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Coordination Polyhedra and Structures of Alloys: Binary Alloys of Niobium (and Tantalum) with Group III*b* and IV*b* Elements

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Abstract

Nb and Ta are found to exhibit a range of coordination numbers (CN) from 10 to 17 in their alloys with Group III*b* and IV*b* elements. The III*b* and IV*b* elements in these binary alloys have a CN ranging from 6 to 14. The polyhedra around Nb, Ta, III*b* and IV*b* elements have been characterized and a description of the polyhedra in terms of certain symbols is suggested. The structures of the binary alloys considered have been described in terms of polyhedra packing. *Most of the structures examined so far could be built up with one or two polyhedra*, only in a few cases are more than two polyhedra required.

Introduction

A fruitful approach to understanding the crystal-chemical features of alloy structures is to consider the coordination spheres around particular atoms. Frank & Kasper (1958, 1959) considered the coordination geometries around an atom as made up of only triangular faces and examined the topological and geometrical properties of the triangulated shells with CN's 12, 14, 15 and 16. The coordination characteristics of structural types with high coordination numbers have been studied by Kripyakevich (1960). He has also deduced the characteristics of the polyhedra with CN's 12 to 17, 20, 22, 24.

A glance through the literature on the crystal structures of alloys shows that very few papers (Brown, 1957, 1959; Girgis, Petter & Pupp, 1975) deal with the coordination polyhedra as building blocks of the structure. Such a description of structures, even though not supported by any specific theory of the structures, arises from observations of their peculiarities and the most general inferences that can be drawn from them (Black, 1956). *An approach to characterize the polyhedra in various known binary alloys and use them to build up the structures* has been introduced by Bhandary & Girgis (1977*b*). Their aim was to present a simple description of the complex alloy structures and to classify the known structure types. The aim of this study is to verify the general applicability of this model for binary intermetallic compounds. We examined for this purpose the alloys of Nb (Ta) with Group III*b* and IV*b* elements.

Coordination polyhedra

In order to define a coordination polyhedron it is essential to limit the coordination sphere of an atom. Brunner (1977) proposed the '$1/d$ method'. The normalized $1/d_n$, where d_n is the interatomic distance between the central atom and the nth neighbour, *versus* the number of atoms, are represented in a histogram. The widest range in which no atoms are present is called the 'max. gap'. The number of neighbours before the 'max. gap' is taken to be the coordination number (CN). The atoms (neighbours) constitute the coordination polyhedron for the corresponding (central) atom.

Nb and Ta exhibit a range of CN's from 10 to 17 in these alloys; the CN of the b elements ranges from 6 to 14. The geometries of these coordinations (coordination polyhedra) have been characterized and are listed

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in Tables 1 and 2. The symmetry given is that found for the polyhedra obtained from the structural parameter of the Nb (Ta) compounds. In some cases the idealized symmetry has been indicated. Each polyhedron has been described in terms of certain symbols according to the arrangement of vertices; hence $1^6 : 4^4 + 2^5 : 2^4 + 3^5 + 1^5$ means that starting from a sixfold vertex at the top there is a plane of four fourfold and two fivefold vertices followed by another plane of two fourfold and three fivefold vertices and a fivefold vertex at the bottom. The starting point of the description is located either on a symmetry axis or a symmetry plane. An *n*-fold vertex is taken to mean a point where *n* edges meet (for the sake of convenience we have not considered the symmetry of the vertex): see Bhandary & Girgis (1977*b*).

