VALENCE ELECTRON STRUCTURE ANALYSIS OF TETRAGONAL PHASE Al_8Fe_4Nd IN RAPID SOLIDIFIED Al-Fe-V-Si-Nd ALLOY

J.X.Lin H.Pang B.J.Zhang M.K.Tseng C.F.Qian X.F.Chen
Department of Material Science , College of Science , Northeastern University, Shenyang 110006, P.R.China

ABSTRACT In this paper, we apply EET theory to research valence electron structure of the complicated alloy phase Al_8Fe_4Nd and the relationship between the phase transforming temperature and the bond broken temperature in RS Al-Fe-V-Si-Nd alloy.
Keywords: *Rapid Solidification Valence Electron Structure Transforming Point*

1.Introduction

The application of rapid solidification for the development of elevated temperature aluminum alloys has resulted in the emergence of several alloys based on the Al-Fe alloy system. Of particular interest are Al- Fe-V-Si alloys which have excellent room temperature and high temperature mechanical properties[1,2].

In the past several years, we had done lots of job about Al-Fe-V-Si and Al-Fe-V-Si-Mm(Nd) alloy. The RS Al-Fe-V-Si alloy contains sub-micron grain α-Al and disperse $Al_{13}(Fe,V)_3Si$ particle, and the RS Al-Fe-V-Si-1.0at%Nd alloy attained at the same experimental conditions are compose of nanometer α-Al grain and Al_8Fe_4Nd particle, after annealing around 400 ℃ the alloys comprise nanameter scale α-Al and $Al_{13}(Fe,V)_3Si$[3]. So it is obvious that RS Al-Fe-V-Si-Nd takes place transformation from Al_8Fe_4Nd to $Al_{13}(Fe,V)_3Si$ during annealing. To understanding its transforming mechanism from electron structure angel, this paper apply S.H.Yu's Empirical Electron Theory of Solids and Molecules(EET)[4] to analysis the valence structure and calculated the transforming point of tetragonal phase Al_8Fe_4Nd.

2.Computation and Results

2.1 Valence structure calculation of Al_8Fe_4Nd

The Al_8Fe_4Nd phase with I4/mmm(a=8.789Å, c=5.054Å) has 26 atoms in the unit cell.The atomic coordinated measured by O.S.ZARECNJUK and P.I.KRIPJAKEVIC [5] were given as follows:

2Nd	in 2(a)	
8Fe	in 8(f)	
8Al(1)	in 8(i)	with x=0.365
8Al(2)	in 8(j)	with x=0.275

Atomic valence electron state of Al_8Fe_4Nd phase was computed by means of the Bond Length Difference(BLD)[4,14] based on EET theory. This theory is further development of L.Pauling's Chemical Bond Theory, Which has successfully applied to many aspects, such as the alloy compositional designed [6], the explanation of $Nd_2Fe_{14}B$ strong magnetic nature[7], the prediction of crystal combination energy[8], the research on the superconductivity[9],etc.

The basic though of the BLD method was described as formula (1):

$$D_{n\alpha} = R_u(I) + R_w(I) - 0.6\log n_\alpha \qquad (1)$$

Where all parameter can be found in reference [14].

Table.1 The neighbor atom kinds, distance and number of every reference atom in Al_8Fe_4Nd phase

reference atom	neighbor atom	distance D_α(Å)	number	reference atom	neighbor atom	distance D_α(Å)	number
Al(1)	Nd	3.20798	1	Nd	Fe	3.35447	8
	Fe	2.72872	4		Al(1)	3.20798	4
	Al(1)*	2.37303	1		Al(2)	3.20879	8
	Al(1)	3.03337	4				
	Al(2)*	2.81065	2				
	Al(2)	2.69250	2				
Al(2)	Nd	3.20879	2	Fe	Fe	2.257	2
	Fe	2.54413	4		Al(1)	2.72872	4
	Al(1)*	2.81065	2		Nd	3.35447	2
	Al(1)	2.69250	2		Al(2)	2.54413	4
	Al(2)*	3.95505	1				
	Al(2)	2.79664	2				

We will obtain the (N-1) bond length difference equations if D_{n1} corresponding to the shortest bond distance is used for the subtraction of $D_{n\alpha}$ (α=2,····· N). In addition, on considering the electric neutrality in the unit cell of crystal, there should exist the relationship, which is the sum of the covalent electron pairs number derived from all the covalent bonds in the unit cell (designated as $n_1\sum_{\alpha=1}^{N} I_\alpha r_\alpha$) is equal to the total covalent electron number provided by all the atoms in the unit cell (designed as $\sum n_c$), so an equation for the covalent electron number (n_1) of the shortest bond can be established, which is expressed as:

