

A New Approach to Limit the Coordination Number in Alloys I: Binary Alloys of Vanadium with III b and IV b Elements

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With 1 Figure

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The present paper is a trial to limit the coordination sphere and hence the coordination number of atoms in alloys. This study shows that the average weighted coordination number of binary alloys as a whole lies in between those of the component atoms. This result seems to be encouraging. The coordination numbers of different atoms in the known 26 binary alloys of vanadium are determined using two different methods, compared and discussed.

Introduction

Many attempts have been made in the past by various authors to limit the coordination sphere of an atom in its alloy. Some of the attempts are mentioned here briefly.

Dehlinger and *Schulze*¹ suggested a weight for the coordination number (CN). For example, for an alloy A_aB_b (a and b are atomic percent concentrations) the mean coordination number $(CN)_m = a \cdot (CN)_A + b \cdot (CN)_B$. *Wieting*² suggested a distance weighted CN . The nearest neighbour distance is given a unit weight and the distance at twice the nearest distance a weight of zero. The intermediate distances are weighted linearly depending on the corresponding distance. *Hoppe*³ tried to describe an effective CN with the help of geometrical polyhedral method or *Maple* (*Madelung Part of Lattice Energy*) values.

Brunner and *Laves*⁴ discussed the different known methods and suggested to describe CN as a number sequence. *Brunner* and *Schwarzenbach*⁵ arranged the number of near neighbours of an atom as a function of their distances in a histogram. For about 90% of the structures treated in this way a clear "maximum gap" i.e. a range of distances without atoms was easily recognised. This gap limits the coordination sphere.

The "conventional coordination number (CCN)" of an atom is taken to be equal to the nearest neighbours before the maximum gap in the histogram. The "weighted coordination number (WCN)" is calculated

by assigning a unit weight to the nearest distance and zero to the distance ratio just after the maximum gap. The distances in between these limits are weighted depending on the ratio d_n/d_{nearest} .

Brunner⁶ proposed a new approach ($1/d$) for calculating the weighted coordination number. The histogram is based on normalised $1/d_n$ where d_n is the interatomic distance between the central atom and the n^{th} neighbour. As in the previous case the nearest $1/d$ is given unit weight and the $1/d$ just after the maximum gap a weight zero. The distances in between are weighted depending on $1/d_n$. This method is in agreement with the energy principle since energy is inversely proportional to the distance between the atoms.

Using the last two methods we have studied the coordination number of all the atoms in the binary alloys of vanadium with group III b and IV b elements.

Average Weighted Coordination Number AWCN

In order to obtain an overall picture of the structure an average weighted coordination number is calculated for the constituents of the alloys and for the structure as a whole using the expression $AWCN = \frac{\sum_n (WCN)_n \cdot E_n}{\sum_n E_n}$, where $(WCN)_n$ is the weighted coordination number of the n^{th} atom and E_n the equivalent point it occupies in the structure. The results are tabulated in Tables 1 and 2. The histograms for all the atoms of the binary alloys studied are given in Fig. 1. It can be seen that for most of the atoms there is a clear biggest gap.

Discussion

V—Al system

Vanadium belongs to the tungsten type structures, bcc, $CCN = 8$ (nearest neighbours) or 14 allowing for a tolerance of 13% in the distances. With the maximum gap approach CCN was found to be equal to 14. Aluminium in the elemental state has a coordination number of 12 with all the interatomic distances equal and hence has a WCN of 12 whilst V has a WCN of 11.9. The present approach gives a higher WCN for ccp than bcc structure thus showing that the ccp structure is more tightly packed.