Description of alloy structures

The binary alloys of Nb (and Ta) with III*b* and IV*b* elements crystallize in one of 20 structure types treated in this work. All these structures could be explained using one or at most only a few polyhedra. The structure-describing polyhedron (polyhedra) and the

Table 1. *Description of polyhedra of the transition elements* (Nb,Ta)

	CN	Polyhedron	Symmetry	Idealized	No. of faces* △	No. of faces* □	Arrangement of vertices†	Found in
I	10	10-verticon of $ZrSi_2$ type	*mm*2		6	5	$3^4:2^3+2^4:3^4$	$TaAl_2$
II	11	11-verticon of β-Ti_6Sn_5 type	*m*		18		$2^5:1^4:1^6:2^5:2^4+2^5:1^6$	Nb_6Sn_5
III	11	11-verticon of Ti_5Ga_4 type	*mm*2		6	6	$1^3:3^4:3^4:3^4:1^3$	Nb_5Ga_4, $Nb_{10}Ge_7$
IV	12	Cubooctahedron [tetragonally distorted (t.d.)]	4/*mmm*	*m*3*m*	8	6	$4^4:4^4:4^4$	Nb_5Ga_{13}, $TaGa_3$
V	12	Cubooctahedron	*m*3*m*	*m*3*m*	8	6	$4^4:4^4:4^4$	Nb_3Si, Ta_3Si, Ta_3Ge
VI	12	Kasper (distorted)	$\bar{1}$	$\bar{5}\bar{3}$ (2/*m*)	20		$2^5:2^5:4^5:2^5:2^5$	Nb_6Sn_5
VII	12	12-verticon of Ni_3Sn type	*mm*2	$\bar{6}$*m*2	8	6	$3^4:6^4:3^4$	Ta_3Si
VIII	12	12-verticon of β-Ti_6Sn_5 type	*mm*2		16	2	$3^5:2^4:1^6+1^4:2^4:3^5$	Nb_6Sn_5
IX	13	13-verticon of Ni_3P type	1		22		$2^5:1^6+1^5+1^4:2^5+1^6:3^5:2^5$	Ta_3Ge
X	14	Kasper (distorted)	*mm*2	$\bar{1}\bar{2}.2m$	24		$3^5:3^5:2^6:3^5:3^5$	‡
XI	14	14-verticon of $CrSi_2$ type	222		20	2	$2^4+2^5:2^6+4^5:2^4+2^5$	$NbSi_2$, $NbGe_2$, $TaSi_2$
XII	14	Tetrakishexahedron (t.d.)	4/*mmm*	$\bar{4}$3*m*	24		$1^4:4^6:4^4:4^6:1^4$	§, Nb_3Ga_2, Nb_5Si_3, Ta_3Ga_2
XIII	14	14-verticon of Ni_3P type	1		24		$3^5:2^6+1^5:2^4+1^6:2^4:3^5$	Ta_3Ge
XIV	15	Kasper (distorted)	*mm*2	$\bar{6}$*m*2	26		$2^5:4^5:2^6:2^5:4^5:1^6$	Nb_6Sn_5
XV	15	15-verticon of Al_2Cu type	*mm*2		22	2	$2^5+1^6:2^4:4^5+1^6:2^4:2^5+1^6$	Ta_2Si
XVI	16	16-verticon of Cr_5B_3 type	*m*		24	2	$2^5+1^6:2^4:4^5+1^6:3^6+2^4+1^3$	Nb_5Si_3, Ta_5Ga_3, Ta_5Si_3
XVII	16	Kasper	$\bar{4}$3*m*	$\bar{4}$3*m*	28		$2^5:2^6:4^5:4^5:2^6:2^5$	$Ta_{17}Al_{12}$
XVIII	17	17-verticon of U_3Si_2 type	*mm*2		26	2	$1^5:1^4+4^5:4^5+1^6:1^4+4^5:1^6$	Nb_3Ga_2, Ta_3Ga_2

* △ Triangular; □ quadrangular.
† Bhandary & Girgis (1977*b*)
‡ Ta_2Al, Nb_2Al, Ta_3Al, Nb_5Ga_4, $Nb_{10}Ge_7$, Nb_3Si, Ta_3Ge, Ta_3Si.
§ Ta_5Ga_3, Ta_5Si_3, Ta_5Ge_3.

