Gd-Cr-Al system have been investigated in the whole concentration region. Three ternary compounds were confirmed and their homogenity regions have been investigated. The crystal structure of all compounds have been refined by Rietveld profile analysis: $GdCr_{2.3\text{-}2.0}Al_{19.7\text{-}20.0}$ ($CeCr_2Al_{20}$ structure type, space group $Fd\bar{3}m$, a=1.44718(3)-1.44822(4) nm), $Gd_6Cr_4Al_{43}$ ($Ho_6Mo_4Al_{43}$ structure type, space group $P6_3/mcm$, a=1.09126(14) nm, c=1.7749(3) nm), $GdCr_{4.0\text{-}2.8}Al_{8.0\text{-}9.2}$ ($ThMn_{12}$ structure type, space group $I4/mmm$, a=0.89780(18)-0.90395(15) nm, c=0.51332(9)-0.51253(9) nm).

INTRODUCTION

Some of the aluminium based alloys and intermetallics possess valuable physical, chemical and mechanical properties and have wide practical application. In order to develop new materials, there is an increasing interest in phase diagrams of relevant alloy systems.

Among the R-Cr-Al (R = rare earth) ternary systems the isothermal sections were investigated partialy for the {Sc, Y, La, Ce, Dy}-Cr-Al systems [1-5] and in the whole concentration region for the Yb-Cr-Al [6] system. The separate alloys of these systems were investigated for the existence of the isostructural ternary compounds found in other related ternary systems R-Cr-Al [7].

Phase equilibria in the Gd-Cr-Al ternary system are not studied to date. Three compounds of the constant composition $GdCr_2Al_{20}$ ($CeCr_2Al_{20}$ structure type) [8], $Gd_6Cr_4Al_{43}$ ($Ho_6Mo_4Al_{43}$ structure type) [9] and $GdCr_4Al_8$ ($ThMn_{12}$ structure type) [10] have been identified in the system earlier. The aim of this investigation is to build phase equilibria in the Gd-Cr-Al system at 500°C and to evaluate regularities of interaction of Al with Cr and rare earth metals.

EXPERIMENTAL

Alloys were prepared by arc-melting of initial components under high purity argon on a water-cooled copper hearth. Starting materials were used in the form of pieces of high purity metals (Gd 99.9 wt.%, V 99.99 wt.%, Al 99.997 wt.%). The samples were remelted twice for better homogenation. Ingots were afterwards sealed in evacuated quartz tubes and annealed at 500°C for 2000 h. After heat treatment the samples were quenched by submerging the silica tubes in cold water.

Phase analysis of the alloys have been determined from the X-ray diffraction pattern obtained on DRON-2.0 diffractometer (Fe*Ka*-radiation) with Ge or Si as internal standard. Diffractograms were obtained in a continuous mode on a chart strip with a rate 2°/min within the 2θ region 20-130°. HZG-4a diffractometer (Cu*Ka*-radiation) was used for the obtaining data for the crystal structure determination of the ternary compounds under the following scanning parameters: 2θ region 10-140°, step scan 0.05°, counting time per step 10-18 s. Theoretical diffractograms were calculated using the PowderCell program [11]. The lattice parameters were obtained by least-squares fits using the Latcon program [12]. All the crystal structure calculations were performed by the Rietveld method using the FullProf program [13].

RESULTS

Binary systems and solid solution ranges of the binary compounds

The Gd-Al, Cr-Al and Gd-Cr boundary binary systems were completely investigated earlier [14-15]. The existence of ten binary compounds at 500°C has been confirmed: $GdAl_3$ ($BaPb_3$ structure type), $GdAl_2$ ($MgCu_2$), GdAl (DyAl), Gd_3Al_2 (Gd_3Al_2), Gd_2Al (Co_2Si), Cr_7Al_{45} (V_7Al_{45}), $CrAl_4$ ($CrAl_4$), Cr_4Al_9 (Cr_4Al_9), Cr_5Al_8 (Cr_5Al_8) and Cr_2Al ($MoSi_2$).

