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Solid solubility by anti-site atoms in the C36-$TiCr_2$ Laves phase revealed by single-crystal X-ray diffractometry

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ABSTRACT

Structure refinements of the C36-$TiCr_2$ Laves phase have been performed on the basis of X-ray diffraction data collected from single crystals containing 33.7 at.% Ti (i.e. near-stoichiometric) and 35.6 at.% Ti (Ti-rich off-stoichiometric). The results indicate that the solid solubility of Ti-rich C36-$TiCr_2$ is predominantly realised by anti-site atoms, i.e. by Ti atoms occupying Cr sites. Constitutional Cr vacancies play at maximum a minor role.

1. Introduction

The occurrence of homogeneity ranges of crystalline, solid phases always raises the question how the changes in composition are realised on the atomic level [1], i.e. by which types of constitutional point defects the required composition changes are realised with respect to an ideal reference structure. Within the field of metals and alloys the most prominent case for extended homogeneity ranges are the simple substitutional (terminal or intermediate) solid solutions of cubic or hexagonal close-packed (Cu and Mg type) or of body-centred cubic structure (W type). In these the same atomic site (“sublattice”) is virtually completely[1] occupied by two (in binary systems) or more (in multinary systems) types of atoms, where the compositional changes are achieved by varying the fractions of atoms occupying completely the mentioned site. This behaviour is contrasted by the interstitial solid solutions and phases. In these (for the simplest, binary cases) one type of sites is virtually completely occupied by metal atoms (in many cases the arrangement of these sites corresponds to the above-mentioned Cu, Mg and W type structures) and another type of sites is partially occupied by some small main-group atoms like H, N, C, O and occasionally B. In these interstitial solid solutions and phases the compositional change is realised by changing the occupancy of the interstitial sites, which is connected with a change of the amount of vacancies “residing” on the same sites.

Based on similar structural principles as described above, compositional changes can also be realised in many, structurally more complex intermetallic phases. As above, an ideal reference structure can be defined for a specific composition, which usually but not necessarily belongs to the homogeneity range of the phase. One of the well-studied cases is a group of CsCl type transition-metal aluminides or gallides, in particular NiAl [2]. The latter has a considerable homogeneity range around the ideal composition NiAl (Ni_1Al_1), where different structural mechanisms, i.e. different types of constitutional point defects are responsible to realise the solid solubility on the Al-poor and Al-rich side (relative to 50 at.% Al) of the homogeneity range. Whereas on the Al-poor side, Ni atoms substitute the Al atoms (formula $(Ni)_1(Al_{1-x}Ni_x)_1$; Ni anti-site atoms), on the Al-rich side vacancies substitute Ni atoms (formula $(Ni_{1-y}Va_y)_1Al_1$ with Va: vacancy; constitutional vacancies).

The Laves phases form a large group of intermetallics [3], with many members attracting considerable interest, e.g. as possible high-temperature materials and as materials for hydrogen storage [4]. The Laves phases belong to the family of Frank–Kasper phases [5] and are often simplistically regarded as line compounds with an AB_2 composition, where A and B are metal atoms with A having a larger atomic radius than B. The ideal ratio of the atomic radii amounts $r_A/r_B = 1.225$, and in all Laves phases of ideal AB_2 composition the A and B atoms occupy definite sites surrounded

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[1] Thermal vacancies and other thermal point defects are not considered in the present paper.

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by Frank–Kasper polyhedra: the *A* atom sites exhibit a coordination number of 16 with 4 *A* and 12 *B* atoms as nearest neighbours whereas *B* atom sites exhibit a coordination number of 12 (a distorted icosahedron) with 6 *A* and 6 *B* atoms as nearest neighbours.

These polyhedra occur in all Laves phase structure types, which can be regarded as a series of polytypes based on certain types of layers [3,6]. These polytypes are 1:1 analogues of the polytypes of the close-packed structures. The simplest and most frequently occurring polytypes are commonly named by the Strukturbericht symbols C15 (XYZ stacking, $MgCu_2$ type), C14 (XY stacking, $MgZn_2$ type) and C36 (XYXZ stacking, $MgNi_2$ type), with X, Y and Z denoting the stacking positions of the layers perpendicular to the stacking direction.