Six binary alloys⁷⁻¹³ of this system have been surveyed. Wherever the structures were solved, the positional parameters reported were used in the calculations and for the others the parameters were taken from the structure type to which the particular alloy belongs. In most of the cases vanadium exhibits a CCN of 12 (in two cases 13 and 14). In the case of Al the CCN is 11 to 13 except in a few cases where it is 14, 16 and 19. The $AWCN$ of V in different structures of this system is around 10.5 except for V_3Al (9.8), while it varies from 9.3 to 11.0 for

Table 1. Summary of Coordination Numbers of Individual Atoms

Compound	Atom	Eq.Pts.	C.N.	Weighted C.N. d_2/d_1 1/d		Compound	Atom	Eq.Pts.	C.N.	Weighted C.N. d_2/d_1 1/d		
V ₃ Al	V	6c	14	11.2	9.8	V ₃ Ge	V	6c	14	11.2	9.8	
	Al	2a	12	12.0	12.0		Ge	2a	12	12.0	12.0	
V ₅ Al ₃	V 1	8c	12	11.1	11.1	V ₅ Ge ₃	V 1	4d	14	10.5	10.8	
	V 2	12e	13	11.6	11.0		V 2	6g	15	11.6	10.2	
	Al 1	8c	12	10.9	10.6		Ge	6g	11	9.6	9.1	
	Al 2	24g	11	9.3	8.9	V ₁₁ Ge ₈	V 1	8d	13	10.5	9.7	
VAl ₃	V	2a	12	11.0	10.7		V 2	8d	14	11.9	9.9	
	Al 1	2b	12	11.0	10.7		V 3	4c	16	12.8	11.3	
	Al 2	4d	12	11.0	10.7		V 4	4c	16	12.6	11.1	
V ₄ Al ₂₃	V 1	2a	12	11.2	10.7		V 5	4c	14	11.0	9.5	
	V 2	16h	12	10.9	10.3		V 6	4c	17	13.9	12.7	
	Al 1	12k	11	9.7	9.5		V 7	4c	15	11.0	9.8	
	Al 2	12k	12	10.2	9.5		V 8	4c	15	11.2	10.1	
	Al 3	12k	12	11.4	11.3	V 9	4c	15	11.1	9.8		
	Al 4	6h	12	9.8	8.9	Ge 1	8d	19	7.9	7.6		
V ₇ Al ₄₅	Al 5	12k	12	11.2	10.8	Ge 2	4c	13	9.7	9.1		
	V 0	2a	12	11.2	10.8	Ge 3	4c	13	10.2	9.5		
	V 1	4i	12	10.7	10.8	Ge 4	4c	11	9.1	8.6		
	V 2	8j	12	10.9	10.4	Ge 5	4c	10	8.1	7.6		
	Al 0	2d	12	11.5	11.1	Ge 6	4c	12	9.4	9.0		
	Al 3	4i	12	10.6	10.1	Ge 7	4c	11	9.1	8.6		
	Al 4	4i	13	11.9	11.2	V ₁₇ Ge ₃₁	V 1	2a	8	7.4	7.3	
	Al 5	4i	12	10.6	9.9		V 2	2c	14	11.0	9.8	
	Al 6	4i	13	11.6	11.1		V 3	4e	14	10.6	9.4	
	Al 7	4i	12	9.7	8.9		V 4	4e	14	10.5	9.7	
	Al 8	4i	12	9.6	8.8		V 5	4e	8	7.4	7.3	
	Al 9	4i	11	10.3	10.0		V 6	4e	14	10.7	9.7	
	Al 10	4i	11	10.7	9.2		V 7	4e	14	10.6	9.5	
	Al 11	8j	12	9.7	8.9		V 8	4e	8	7.5	7.2	
	Al 12	8j	11	10.1	9.9		V 9	4e	14	10.9	9.6	
	Al 13	8j	12	9.7	8.8		V 10	4e	8	7.2	6.9	
	Al 14	8j	12	9.4	8.6		V 11	4h	8	7.5	7.3	
Al 15	8j	13	11.4	10.9	V 12		4h	14	10.9	9.6		