$$n_1 = \sum n_c / \sum_{\alpha=1}^{N} I_\alpha r_\alpha \quad (2)$$

where I_α is the number of α-bond in the unit cell of crystal. r_α express the relative value of the covalent electron number between the α-bond and the shortest bond in the unit cell. Thus there are N equations as a whole. From there equations, N different theoretical bond length ($\overline{D}_{n\alpha}$)(α=1,2,⋯⋯ N) can be calculated through selecting hybrid states of the various kinds of atoms. Comparing $\overline{D}_{n\alpha}$ with covalent experimental bond lengths $D_{n\alpha}$, if the condition of $|\Delta D_{n\alpha}| = |\overline{D}_{n\alpha} - D_{n\alpha}| \le 0.05A$ is satisfied, the selected atomic hybrid state during computing is supposed to represent the existing real state of atoms in crystal. Here, we need to emphasize the selecting rule of the atomic hybrid states. Based on L.Pauling's the atomic double-state hybrid model[11],S.H.Yu proposed that the atomic hybrid state in the actual crystal is not continuous and drew up the table of hybrid state corresponding to every element by means of the quantum-mechanical treatment of valence bond together with the empirical analysis of various atom hybrids state in a vast amount of substance[4]. From this table it can be obtained that there are 64, 28 and 6 kinds of hybrid states for Fe, V and Al atoms. Example for bond-forming Al atom, there are 6 kinds of the covalent electron number (n_c=1.0000, 1.0330, 1.1734, 2.5296, 2.8970, 3.0000) corresponding to 6 different hybrid states. In this paper, the covalent electron number of Al, Fe, Nd atoms in the Al_8Fe_4Nd phase used for the BLD method computing have been taken from the hybrid state table of elements.

table.2 Valence Electron Configuration of Al, Fe, Nd atoms in Al_8Fe_4Nd

ΔD = 0.01208 Å	R_{Fe}=1.0408 Å	R_{Al}=0.7980 Å	R_{Nd}=1.4932 Å
n_{Fe}=4.6904	$n_{Al(1)}$=1.1734	$n_{Al(2)}$ =2.5296	n_{Nd} =2

2.2 Transformation point of Al_8Fe_4Nd phase

Furthermore, using above achieved valence electron structural parameters the melting point of every kind of bond in a cell unit of crystal can be obtained. The formulate for calculating melting point is written as [12]:

$$T_m = \frac{b}{3R}\{\frac{n_\alpha}{D_{n\alpha}} f + \frac{n_l f'}{I_s \overline{D}} - \frac{CW}{I_s}\} \times 10^3 \quad (3)$$

Here, T_m is the melting temperature of every kind of bond in a cell unit of crystal, n_α is the α-bond covalent electron pairs number, $D_{n\alpha}$ is the bond length, n_l is the number of crystal lattice electron, $I_s = \sum I_\alpha r_\alpha$, $\overline{D} = \frac{\sum I_\alpha D_{n\alpha}}{\sum I_\alpha}$, $f' = \sqrt{2\alpha'}$, $\alpha' = \frac{n_l}{n_T}$, n_T is the total covalent electron pairs number of α-bond. C and W are parameter, in here $C = 0.907P$. Because in the three element (Al, Nd, Fe) only Fe have C and W, so only provide C and W of Fe here. C and W of Fe are 3 and 0.29247, respectively. b of Fe, Al and Nd are 156.975, 191.433 and 133.155KJ·Å /mol [4,13], respectively. So we gain all parameter for calculating the melting temperature of every kind of bond in a cell unit of

crystal, listing in table 3. The result of calculation list in the table 4.

3. Discussion

Experiments indicated that when Rapidly Solidified Al-Fe-V-Si-Nd were heated around 400 ℃ there was a phase transformation from Al_8Fe_4Nd to α-$Al_{13}(Fe,V)_3Si$. In general, the procedure of transformation from metastable phase to stable phase was controlled by diffusion, corresponding to the decomposition of old phase and formation of new phase. Considering from atoms angle, the decomposition of phase is the results of atoms bonds break in phase unit. To Al_8Fe_4Nd, people did not know the break of what bonds control transformation procedure. Seeing from table 5, we knew that the break temperatures of Fe-Fe, Al(1)-Al(1)*, Fe-Al(2), Al(1)-Al(2), Al(2)-Al(2), Al(1)-Al(2)' are above 500 ℃, the break temperatures of Fe-Al(1), Al(1)-Al(1), Nd-Fe, Al(2)-Al(2) are below 314 ℃ and that of Nd-Al(1), Nd-Al(2) are 367.196 ℃ and 379.296 ℃, respectively. Combining the experimental results, it is obvious that the breaks of Nd-Al(1), Nd-Al(2), Nd-Fe is related to transformation of Al_8Fe_4Nd. When temperatures reached 380 ℃, Nd-Al(1), Nd-Al(2), Nd-Fe broke. At this time, Nd was in free state, and it would leave unit. So Al_8Fe_4Nd was decomposed. At the other side, in spite of the breaks of Nd-Al(1), Nd-Al(2), Nd-Fe, other atoms still keep Al-Al, Al-Fe short distance order near neighbor because of the effect of strong bonds group such as Fe-Fe, Al(1)-Al(1), Fe-Al(2), Al(1)-Al(2) and so on. At the same time, because of the leave of Nd, strong repulsive interaction between Nd and V atoms decreased, so V atoms can easily diffuse to the location of original unit and create nucleation conditions for $Al_{13}(Fe,V)_3Si$.