Among the Gd-Al binary compounds maximum solid solubility of Cr was found for $GdAl_2$, which dissolves ~16 at.% Cr. Lattice parameters change from a=0.79052(6) nm for $GdAl_2$ to a=0.78842(3) nm for $GdCr_{0.48}Al_{1.52}$. Other Gd-Al binary compounds solute no more than 3 at.% Cr. Practically no solubility of Gd in the Cr-Al binary compounds was observed.

Gd-Cr-Al ternary system and crystal structure of the ternary compounds

Three ternary compounds were confirmed. The lattice paremeters of the compounds are presented in Table 1.

Table 1. Crystal structure data of the Gd-Cr-Al ternary compounds

Compound	Structure type	Space group	Lattice parameters (nm)		Ref.
			a	*c*	
$GdCr_2Al_{20}$	$CeCr_2Al_{20}$	$Fd\bar{3}m$	1.440	-	[8]
$GdCr_{2.3\text{-}2.0}Al_{19.7\text{-}20.0}$			1.44718(3)-1.44822(4)	-	*
$Gd_6Cr_4Al_{43}$	$Ho_6Mo_4Al_{43}$	$P6_3/mcm$	1.0886	1.7725	[9]
			1.09126(14)	1.7749(3)	*
$GdCr_4Al_8$	$ThMn_{12}$	$I4/mmm$	0.8967	0.5128	[10]
$GdCr_{4.0\text{-}2.8}Al_{8.0\text{-}9.2}$			0.89780(18)-0.90395(15)	0.51332(9)-0.51253(9)	*

* this work

Isothermal section at 500°C of the Gd-Cr-Al phase diagram is presented in Fig.1.

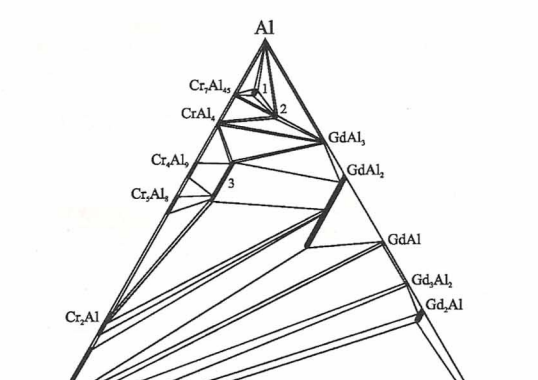

Figure 1. Gd-Cr-Al isothermal section at 500°C. Ternary compounds: (1) $GdCr_{2.3\text{-}2.0}Al_{19.7\text{-}20.0}$; (2) $Gd_6Cr_4Al_{43}$; (3) $GdCr_{4.0\text{-}2.8}Al_{8.0\text{-}9.2}$

The crystal structure of all compounds have been refined by Rietveld profile analysis. The crystal structure of $GdCr_{2+x}Al_{20-x}$ and $Gd_6Cr_4Al_{43}$ compounds was investigated by means of profile analysis of X-ray powder pattern using multiphases samples with the nominal compositions $Gd_5Cr_{10}Al_{85}$ and $Gd_{12}Cr_8Al_{80}$, respectively (Fig. 2*a*, *b*). Atomic coordinates and isotropic temperature parameters are given in Tables 2 and 3.

Table 2. Atomic coordinates and isotropic temperature parameters for the $GdCr_{2+x}Al_{20-x}$ (x=0.3) compound (structure type $CeCr_2Al_{20}$, $Fd\bar{3}m$ space group, a=1.44718(3) nm, R_p=2.04%, R_{wp}=2.68%)

Atoms	Site	*x*	*y*	*z*	B_{iso}, 10^{-2} nm
Gd	*8a*	1/8	1/8	1/8	0.9(1)
Cr	*16d*	1/2	1/2	1/2	0.9(2)
Al1	*16c*	0	0	0	1.1(3)
Al2	*48f*	0.4872(8)	1/8	1/8	1.1(3)
M*	*96g*	0.0590(4)	x	0.3275(5)	1.2(2)

* M=0.97Al + 0.03Cr

The impurity phases in these samples were $Gd_6Cr_4Al_{43}$ and $GdAl_3$, respectively. According to the X-ray data of the Al-rich alloys the $GdCr_{2+x}Al_{20-x}$ ternary compound has narrow homogeneity region about 2 at.% Al(Cr) at 500°C.