Table 2. *Description of polyhedra of b elements*

	CN	Polyhedron	Symmetry	Idealized	No. of faces* △	No. of faces* □	Arrangement of vertices†	Found in
XIX	6	Bicapped rhombohedron	3*m*		8		$3^4:3^4$	Nb_2AlC, Nb_2SnC, Ta_2AlC
XX	7	7-verticon of β-Ti_6Sn_5 type	*m*		8	1	$2^4:2^3:1^6:2^4$	Nb_6Sn_5
XXI	8	8-verticon of $ZrSi_2$ type	*mm*2		4	4	$2^4+1^3:2^3:2^4+1^3$	$TaAl_2$
XXII	8	8-verticon of β-Ti_6Sn_5 type	*mm*2		10	1	$3^4:2^5:3^4$	$TaAl_2$, Nb_6Sn_5
XXIII	8	8-verticon of β-Ti_6Sn_5 type	*mm*2		12		$1^3:2^4:1^4+1^6:2^6:1^3$	Nb_6Sn_5
XXIV	9	9-verticon of Cr_5B_3 type	*mm*2		14		$3^5:3^4:3^5$	‡
XXV	10	Bicapped square antiprism	422	$\bar{8}$2*m*	16		$1^4:4^5:4^5:1^4$	§
IV	12	Cubooctahedron (t.d.)	*mmm*	*m*3*m*	8	6	$4^4:4^4:4^4$	$TaGa_3$
VI	12	Kasper (distorted)	*m*	$\bar{5}\bar{3}$ (2/*m*)	20		$2^5:2^5:4^5:2^5:2^5$	Ta_2Al, Nb_2Al, Ta_3Al
VII	12	12-verticon of Ni_3Sn type	$\bar{6}$*m*2		8	6	$3^4:6^4:3^4$	¶
XXVI	13	13-verticon of Ti_5Ga_4 type	*mm*2		14	4	$2^4:2^5+1^4:3^4:2^5+1^4:2^4$	Nb_5Ga_4, $Nb_{10}Ge_7$
XXVII	13	13-verticon of α-Mn type	*m*		20	1	$1^6:2^4:2^5:2^5:2^5:2^5:1^5:1^5$	$Ta_{17}Al_{12}$
XI	14	14-verticon of U_3Si_2 type	2		20	2	$2^4+2^5:2^6+4^5:2^4+2^5$	$NbSi_2$, $NbGe_2$, $TaSi_2$, $TaGe_2$
XII	14	14-verticon of Ti_5Ga_4 type	$\bar{3}$*m*		24		$1^6:3^4+3^6:3^4+3^6:1^6$	Nb_5Ga_4, $Nb_{10}Ge_7$
XIV	15	Kasper (distorted)	*mm*2	$\bar{6}$*m*2	26		$1^6:4^5:2^5:4^5:2^6:2^5$	Nb_6Sn_5

* △ Triangular; □ quadrangular.
† Bhandary & Girgis (1977*b*).
‡ Nb_3Ga_2, Nb_5Si_3, Ta_3Ga_2, Ta_5Ga_3, Ta_5Si_3, Ta_5Ge_3, Ta_3Ge, Nb_3Si, Ta_3Ge.
§ Nb_5Si_3, Ta_2Si, Ta_5Ga_3, Ta_5Si_3, Ta_5Ge_3.
¶ Ta_3Si, Nb_2AlC, Nb_2SnC, Ta_2AlC.

Table 3. *Structures of* (Nb, Ta)–(III*b*, IV*b*) *phases described by polyhedra packing*

The structure types are ordered according to their Pearson symbol.