Al 16	8j	12	10.0	9.3	V 13		4h	8	6.9	6.7		
Al 17	8j	11	9.4	8.9	V 14		4h	8	7.1	7.0		
VAl ₁₀ (a)	V	16c	12	11.3	10.7		V 15	4h	14	10.7	9.8	
	Al 1	96g	19	13.4	10.6	V 16	4h	14	10.8	9.6		
	Al 2	48f	12	8.5	8.7	V 17	4h	8	7.4	7.2		
	Al 3	16d	12	12.0	12.0	V 18	4h	14	10.9	9.8		
VAl ₁₀ (b)	V	16c	12	11.3	10.7	Ge 1	8i	10	7.3	6.8		
	Al 1	96g	12	9.8	8.8	Ge 2	8i	10	6.4	6.0		
	Al 2	48f	12	10.2	9.5	Ge 3	8i	12	7.2	6.5		
	Al 3	16d	14	13.9	13.8	Ge 4	8i	14	9.9	8.7		
	Al 4	8b	16	15.8	15.8	Ge 5	8i	14	10.5	9.4		
V ₃ Ga	V	6c	14	11.2	9.8	Ge 6	8i	14	10.3	9.0		
	Ga	2a	12	12.0	12.0	Ge 7	8i	14	10.1	8.9		
V(Ga)	V	2a	14	12.5	11.9	Ge 8	8i	12	7.4	6.8		
	Ga	2a	14	12.5	11.9	Ge 9	8i	12	6.1	7.4		
V ₆ Ga ₅	V 1	6h	11	8.4	7.7	Ge 10	8i	10	7.0	6.5		
	V 2	6g	12	11.2	10.8	Ge 11	8i	10	7.5	7.0		
	Ga 1	6h	14	10.7	9.8	Ge 12	8i	10	6.9	6.5		
	Ga 2	2b	14	10.9	9.9	Ge 13	8i	12	7.9	7.1		
V ₆ Ga ₇	Ga 3	2c	15	11.5	10.2	Ge 14	8i	14	9.8	8.7		
	V 1	8c	12	11.2	10.9	Ge 15	8i	14	10.2	8.8		
	V 2	12e	13	11.6	10.9	Ge 16	8i	14	10.5	9.3		
V ₆ Ga ₅	Ga 1	8c	12	10.5	10.2	V ₃ Sn	V	6c	14	11.2	9.8	
	Ga 2	24g	11	9.4	9.1		Sn	2a	12	12.0	12.0	
	V ₂ Ga ₅	V	4h	12	11.6	11.4	V ₂ Sn ₃	V	16g	10	9.6	9.4
Ga 1		2d	10	9.8	9.8	Sn 1		16g	15	11.8	10.5	
V ₈ Ga ₄₁	Ga 2	8i	10	9.6	9.5	Sn 2	16c	15	11.6	11.0		
	V ₈ Ga ₄₁	V 1	6c	10	9.4	9.0	V ₃ In	V	6c	14	11.2	9.8
		V 2	18f	10	9.6	9.3		In	2a	12	12.0	12.0
		Ga 1	3a	12	11.9	11.8	V ₃ Pb	V	6c	14	11.1	9.8
		Ga 2	3b	8	7.6	7.5		Pb	2a	12	12.0	12.0
		Ga 3	9d	10	8.4	7.8	V ₃ Tl	V	6c	14	11.2	9.8
		Ga 4	18f	13	10.6	9.8		Tl	2a	12	12.0	12.0
		Ga 5	18f	13	11.2	10.6	Element	Atom	Eq.Pts.	C.N.	Weighted C.N.	
		Ga 6	18f	10	7.8	7.2		V	V	2a	14	12.5
Ga 7		18f	10	8.0	7.5	Al		Al	4a	12	12.0	12.0
Ga 8	18f	10	7.6	6.9	Ga	Ga		8f	7	5.8	5.4	
Ga 9	18f	9	7.7	7.2	Si	Si		8a	4	4.0	4.0	
V ₃ Si	V	6c	14	11.2	9.8	Ge		Ge	8a	4	4.0	4.0
	Si	2a	12	12.0	12.0	Sn		Sn	8a	4	4.0	4.0
V ₅ Si ₃	V 1	4b	14	10.1	8.8	V ₆ Si ₅		V 1	8j	17	13.6	12.1
	V 2	16k	15	11.9	12.1			V 2	8j	15	10.9	9.5
	Si 1	4a	10	9.2	8.8		V 3	8f	14	11.6	11.6	
	Si 2	8h	10	8.1	7.7		Si 1	8j	11	9.2	8.4	
V ₆ Si ₅	Si 2	8h	10	8.1	7.7		Si 2	8j	10	7.8	7.0	
	V 1	8j	17	13.6	12.1		Si 3	4a	10	8.8	8.3	
	V 2	8j	15	10.9	9.5		VSi ₂	V	6c	14	11.2	9.8
	V 3	8f	14	11.6	11.6			Si	2a	12	12.0	12.0