Table 3. Atomic coordinates and isotropic temperature parameters for the $Gd_6Cr_4Al_{43}$ compound (structure type $Ho_6Mo_4Al_{43}$, $P6_3/mcm$ space group, a=1.09126(14) nm, c=1.7749(3) nm, R_p=1.76%, R_{wp}=2.30%)

Atom	Site	x	y	z	B_{iso}, 10^{-2} nm
Gd	*12k*	0.5308(6)	0	0.0954(4)	0.5(2)
Cr1	*6g*	0.737(4)	0	1/4	0.4(3)
Cr2	*2b*	0	0	0	0.4(3)
Al1	*24l*	0.165(3)	0.396(3)	0.158(2)	0.4*
Al2	*12k*	0.161(3)	0	0.613(3)	0.4*
Al3	*12k*	0.255(5)	0	0.030(2)	0.4*
Al4	*12j*	0.159(4)	0.598(5)	1/4	0.4*
Al5	*12i*	0.240(5)	2x	0	0.4*
Al6	*8h*	1/3	2/3	0.129(3)	0.4*
Al7	*6g*	0.139(6)	0	1/4	0.4*

* fixed parameter

The X-ray analysis of the annealed at 500°C alloys of the 7.7 at.% Gd isoconcentrate showed, that the homogeneity region of the $GdCr_4Al_8$ ternary compound is wide and extends from 20 to 30 at.% Cr, i.e. it's composition is as follows $GdCr_{4.0\text{-}2.8}Al_{8.0\text{-}9.2}$. Crystallographic data for the $GdCr_xAl_{12\text{-}x}$ (x=4.00, 3.65, 3.25 and 2.80) alloys, final atomic coordinates and their displacement parameters are summarized in Table 4.

Table 4. Crystallographic data, final atomic coordinates and displacement parameters for the $GdCr_xAl_{12\text{-}x}$ (x=4.00, 3.65, 3.25 and 2.80)

$GdCr_xAl_{12\text{-}x}$	**x=4**	**x=3.65**	**x=3.25**	**x=2.80**
a, nm	0.89780(18)	0.89913(10)	0.90119(15)	0.90377(15)
c, nm	0.51332(9)	0.51221(6)	0.51118(9)	0.51260(8)
V, nm^3	0.4138	0.4141	0.4152	0.4187
R_p, %	3.00	2.60	2.27	2.29
R_{wp}, %	3.82	3.38	3.06	3.03
Gd 2*a* (0,0,0)				
B_{iso}, 10^{-2} nm	0.2(3)	0.9(3)	1.5(3)	1.1(3)
M1 8*f* (¼, ¼, ¼)				
B_{iso}, 10^{-2} nm	0.6(4)	0.5(3)	1.3(4)	0.5(4)
Occ (Al, Cr)	8Cr	2.1Al + 5.9Cr	2.7Al + 5.3Cr	3.3Al + 4.7Cr
M2 8*i* (*x*, 0, 0)				
x	0.350(3)	0.344(3)	0.348(3)	0.356(3)
B_{iso}, 10^{-2} nm	0.5(6)	0.4(5)	1.3(6)	0.5(6)
Occ (Al, Cr)	8Al	8Al	8Al	7.7Al + 0.3Cr
M3 8*j* (*x*, ½, 0)				
x	0.282(3)	0.276(3)	0.277(2)	0.279(3)
B_{iso}, 10^{-2} nm	0.5(5)	0.6(5)	1.3(5)	0.6(6)
Occ (Al, Cr)	8Al	6.6Al + 1.4Cr	6.8Al + 1.2Cr	7.4Al + 0.6Cr

Results of the Rietveld profile refinement of the $GdCr_xAl_{12-x}$ XRD data are presented in Fig. 2*c-f*.