Structure type	Representative	Pearson symbol	Space group	Atom	CN	Polyhedra used and their symmetry [idealized]	Type of packing*
$ZrSi_2$	$TaAl_2$	*oC*12	*Cmcm*	Ta	10	10-verticon of $ZrSi_2$ type; $mm2$ (C_{2v})	I
Nb_5Ga_{13}	Nb_5Ga_{13}	*oA*36	*Ammm*	Nb_1	12	Cubooctahedron (*D*); mmm (D_{2h})	I
				Nb_2	12	Cubooctahedron (*D*); $mm2$ (C_{2v})	
				Nb_3	12	Cubooctahedron (*D*); $mm2$ (C_{2v})	
β-Ti_6Sn_5	Nb_6Sn_5	*oI*44	*Immm*	Nb_3	15	15-Kasper (*D*); $mm2$ (C_{2v})	I
				Nb_4	12	12-verticon of β-Ti_6Sn_5 type; $mm2$ (C_{2v})	
$CuMg_2$	$NbSn_2$	*oF*48	*Fddd*	Nb	10	Bicapped dodecahedron; 2 (C_2)[222 (D_2)]	I
$CuTi_3$	$TaGa_3$	*tP*4	*P*4/*mmm*	Ga_1	12	Cubooctahedron (*D*); $4/mmm$ (D_{4h})	II
U_3Si_2	Nb_3Ga_2	*tP*10	*P*4/*mbm*	Nb_1	14	Tetrakishcxahedron; $4/mmm$ (D_{4h})	I
σ-FeCr	Nb_2Al	*tP*30	*P*4$_2$/*mnm*	Al_2	12	Icosahedron (*D*); $2/m$ (C_{2h})[$\bar{5}\bar{3}(2/m)$ (I_h)]	II
Ti_3P	Nb_3Si	*tP*32	*P*4$_2$/*n*	Si	9	9-verticon of Cr_5B_3 type; 1 (C_1)	I
$TiAl_3$	$NbAl_3$	*tI*8	*I*4/*mmm*	Nb	12	Cubooctahedron; $m3m$ (O_h)	II
Al_2Cu	Ta_2Si	*tI*12	*I*4/*mcm*	Si	10	Bicapped square antiprism; 422 (D_4)	II
Cr_5B_3	Nb_5Si_3	*tI*32	*I*4/*mcm*	Nb_1	14	Tetrakishexahedron; $4/mmm$ (D_{4h})	II
W_5Si_3	Nb_5Ga_3	*tI*32	*I*4/*mcm*	Nb_1	14	14-Kasper (*D*); $\bar{4}2m$ (D_{2d})[$\bar{6}m$ (D_{6d})]	II
				Ga_1	10	Bicapped square antiprism; $\bar{8}2m$ (D_{4d})	
Ni_3P	Ta_3Ge	*tI*32	$I\bar{4}$	Ge	9	9-verticon of Cr_5B_3 type; 1 (C_1)	I
Ni_3Sn	$Ta_3(Ta_{0.28}Si_{0.72})$	*hP*8	*P*6$_3$/*mmc*	Si	12	12-verticon of Ni_3Sn type; $\bar{6}m2$ (D_{3h})	I
$CrSi_2$	$NbSi_2$	*hP*9	*P*6$_2$22	Nb	14	14-verticon of $CrSi_2$ type; 222 (D_2)[$6/mmm$ (D_{6h})]	I
Mn_5Si_3	$Nb_5Ga_3O_x$	*hP*16	*P*6$_3$/*mcm*	Nb_1	14	14-Kasper like; 32 (D_3)	II
Ti_5Ga_4	Nb_5Ga_4	*hP*18	*P*6$_3$/*mcm*	Nb_1	14	14-Kasper (*D*); 32 (D_3)	I
				Ga_1	14	14-verticon of Ti_5Ga_4 type; $\bar{3}m$ (D_{3d})	
Cu_3Au	Nb_3Si	*cP*4	*Pm*3*m*	Nb	12	Cubooctahedron; $m3m$ (O_h)	II
Cr_3Si	Nb_3Al	*cP*8	*Pm*3*n*	Nb	14	14-Kasper (*D*); $\bar{4}2m$ (D_{2d})[$\overline{12}.2m$ (D_{6d})]	II
α-Mn	$Ta_{17}Al_{12}$	*cI*58	$I\bar{4}3m$	Ta_2	16	16-Kasper (*D*); $\bar{4}3m$ (T_d)	I

* Types of packing: (I) three-dimensional arrangement of discrete polyhedra sharing corners, edges or faces. (II) A layer-like distribution of polyhedra (sheet polyhedra packing).

kind of linkage of the polyhedra are summarized in Table 3. The structures considered can be described as being of two types.