Table 2. *Average Weighted Coordination Number (AWCN) of the Alloys*

Compound	Ref.	Struct. Type	Space Group	At. % V	Av. Weighted		C.N.* Str.
					V	B	
V ₃ Al	7	Cr ₃ Si	Pm3n	75.0	9.8	12.0	10.4
V ₅ Al ₈	8	Cu ₅ Zn ₈	I43m	38.5	11.1	9.3	10.0
VAL ₃	9	TiAl ₃	I4/mmm	25.0	10.7	11.0	11.0
V ₄ Al ₂₃	10		P6 ₃ /mmc	14.8	10.4	10.1	10.1
V ₇ Al ₄₅	11		C2/m	13.5	10.6	9.6	9.7
VAL ₁₀ (a)	12		Fd3m	9.1	10.7	10.8	10.2
VAL ₁₀ (b)	13		Fd3m	9.1	10.7	9.8	9.9
V ₃ Ga	14	Cr ₃ Si	Pm3n	75.0	9.8	12.0	10.4
V(Ga)	14	W	Im3m	62.5	11.9	11.9	11.9
V ₆ Ga ₅	15	α-Ti ₆ Sn ₅	P6 ₃ /mmc	55.0	9.3	9.9	9.6
V ₆ Ga ₇	15	Cu ₅ Zn ₈	I43m	46.0	10.9	9.4	10.0
V ₂ Ga ₅	16	Mn ₂ Hg ₅	P4/mbm	28.6	11.4	9.6	10.1
V ₈ Ga ₄₁	17	V ₈ Ga ₄₁	R3̄	16.3	9.2	8.2	8.4
V ₃ Si	18	Cr ₃ Si	Pm3n	75.0	9.8	12.0	10.4
V ₅ Si ₃	19	W ₅ Si ₃	I4/mcm	62.5	11.5	8.1	10.2
V ₆ Si ₅	20		Ibam	54.5	11.1	7.8	9.6
VSi ₂	21	CrSi ₂	P6 ₂ 22	33.3	11.1	11.1	11.1
V ₃ Ge	22 a	Cr ₃ Si	Pm3n	75.0	9.8	12.0	10.4
V ₅ Ge ₃	22 b	Mn ₅ Si ₃	P6 ₃ /mcm	62.5	10.4	9.1	9.9
V ₁₁ Ge ₈	23	Cr ₁₁ Ge ₈	Pnma	57.9	10.3	8.5	9.5
V ₁₇ Ge ₃₁	24		P4n2	35.4	8.5	7.7	8.0
V ₃ Sn	25	Cr ₃ Si	Pm3n	75.0	9.8	12.0	10.4
V ₂ Sn ₃	26	CuMg ₂	Fddd	40.0	9.4	10.8	10.3
V ₃ Pb	27	Cr ₃ Si	Pm3n	75.0	9.8	12.0	10.4
V ₃ In	28	Cr ₃ Si	Pm3n	75.0	9.8	12.0	10.4
V ₃ Tl	28	Cr ₃ Si	Pm3n	75.0	9.8	12.0	10.4

* determined in the present work

V₆Ga₇: given as VGa^h in [14] may be pseudo cubic

Al. However, when the structure as a whole is considered the *AWCN* does not change much (9.7 to 10.4; for VAL₃ it is 11) even when the composition varies from one compound to another. This may be attributed to the fact that both elements have nearly the same *WCN*. In V₃Al and other Cr₃Si type structures considered in this paper the vanadium atom has a *CCN* of 14 and *WCN* of 9.8 while the b-element has a *CCN* and *WCN* of 12.0.