In spite of the commonly used simple formula AB_2,[2] many binary Laves phase systems exhibit (large) homogeneity ranges [3,7], extending on the *A*-poor (<33.3 at.% *A*) and/or on the *A*-rich side (>33.3 at.% *A*). This rises – as above – the question how possibly existing solid solubility involving the indicated deviations from ideal AB_2 composition is realised. In most works as constitutional point defects the possibilities of anti-site atoms or of constitutional vacancies have been considered [8].[3]

Anti-site substitution has been reported on the basis of macroscopic density measurements in comparison with calculated densities (based on the measured lattice parameters and the corresponding structure model) for several binary Laves phase alloys (for both excess of *A* and *B* atoms) such as $NbCo_2$ [9,10], $NbFe_2$ [9], $ZrCo_2$ [11], $TiFe_2$ [12], $ZrMn_2$ [13], and $HfCo_2$ [14]. Similarly, X-ray diffraction investigations on single crystals indicated the presence of anti-site atoms for (C36-)$NbCo_2$ Laves phase [15]. However, constitutional vacancies have been suggested to exist on the *A*-rich side of the homogeneity range (*B* vacancies) for $MgZn_2$ [16], $ZrCr_2$ [17] and $TiCr_2$ [18] by the same type of density measurements and for $NbCr_2$ [19] by combination of geometrical considerations and the concentration dependence of the lattice parameters. Similarly, constitutional vacancies have been suggested to exist for *A*-poor (*A* vacancies) rare earth-(RE)-nickel Laves phases (e.g. $La_{1-x}Ni_2$) on the basis of diffraction methods and density measurements [20,21].

However, for some systems, except perhaps for the $RENi_2$ systems, the experimental evidence for occurrence of constitutional vacancies seems to be relatively poor. Sometimes the conclusions have been drawn from only few density-data points, which by the presence of often unavoidable pores may also misleadingly indicate the presence of vacancies. Indeed, alternative investigations on $NbCr_2$ (density measurements [22]) and also on $ZrCr_2$ (density measurements [23], first principles calculations [24]) seem to indicate explicitly the predominance of anti-site atoms instead of constitutional vacancies as mechanism for solid solubility in these Laves phases.

The present work focuses on the constitutional defects realising solid solubility in C36-$TiCr_2$. In the Ti–Cr system all three above-mentioned, main Laves phase polytypes occur, where the homogeneity ranges comprise compositions, which are Ti-rich with respect to the ideal 33.3 at.% Ti [25]. The C36 phase is the medium-temperature phase, whereas the C14 high-temperature phase is stable above 1550 K and the C15 low-temperature phase is stable below a strongly composition-dependent transformation temperature of 1050–1480 K. However, formation of the C15 phase requires relatively long annealing times so that the C36 phase is easily retained at room temperature upon cooling $TiCr_2$ Laves phase alloy from temperatures, at which the C36 polytype is stable. In the course of a project mainly devoted to studying the C36 $\leftrightarrows$ C14 transformation of $TiCr_2$ [26,27], single crystals became available of C36-$TiCr_2$ having different Ti contents. The structure refinements on the basis of X-ray diffraction data collected from these single-crystal allow to reject the previously proposed major (at least 50%) contribution of constitutional vacancies to non-stoichiometry in Ti-rich C36-$TiCr_2$ [18] and suggest that instead predominantly anti-site atoms are responsible for establishing the solid solubility.

2. Experimental

2.1. Sample preparation

Two C36-$TiCr_2$ alloys with different compositions (alloy I: 33.0 at.% Ti/67.0 at.%; alloy II: 35.8 at.% Ti/64.2 at.% Cr; as weighed in) were prepared by arc melting high-purity metals (titanium purity 99.999%; chromium purity 99.999%) under a titanium-gettered argon atmosphere. Afterwards the $TiCr_2$ ingots were subjected to further heat treatments, where the final annealing step was 50 h at 1473 K followed by rapid cooling by switching off the employed induction furnace. For a detailed description of the sample production process, see Ref. [26]. The ingots were then smashed in a mortar. From the resulting particles single crystals were selected, referred to as near-stoichiometric single-crystal I and Ti-rich single-crystal II, where the Roman numbers refer to the respective alloys.