Type I: a three-dimensional distribution of discrete polyhedra sharing corners, edges and faces.

Type II: a layer-like distribution of polyhedra (sheet polyhedra packing).

The α-Mn type represents an example of type I. $Ta_{17}Al_{12}$ crystallizes in the cubic space group $I\bar{4}3m$ and belongs to the α-Mn type with 58 atoms per cell. This complicated structure can be described using only one polyhedron. These polyhedra share with the surrounding ones (alternately) an edge and a triangular face building a plane of polyhedra. A similar plane, rotated by 90° with respect to the lower one, lies over it, sharing the shaded triangular faces (see Fig. 1).

The σ-FeCr type ($AlNb_2$) represents an example of type II. $AlNb_2$ crystallizes in the tetragonal space group $P4_2/mnm$ and has 30 atoms in the unit cell. Al(2) [8(*i*)] is twelve coordinated building a 'distorted icosahedron' having *mm*2 symmetry. The structure can be described by packing Al(2) ($z = 0$) polyhedra which build a zigzag chain along the *b* axis (Fig. 2) sharing a corner and an edge alternately with each other. A similar chain of Al(2) ($z = \frac{1}{2}$) polyhedra is also present. These two chains share atoms with each other as shown in Fig. 2. Along the *c* axis the Al(2) polyhedra share the upper edges with each other.

Conclusions

Nb and Ta exhibit CN's ranging from 10 to 17 and a wide variety of coordination polyhedra. The *b* elements have CN's 6 to 14.

The relation between the CN and the number of triangular and quadrangular faces forming the polyhedron can be expressed as follows:

$$\mathrm{CN} = (n + 2m + 4)/2,$$

where *n* and *m* are the number of triangular and quadrangular faces respectively (derived from the Euler formula). If we restrict the CN to 6–17 as found in this study and by Bhandary & Girgis (1977*a*) we achieve 142 theoretically possible polyhedra (only formed by triangular and quadrangular faces, without consideration of symmetry). The 39 polyhedra found in this work and in the literature show a high number of triangular faces. It seems that the intermetallic compounds preferably form polyhedra with the highest possible number of triangular faces.

All structures examined can be described in terms of the packing of one or two polyhedra. This model gives a simple description of even quite complicated structures. *The polyhedra-packing model can be used for all representatives of a certain structure type.*

Icosahedra, Kasper (14-verticon) polyhedra, tetrakishexahedra and cubooctahedra play an important