V—Ga System

Gallium metal has a *CCN* of 7 and *WCN* of 5.4. In the six binary alloys^{14–17} surveyed vanadium shows a range of *CCN* (10, 12, 13, 14 and 16) with a tendency to increase with increasing V content. The *CCN* for

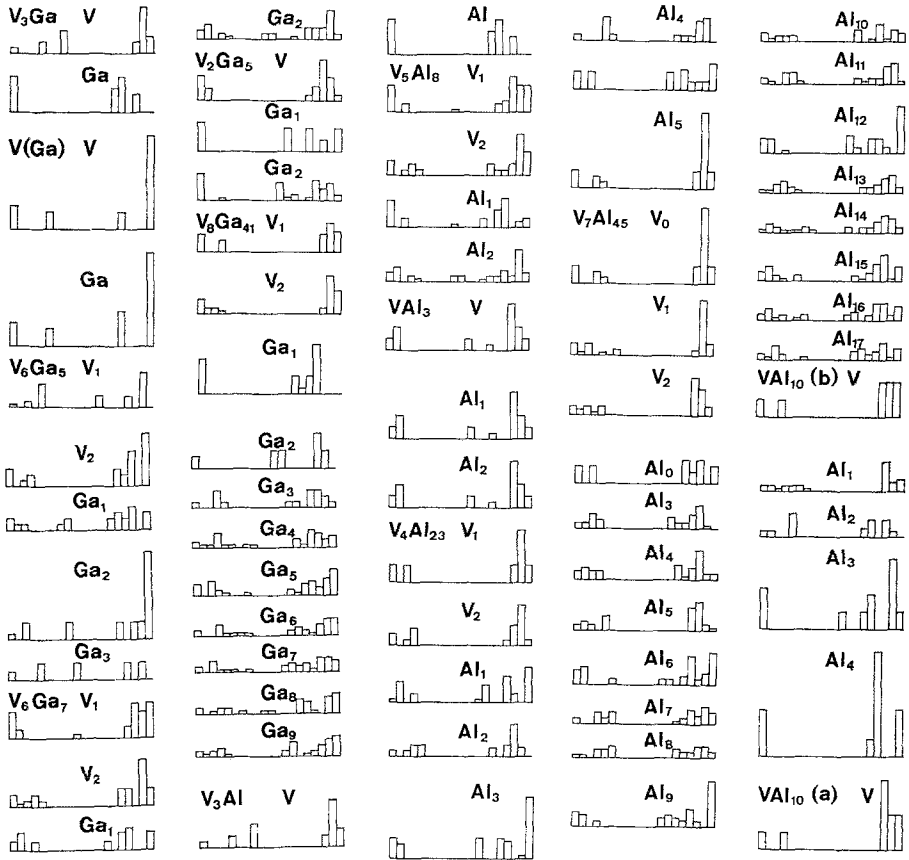


Fig. 1 a

Fig. 1. Distribution of near neighbours as function of their normalised reciprocal distance ($1/d_n$). The sequence of atoms in the figure is columnwise and the atoms belonging to a particular alloy are under each other

Ga ranges from 8 to 15. The *AWCN* of V and Ga vary between 12 and 9.2 and 12 to 8.2, resp., showing a decrease with decrease of V content. *AWCN* of the structure as a whole also shows a decrease (12 to 8.4) with decrease of V content in the alloy. This means that the *AWCN* of vanadium rich alloys is nearer to that of V and for gallium rich ones it is nearer to that of Ga. The *AWCN* of the structure lies in between those of the constituents of the alloys.