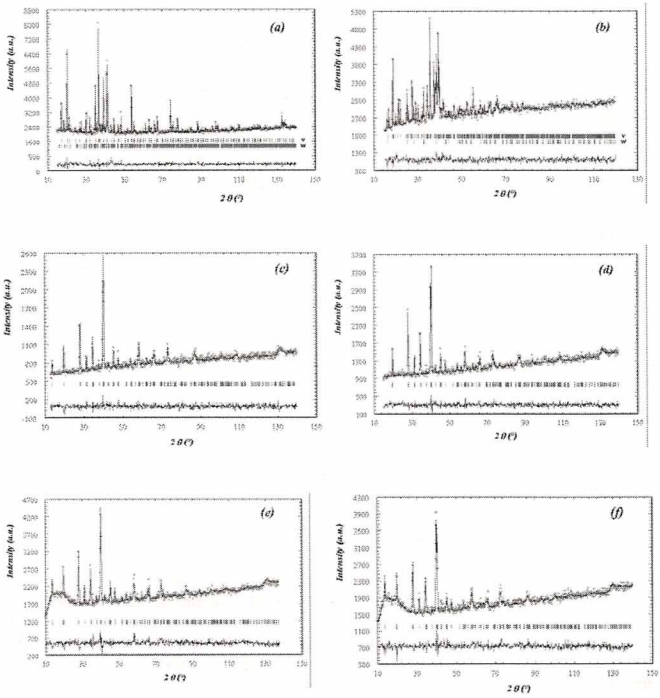

Figure 2. Results of the Rietveld refinement of the $Gd_5Cr_{10}Al_{85}$ (v - $GdCr_{2.3}Al_{19.7}$, w - $Gd_6Cr_4Al_{43}$) (*a*), $Gd_{12}Cr_8Al_{80}$ (v - $Gd_6Cr_4Al_{43}$, w - $GdAl_3$) (*b*), $Gd_{7.7}Cr_{31}Al_{61.3}$ ($GdCr_4Al_8$) (*c*), $Gd_{7.7}Cr_{28}Al_{64.3}$ ($GdCr_{3.65}Al_{8.35}$) (*d*), $Gd_{7.7}Cr_{25}Al_{67.3}$ ($GdCr_{3.25}Al_{8.75}$) (*e*) and $Gd_{7.7}Cr_{22}Al_{70.3}$ ($GdCr_{2.80}Al_{9.20}$) (*f*) alloys. Observed (dots), calculated (line) and difference (bottom) profiles.

CONCLUSIONS

The summarized data on investigation of the R-Cr-Al systems are presented in Table 5.

Table 5. Summarized data on investigation of the R-Cr-Al systems

R	Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu
Phase diagram	Δ	Δ	Δ	Δ	—	—	—	—	—
Number of ternary compounds	0	3	3	3	2	3	-	3	1
$CeCr_2Al_{20}$*	-	+	+	+	+	+	-	+	+
$Ho_6Mo_4Al_{43}$*	-	+	-	-	-	+	-	+	-
$CeMn_4Al_8$*	-	+	-	-	+	+	-	+	-
$ThMn_{12}$*	-	-	+	+	-	-	-	-	-
Th_2Zn_{17}*	-	-	+	+	-	-	-	-	-

R	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Phase diagram	Δ	—	Δ	—	—	—	Δ	—
Number of ternary compounds	3	3	3	3	3	2	3	-
$CeCr_2Al_{20}$*	+	+	+	+	+	-	+	-
$Ho_6Mo_4Al_{43}$*	+	+	+	+	+	+	+	-
$CeMn_4Al_8$*	-	+	+	+	+	+	-	-
$ThMn_{12}$*	+	-	-	-	-	-	+	-
Th_2Zn_{17}*	-	-	-	-	-	-	-	-

Δ - isothermal section of the ternary system is investigated
— - isothermal section of the ternary system is not investigated
+ - the ternary compounds exist in the system
- - there are no data
* - structure type of ternary compounds

Apparently phase equilibria of the investigated ternary system are similar. Only the Sc-Cr-Al ternary system is in contrast with other systems. In all investigated R-Cr-Al systems the ternary compounds occur in the region with the high aluminium content above 50 at.%. Formation of the ternary phases with the $CeCr_2Al_{20}$, $Ho_6Mo_4Al_{43}$ and $ThMn_{12}$ ($CeMn_4Al_8$) structure types is typical almost for all investigated R-Cr-Al systems.

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