2.2. X-ray powder diffraction on the alloys

From both alloys powder diffraction patterns for lattice parameter determination have been recorded. For that purpose the alloy powders were mixed with silicon powder as internal standard and the overall powder was sedimented as a thin layer on (5 1 0)-cut Si crystals. X-ray powder diffraction patterns were recorded using an X'Pert MPD diffractometer (Philips/Panalytical) equipped with a germanium monochromator in the primary beam using Cu Kα1 radiation (λ = 1.54056 Å). The lattice parameters *a* and *c* of the Laves phase have been extracted by a two-phase Rietveld fit using TOPAS [28], adopting a fixed lattice parameter for the Si reflections (*a* = 5.4310 Å), and allowing for refined zero-point off-set and height errors.

2.3. X-ray diffraction on single crystals

The single-crystal X-ray diffraction data was gathered using a Bruker AXS Smart-CCD diffractometer equipped with a graphite-monochromator, using Mo Kα radiation. The intensities were corrected for Lorentz and polarisation effects, and a multi-scan absorption correction was applied [29]. The diffraction data were basis for structure refinements using the software Jana2006 [30]. Details on the crystals, on data collection and on structure refinements have been compiled in Table 1.

3. Results and discussion

The main aim for the structure analysis of the two C36-$TiCr_2$ crystals of different compositions was the determination of the types of constitutional point defects by which the Laves phase crystal structure adapts to the deviation of the crystals' composition from 33.3 at.% Ti, considering the possibility of anti-site atoms and of constitutional vacancies. However, the small scattering contrast between Ti and Cr forbids an indiscriminate refinement of the crystal structure including refinement of site occupancies for these atoms for identification of the types of constitutional point defects present. Therefore, the composition of the crystals is taken as input information for the structure refinements. Moreover, two idealised models are considered (Table 2), emanating from the ideal C36 type Laves phase structure and considering the fact that both crystals are Ti-rich with respect to the ideal composition (33.3 at.% Ti; see what follows). While refining the occupancies of the Cr1, Cr2 and Cr3 sites according to both models, the composition was respectively held fixed by introducing constraints in the restrictions menu in Jana2006.

The compositions of the two crystals I and II to be used as input information for the structure refinements were assessed on the basis of the lattice parameters determined by X-ray powder diffraction of the alloys, from which the crystals had been isolated. To interpret these lattice parameter values in terms of composition,

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[2] Also in the present paper, the formula AB_2 indicates the Laves phase in general, without specifying a specific composition, which is instead indicated by the molar fraction of the *A* component.

[3] Indeed also the occurrence of substitution of *A* atoms by *B* tetrahedra has been suggested [8], but never experimental evidence for this type of more complex constitutional point defects has been presented.

Table 1

Details of X-ray diffractometry and structure refinement on crystal I and II using a constitutional vacancy (left subcolumn) and an anti-site atom model (right subcolumn, see also Tables 2 and 3).

Formula	Crystal I ≈ $TiCr_2$ (close to stoichiometric)		Crystal II ≈ $TiCr_2$ (Ti-rich)	
Diffractometer	Bruker AXS Smart-CCD			
Radiation, wavelength	Mo Kα1			
Crystal system, space group	*Hexagonal*, $P6_3/mmc$ (No. 194)			
Crystal shape and size (mm^3)	0.08 × 0.07 × 0.02		0.2 × 0.12 × 0.09	
Index range				
h	−8, 7		−7, 7	
k	−8, 7		−7, 7	
l	−19, 19		−25, 25	
Software	Jana2006			
Cell parameters of alloy[a]				
a (Å)	4.9090		4.9226	
c (Å)	15.9675		15.9975	
Ti content derived from cell parameters of alloy (adopted for refinement)	33.7 at.%		35.6 at.%	
Cell parameters of crystal				
a (Å)	4.9031(4)		4.9216(8)	
c (Å)	15.953(1)		15.992(3)	
Ti content derived from cell parameters of crystals (not considered for refinement)	32.9 at.%		35.4 at.%	
Cell volume (Å)	332.13		335.58	
No. of formula units per unit cell	4		4	
Calculated density/(Mg m^{-3})	6.01	6.07	5.62	6.00
Absorption coefficient (mm^{-1})	16.7	16.9	15.6	16.6
No. of measured reflections	5242		4781	
No. of independent reflections all/$I \geq 3\sigma(I)$	317/238		320/271	
R_{int}	0.0315		0.0334	
No. of structural parameters	20	20	20	20
Min/max residual electron density $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/$Å^{-3}$)	−0.95/2.67	−1.50/1.86	−0.88/0.91	−0.84/0.97
R ($F^2 \geq 3\sigma(F^2)/R$(all))	0.0166/0.0259	0.0174/0.0266	0.0349/0.0398	0.0280/0.0327
wR ($F^2 \geq 3\sigma(F^2)/R$(all))	0.0230/0.0253	0.0231/0.0253	0.0550/0.0563	0.0343/0.0363
CSD number	–	CSD-421648	–	CSD-421647