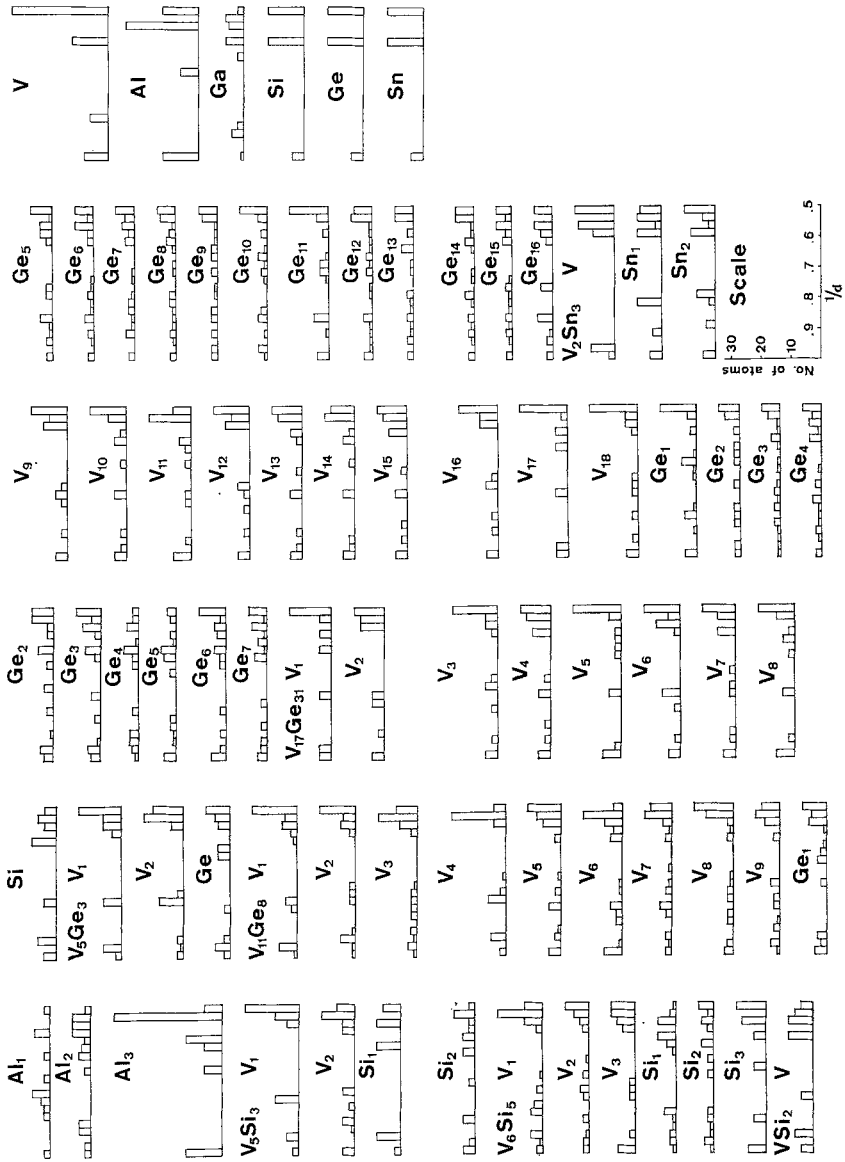


Fig. 1 b

V—Si System

Silicon has four nearest neighbours with the same interatomic distance in its elemental state. Four binary alloys¹⁸⁻²¹ of this system have been characterised. Vanadium atoms have 14, 15 and 17 as the

CCN in these alloys while silicons exhibit *CCN* of 10, 11, 12 and 14. The *AWCN* of V remains almost the same at about 11 except for V_3Si while it varies from 7.8 to 12.0 in the case of silicon. The *AWCN* of the structures show a tendency to decrease as the atomic percent of V is decreased (VSi_2 is an exception). The situation in this system seems to be the same as that in the V—Ga system.