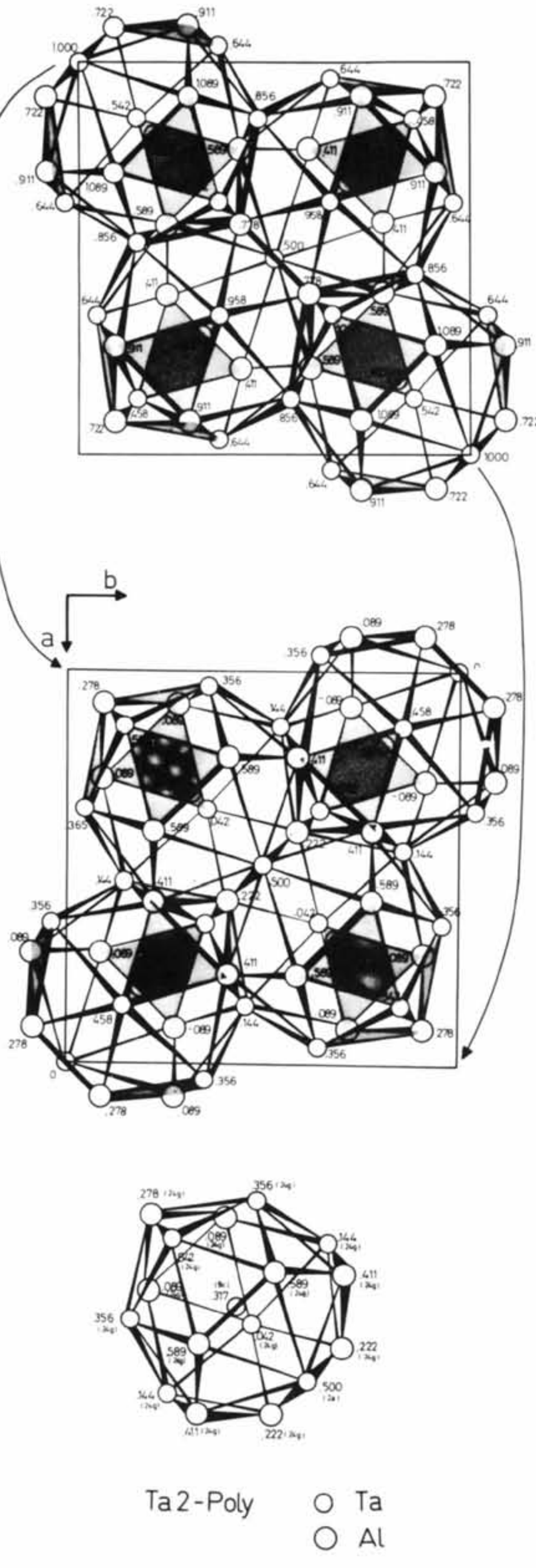

Fig. 1. Polyhedra packing of the α-Mn type (*cI*58) ($Al_{12}Ta_{17}$).

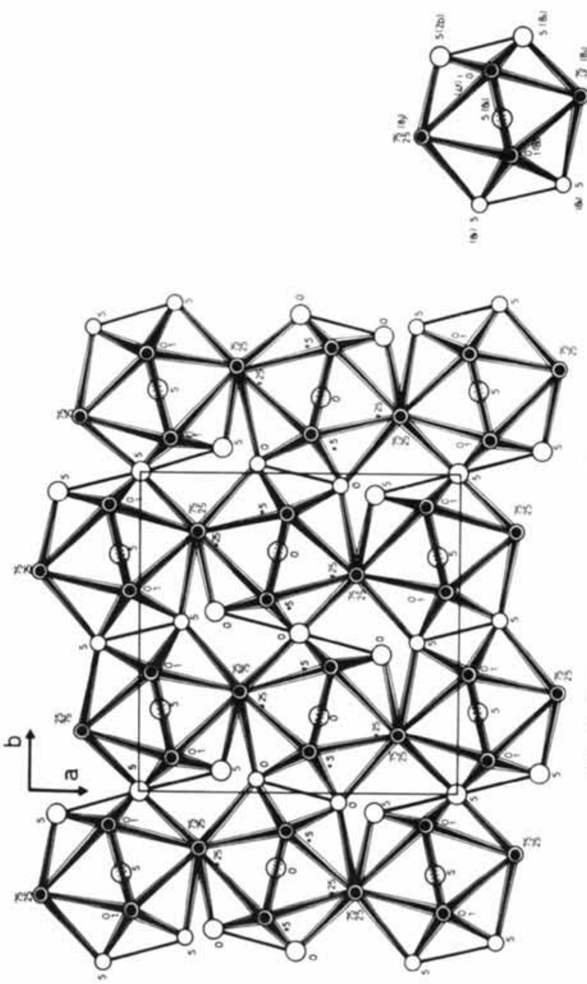

Fig. 2. Polyhedra packing of the σ-FeCr type (*tP*30) ($AlNb_2$).

role in the explanation of these structures which belong to different structure types.

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