[a] The Rietveld-type standard deviations are ≤0.0001 Å.

linear functions were fitted to lattice parameter vs. composition data reported in Ref. [27]. In that work the lattice parameters had been determined on the basis of measurements similar to those described in the present paper and the compositions were determined by electron-probe microprobe analysis (EPMA; standard deviations are given here and elsewhere in parentheses; the present ones result from the scatter of the data points):

$$\begin{aligned} a &= 4.9067(5)\ \text{Å} + 0.70(4)\,\text{Å}\ (f_{Ti} - 1/3) \\ c &= 15.9598(5)\ \text{Å} + 1.62(3)\,\text{Å}\ (f_{Ti} - 1/3) \end{aligned} \tag{1}$$

where f_{Ti} is the mole fraction of Ti in $TiCr_2$.

These expressions yield as average values from a and c 33.7 at.% Ti for alloy I and thus for crystal I and 35.6 at.% Ti for alloy II and thus for crystal II (see Table 1). It must be noted that the values pertaining to the lattice parameters determined from the single crystals lead to 32.9 at.% and 35.4 at.% Ti for crystal I and II, i.e. different values than determined from powder diffractometry of the alloys (Table 1). Whereas for crystal II the results are relatively close, the differences seem considerable for crystal I. However, both values for alloy I/crystal I are close to the ideal 33.3 at.% Ti such that crystal I can, in any case, represent for the present study the close to stoichiometric state of the Laves phase with only very few constitutional point defects.

The structure refinements on the basis of the diffraction data from crystals I and II converged for both models, respectively. The respective results have been listed in Table 3 and the residuals in Table 1.

For the Ti-rich crystal II the structure refinements clearly yield much better residuals for the anti-site atom model than for the constitutional vacancy model, indicating adequateness of the anti-site atom model for crystal II. The occupancy data in Table 3 suggest a preference of Ti for the Cr3/4f site. However, the reliability of this statement is low due to the small scattering contrast between Ti and Cr (see above).

Although the refinements on the basis of the two ideal models clearly favour the anti-site atom model, the question remains, to what extent a minor amount of constitutional vacancies defects may be present. For this reason test refinements have been performed assuming the mutual presence of constitutional vacancies and anti-site atoms corresponding the fixed formulas (with increasing constitutional vacancy

Table 2

Occupancies resulting for the constitutional vacancy model and for the anti-site atom model for realisation of solid solubility for Ti contents larger than 33.3 at.%.

Site	Wyckoff symbol	x	y	z	Constitutional vacancy model	Anti-site atom model
Ti1	4f	1/3	2/3	z_{Ti1} (≈21/32)	1	1
Ti2	4e	0	0	z_{Ti2} (≈3/32)	1	1
Cr1	6h	x_{Cr1} (≈1/6)	$2x_{Cr1}$	1/4	$(1-occ1)$ Cr $occ1$ Va	$(1-occ'1)$ Cr $occ'1$ Ti
Cr2	6g	1/2	0	0	$(1-occ2)$ Cr $occ2$ Va	$(1-occ'2)$ Cr $occ'2$ Ti
Cr3	4f	1/3	2/3	z_{Cr3} (≈1/8)	$(1-occ3)$ Cr $occ3$ Va	$(1-occ'3)$ Cr $occ'3$ Ti
Formula					$Ti(Cr_{1-p}Va_p)_2$ $f_{Ti} = \frac{4}{12-3occ1-3occ2-2occ3} = \frac{1}{3-2p}$	$Ti(Cr_{1-q}Ti_q)_2$ $f_{Ti} = \frac{4+3occ'1+3occ'2+2occ'3}{8} = \frac{1+2q}{3}$