V—Ge System

Only four binary alloys²²⁻²⁴ have been reported in the literature. Germanium has four nearest neighbours at equal distances. In the binary alloys of this system vanadium shows a range of *CCN* of 8, 13, 14, 15, 16 and 17 and Ge atoms have a *CCN* of 9 to 14. In $V_{11}Ge_8$ which is isotypic with $Cr_{11}Ge_8$ the V atoms have a *CCN* of 13 to 17 while the Ge atoms 9 to 11 and 13. It is interesting to note that the *CCN* obtained by us is different for a few atoms from those reported by *Israiloff* et al.²³ for $Cr_{11}Ge_8$. The atoms V (6), V (7) and V (8) have *CCN* of 17, 15 and 15 respectively as against 16, 14 and 14 reported for Cr (6), Cr (7) and Cr (8) respectively. This has been found to be due to the arbitrary limit of 3.35 Å set for the coordination sphere boundary by them since bond length calculations on $Cr_{11}Ge_8$ gave distances of 3.39 [Cr (6)—Cr (7)], 3.39 [Cr (7)—Cr (6)], and 3.36 [Cr (8)—Cr (4)]. We feel that these atoms should also have been taken into account when the *CCN* is determined. However for Ge (1) the *CCN* obtained by us is 9 as against 11 reported. Though the last two atoms lie within 3.35 Å they do not fall before the biggest gap in the coordinating distances. It must be mentioned here that though the present approach gives a *CCN* 9, a *CCN* of 11 should be taken in order to have a closed polyhedron around Ge (1).

The *WCN* of individual vanadium atoms in this system varies from 6.7 to 12.7 while that for Ge is between 6.5 and 12.0. The *AWCN* for V and Ge varies from 8.5 to 10.4 and 7.7 to 12.0 respectively. As in the case of V—Ga and V—Si systems the *AWCN* of the structure as a whole varies from 10.3 to 8.0 showing a clear tendency to decrease as the atomic percent of vanadium is decreased.

V—Sn, V—Pb, V—In, and V—Tl Systems

In V—Pb, V—In, and V—Tl systems only the A-15 type compounds^{27, 28} have been reported. In V—Sn system apart from the A-15 alloy²⁵ another alloy²⁶ V_2Sn_3 has been reported. In V_2Sn_3 the vanadium atom exhibits a *CCN* of 10 while the Sn atoms have a *CCN* of 15. The *WCN* of V is 9.4 and that of Sn is 10.8. The *AWCN* of the structure as

a whole is 10.3 while that of V_3Sn is 10.4. A correlation like the ones obtained in other systems is hard to make due to lack of binary alloys reported in the literature in these systems.

Conclusions

As mentioned earlier *Brunner* and *Schwarzenbach*⁵ suggested the so called "maximum gap" and dn/d_1 weighting procedure to limit the *CCN*. *Brunner*⁶ proposed a $1/d$ weighting procedure. In this paper we used both approaches and find that the latter gives more reasonable results and hence have used the values obtained by this weighting procedure for the purposes of discussion and drawing the following conclusions.

1. When the two elements in the binary alloy have almost the same *WCN* as in the case of V—Al system the *AWCN* of the phases does not change appreciably with change in composition of the alloys. The *AWCN* of the phases lie in between those of the components; eventhough the structure types are different.

2. When there is an appreciable difference in the *CCN* of the constituting elements of the binary alloys as is the case with V—Ga, V—Si and V—Ge systems there is a tendency for the *AWCN* of the structure to decrease with decrease of V content of the alloy (V has a higher *CN* than the other elements). The *AWCN* of the phases in this case also lies in between those of the components.

3. The close packed structures possess the uppermost *CN* of 12. The present study shows that although the atoms individually have *CN* of more than 12 the structure as a whole has a lower *AWCN*.

4. In most of the alloys considered the vanadium atom has a higher *AWCN* than the b-element though it has a smaller radius. This corresponds to the metallic character of V.

5. In a particular structure type the coordination number and hence the packing does not depend on the elements constituting the alloy but on the structure type itself as evidenced by the Cr_3Si type alloys (V_3Al , V_3Ga , V_3Si , V_3Ge , V_3Sn , V_3Pb , V_3In , and V_3Tl). This has also been found to be the case with $CrSi_2$ and $TiAl_3$ type alloys. Hence it seems worthwhile to take the coordination number as a characteristic feature of the alloys belonging to a particular structure type.

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