table.3 Parameter for calculating the melting temperature of Al_8Fe_4Nd phase

Bond	b(KJ ·Å /mol)	n_α	$D_{(n\ \alpha)}$ Å	f	n_l	I_s	$\overline{D}$(Å)	f'	CW
1.Fe-Fe	156.975	0.48700	2.257	2.05315	0.8731	73.046	2.86215	0.5602	0.79582
2.Al_1-Al_1*	191.433	0.98069	2.37303	1.21245	1.8266	73.046	2.86215	1.10351	0
3.Fe-Al_2	173.349	0.28699	2.54413	1.94326	0.67175	73.046	2.86215	0.5601	0.26527
4.Al_1-Al_2	191.433	0.28831	2.69251	1.52291	1.1485	73.046	2.86215	0.83176	0
5.Fe-Al_1	173.349	0.14164	2.72872	1.6328	1.34985	73.046	2.86215	0.83186	0.26527
6.Al_2Al_2	191.433	0.19269	2.79664	1.83337	0.4704	73.046	2.86215	0.5600	0
7.Al_1-Al_2*	191.433	0.18261	2.81065	1.52291	1.1485	73.046	2.86215	0.83176	0
8.Al_1-Al_1	191.433	0.07789	3.03338	1.21245	1.8266	73.046	2.86215	1.10351	0
9.Nd-Al_1	159.657	0.12740	3.20799	2.20357	1.4133	73.046	2.86215	0.96	0
10.Nd-Al_2	159.657	0.12692	3.20879	2.51403	0.7352	73.046	2.86215	0.68825	0
11.Nd-Fe	144.576	0.04104	3.35447	2.62392	0.9365	73.046	2.86215	0.68836	0.63666
12.Al_2-Al_2	191.433	0.00226	3.95505	1.83337	0.4704	73.046	2.86215	0.56	0

4.Conclusion

The calculating results show that Al_8Fe_4Nd phase produce transformation at 379 ℃, it concur well with the experimental results. It is obvious that the breaks of Nd-Al(1), Nd-Al(2) and Nd-Fe is the key factor for the dissolution of Al_8Fe_4Nd phase. At the other side, strong bonds, such as Fe-Fe, Al(1)-Al(1)*, Fe-Al(2), Al(1)-Al(2) and so on, keep atoms in short-range order.

Table.4 The calculating results of Al_8Fe_4Nd phase melting point

Bond	Broken Temperature(℃)	Bond	Broken Temperature(℃)
1.Fe-Fe	2301.258	7.Al(1)-Al(2)*	521.783
2.Al(1)-Al(1)*	3648.666	8.Al(1)-Al(1)	40.155
3.Fe-Al(2)	1189.749	9.Nd-Al(1)	367.196
4.Al(1)-Al(2)	1014.534	10.Nd-Al(2)	379.296
5.Fe-Al(1)	300.466	11.Nd-Fe	-96.230
6.Al(2)-Al(2)	706.55	12.Al(2)-Al(2)	-255.266

References

1. J.C.Lee, S.Lee, D.Y.Lee and N.J.Kim, Metall.Trans., 22A,853(1991).
2. B.C.Go and B.Wilshire, Scripta Meatll.,26,435(1992).
3. J.Q.Wang, Ph.D.Dissertation, Northeasten University of China, 1996
4. R.L.Zhang, The Empirical Electron Theory of Solids and Molecules,p.427, Changcun, China, Jilin Science and Technology Press, 1993.
5. O.S.ZARECNJUK and P.I.KRIPJAKEVIC, 1962.Kristallografija, SSSR,7,543-554
6. Z.L.Liu, C.M.Liu, L.M.Zhao, R.L.Zhang and B.Wang, Science in China, A32, 367(1989).
7. R.L.Zhang, S.C.Wu and S.H.Yu, Science in China, 2A,197(1988).
8. W.D.Xu, R.L.Zhang and S.H.Yu, Science in China, 3A, 323(1988).
9. S.H.Yu, Inter.J.Modern Phy., B2,599(1987).
10. L.Pauling, Phys.Rev.,(ii)54,899(1938).
11. L.Pauling, The Nature of the Chemical Bond, P.60, third edition, Itace, New York, Cornell University Press, (1960).
12. J.M.Zhang, R.L.Zhang, W.T.Zheng etc. ActaScientiarum Naturalium Universitatis Jilinensis,4(1994)75
13. Sh.K.Wang, Zh.J.L ü . Acta of the Electromechanical institute (Shenyang, China),7(1979)2
14. J.Q.Wang, C.F.Qian, B.J.Zhang, M.K.Tseng and S.W.Xiong, Scripta Materialia, Vol.34.No.10,1509(1996)