Table 3
Refined fractional coordinates, occupancies and equivalent isotropic displacement parameters (U_{eq}, in Å^2) in C36-TiCr$_2$ for crystal I and crystal II for both the constitutional vacancy model and the anti-site atom model for realisation of solid solubility.

Crystal	Model formula	z_{Ti1} z_{Ti2} x_{Cr1} [b] z_{Cr3} [b]	Occupation Cr1[a] Occupation Cr2[a] Occupation Cr3[a]	U_{eq}(Ti1) U_{eq}(Ti2) U_{eq}(Cr1)[b] U_{eq}(Cr2)[b] U_{eq}(Cr3)[b]
Crystal I	Constitutional	0.65619(5)	0.986(3) Cr	0.00662(19)
	vacancies	0.09426(5)	0.980(2) Cr	0.00659(18)
	(rejected)	0.16279(5)	0.986(3) Cr	0.00566(19)
	Ti($Cr_{0.984}Va_{0.016}$)$_2$	0.12439(5)		0.00532(18)
				0.00564(17)
	Anti-site	0.65619(5)	1.00(2) Cr/0.00(2) Ti	0.00605(19)
	atoms	0.09427(5)	0.962(19) Cr/0.038(19) Ti	0.00602(18)
	(approved)	0.16278(5)	1.00(2) Cr/0.00(2) Ti	0.00539(17)
	Ti($Cr_{0.995}Ti_{0.005}$)$_2$	0.12440(5)		0.00539(17)
				0.00560(17)
Crystal II	Constitutional	0.65622(8)	0.904(5) Cr	0.0110(3)
	vacancies	0.09440(9)	0.897(3) Cr	0.0114(3)
	(rejected)	0.16300(9)	0.916(5) Cr	0.0070(4)
	Ti($Cr_{0.904}Va_{0.096}$)$_2$	0.12420(8)		0.0068(3)
				0.0076(3)
	Anti-site	0.65627(5)	0.98(3) Cr/0.02(3) Ti	0.0078(2)
	atoms	0.09440(6)	0.97(2) Cr/0.03(2) Ti	0.0080(2)
	(approved)	0.16298(6)	0.93(3) Cr/0.07(3) Ti	0.0074(2)
	Ti($Cr_{0.966}Ti_{0.034}$)$_2$	0.12423(5)		0.0075(2)
				0.0075(2)

[a] These occupancies have been refined under the restriction that the weighted sums of the occupancies are compatible with the assessed composition of the respective crystal (see Table 1).

[b] For the anti-site atom model, these parameters also pertain to the Ti atoms residing on the corresponding Cr sites.

contents) Ti($Cr_{0.966}Va_0Ti_{0.034}$)$_2$, Ti($Cr_{0.960}Va_{0.010}Ti_{0.030}$)$_2$, Ti($Cr_{0.953}Va_{0.020}Ti_{0.027}$)$_2$, Ti($Cr_{0.940}Va_{0.040}Ti_{0.020}$)$_2$, Ti($Cr_{0.927}Va_{0.060}Ti_{0.013}$)$_2$, Ti($Cr_{0.914}Va_{0.080}Ti_{0.006}$)$_2$, and Ti($Cr_{0.904}Va_{0.096}Ti_0$)$_2$, keeping thus the Ti content constant at 35.6 at.%. Among these formulas the two end members correspond to exclusive occurrence of anti-site atoms and constitutional vacancies. For simplicity it was assumed that for each of the vacancy contents, the fraction of vacancies and of anti-site Ti atoms was equal on the Cr1, Cr2 and Cr3 sites (compare Table 2). These refinements indicate a broad minimum of the residual parameters for small vacancy contents close to Ti($Cr_{0.960}Va_{0.010}Ti_{0.030}$)$_2$, i.e. close to the pure anti-site atom model (see Supplementary material). The residual parameters considerably increase if more and more vacancies are introduced. On this basis it can be concluded that the presence of a small amount of constitutional vacancies cannot be excluded. However, the data would also be compatible (due to the broad minimum of the residuals) with a complete absence of constitutional vacancies. The present data thus disagree with the conclusion from previous density measurements [18] which suggested that at least half of the compositional change should be accommodated by constitutional vacancies in Ti-rich TiCr$_2$.

In contrast to the clear results for the Ti-rich crystal II, the structure refinements on the basis of the data recorded from the near-stoichiometric crystal I yield quite similar residuals both for the anti-site atom model and for the constitutional vacancy model. This is indeed expected, because, although the two models differ by the type of constitutional point defects assumed to be present, the concentration of defects is very small for both models taking into account the assessed composition of crystal I (as compared to crystal II). Thus both models feature nearly the same crystal structure for crystal I (they become identical for 33.3 at.% Ti). In fact, the differences in the residual parameters may even be accidental, and a clear distinction of the models is probably beyond the sensitivity of single-crystal structure analysis. Consequently, the residuals of the refinements for crystal I pertaining to the two structure models alone cannot confirm the anti-site atom model found applicable for crystal II, but they also do not contradict it.

The larger atomic displacement parameters obtained for crystal II, as compared to crystal I (see Table 3), can be attributed to static displacements of the atoms due to the local disorder in the crystal structure [31]. Indeed, in favourable cases the information associated with the corresponding atomic displacements, which in general can be distinctly non-Gaussian, e.g. due to a superposition of the atomic probability density functions pertaining to the components of “split atoms” [32], can be used to extract information about the local atomic configuration. This succeeded, e.g. in non-stoichiometric intermetallic phases [33,34] and in particular also in Co-rich C36-NbCo$_2$ Laves phase [15]. However, in the present case the small scattering contrast between Ti and Cr and the probably not very large magnitude of the static displacements make it unlikely that detailed information can be extracted. Indeed, for crystal II a refinement of non-Gaussian displacement parameters gave only moderate improvement of the refinement results, which are of the same order of magnitude as the improvements for crystal I, for which no static displacements are expected.

The refined fractional coordinates partially agree and partially disagree with the results from other structure refinements of C36-Laves phases MgNi$_2$ [6] and NbCo$_2$ [15]. For example, the previously observed and well-understood [6,15] bond-distance differences within one type of Kagomé layers of B atoms on $z = 1/4$ as resulting from $x_{Cr1} < 1/6$ is found for both C36-TiCr$_2$ crystals, see Table 3. However, for both C36-TiCr$_2$ crystals $z_{Cr3} < 1/8$ is observed here (test refinements confirm this deviation to be well significant; see Table 3) whereas for both C36-MgNi$_2$ and C36-NbCo$_2$ $z_{Cr3} > 1/8$ was obtained. Discussion of the reasons for these differences of the crystal structures is, however, beyond the scope of the present work.

The preferential formation of Ti anti-site atoms in Ti-rich TiCr$_2$ agrees with trends in most binary Laves phase systems AB_2 with A and B being 3d/4d/5d metals (see Section 1). From a geometric point of view substitution of smaller Cr by larger Ti atoms does not seem to be too surprising due to the atomic radius ratio $r_{Ti}/r_{Cr} = 1.17$ being considerably smaller than the ideal value of 1.225 [35]. Note that in contrast to that the atomic radius ratio of $La_{1-x}Ni_2$, within which presence of La constitutional vacancies seems to be well established [20,21], assumes an exceptionally large value of $r_{La}/r_{Ni} = 1.506$ [20].

4. Conclusion

Solid solubility in Ti-rich (with respect to 33.3 at.% Ti) C36-TiCr$_2$ is, in contrast to previous suggestions, realised by Ti anti-site atoms. This situation conforms to that found for most other Laves phases AB_2 with both A and B being 3d/4d/5d metals.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2010.06.117.

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