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Fracture behavior of DO_3-ordered Fe-Al alloy with V addition①

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Abstract: The fracture behaviors of DO_3-ordered Fe-28Al alloys with or without V addition were studied. The results show that addition of element V into Fe-Al alloy can improve the mechanical properties of the alloy. Contrasted with transgranular fracture of Fe_3Al alloy at room temperature, the Fe_3Al containing V has intergranular and transgranular cleavage mixed fracture mode. The theoretical calculation conforms that V addition could increase cleavage strength of Fe_3Al alloy from 98.405 7 kJ/mol to 173.144 5 kJ/mol in ⟨111⟩ direction and from 29.660 4 kJ/mol to 47.673 0 kJ/mol in ⟨100⟩ direction.

Key words: fracture; cleavage strength; DO_3-ordered Fe-Al alloy; vanadium
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1 INTRODUCTION

There has been more and more research on the ordered iron aluminides based on the Fe-Al system in recent years. The iron aluminide Fe_3Al occurs when the content of aluminum is in the range of 24%-32% (mass fraction). It has two ordered structures: DO_3-ordered structure which exists below the critical temperature of 540 ℃ and B2-ordered structure between 540 and 760 ℃. The ordered iron aluminides have excellent oxidation resistance, low cost, enrichment in resources and some other advantages, which leads them to many engineering applications[1, 2]. However, the brittleness and lack of ductility at room temperature have been the major obstacles to their uses as structural materials. Recently many research reports showed that alloying elements could improve their mechanical properties. For example, addition of alloying elements such as Cr, Mn, Ce could improve their ductility at room temperature[3, 4].

Despite the changes in grain size, APB energy and superdislocation structure were suggested to be the major effects of ternary additions on the properties of the aluminides, and have been studied for many years, but relatively little attention has been paid to the changing valence electron structure, which is considered to be the cause of brittleness of the ordered aluminides.

The purpose of this paper is to report the effect of V on the fracture behavior of DO_3-ordered Fe_3Al at room temperature and explain the mechanism by solid valence electron theory[5] as a depletion of valence bonding strength among Fe, Al and V atoms.

2 EXPERIMENTAL

Two DO_3-type Fe_3Al alloys were studied. They were Fe-28Al and Fe-28Al-1.5V (mole fraction, %). The alloys were smelted in a vacuum induction furnace and cast into molds. After homogenizing at 950 ℃ for 4 h, the alloys were hot-rolled at 950 ℃ and warm-rolled at 650 ℃ from 7 to 0.7 mm. The rolled sheets were cleaned in a solution of 95% H_2O and 5% hydrochloric acid to remove surface oxide layer. Tensile samples with a gauge section of 0.7 mm × 5 mm × 20 mm were punched from the sheet and then heat treated in air at 800 ℃ for 1 h for recrystallizing and at 450 ℃ for DO_3 ordering. The tensile samples were tested at temperature between 25 and 850 ℃ in air at a strain rate of $(3.3-5.0)\times 10^{-2}\ s^{-1}$ on an LX-2 500 N tensile machine. The fracture surfaces were examined by DXS-X2 scanning electron microscopy (SEM).

3 RESLUTS AND DISCUSSION

Tensile results are listed in Table 1. It can be seen from Table 1 that the two alloys are characteristic of brittle material at room temperature, but Fe_3Al has lower strength than that containing V, which indicates that the addition of V into Fe_3Al can slightly improve its ductility at room temperature. The tensile samples of Fe_3Al containing V show some increase in tensile strength at room temperature. SEM observation in our experiment shows that V element dis-

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tributes uniformly in the alloy and the gain sizes are smaller in the alloy with V than that in the alloy without V, suggesting that V addition improves mechanical properties of DO_3-ordered Fe_3Al alloy.

Table 1 Mechanical properties of two alloys at room temperature

Alloy	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%
Fe-28Al	441.2	375.2	2.0
Fe.28Al-1.5V	533.1	446.5	2.5

The tensile fracture modes of alloys were observed by SEM. The results show some differences in fractures, crack shapes, and distribution in the alloy with or without V, as shown in Fig. 1. DO_3-ordered Fe_3Al had transgranular cleavage fracture mode at room temperature. It can be seen from Fig. 1(a) that cleavage planes are large and there are many parallel secondary transgranular cracks from grain boundaries to inside, indicating easy crack propagation during the fracture of Fe-28Al alloy. On the other hand, the DO_3-ordered alloy with V had transgranular cleavage-intergranular fracture mode at room temperature, as shown in Fig. 1(b). Its cleavage planes are small and consist of small cleavage steps and ripple ridges, which suggests higher cleavage strength in the alloy with V, as contrasted with the alloy without V.

The optical microscope observation of crack propagation was also done during the tensile test. The crack in the alloy with V addition appears zigzag and there are a lot of slender slip lines around the tip of crack while the crack in the alloy without V looks rather straight and no obvious plastic deformation at crack tip is found, indicating that the addition of V improves the ductility of the alloy and crack propagation are somehow retarded due to plastic deformation arising from the emission of dislocations at crack tip after addition of V.

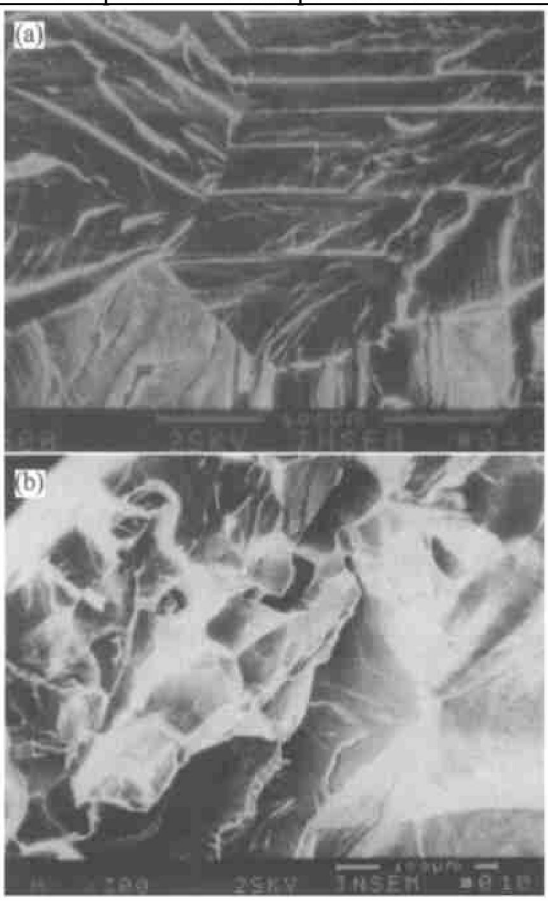

Fig. 1 SEM morphologies of fracture
(a) —Fe-28Al alloy; (b) —Fe-28Al-1.5V alloy

For brittle alloy, its cleavage strength is related to atom bonds on cleavage plane. From the above results, it is suggested that the V addition into Fe-28Al alloy does not change the brittleness feature of the alloy, but can raise cleavage strength and then lead to large plastic deformation in the alloy before fracture. Those results could be reasonably explained by theoretical analyzing of bond energy strength for the alloys with or without V, based on solid-valence electron theory, as a depletion of valence bonding strength among Fe, Al and V atoms[6-8]. The theoretical model is described as follows.

Firstly, the DO_3 superlattice mode is considered at the stochiometric composition of Fe_3Al. In order to give the most general treatment of DO_3 superlattice formed in this alloy, it is convenient to picture the unit cell as being composed of four interpenetrating face-centered cubic sublattices, and call the knots of them sites Ⅰ, Ⅱ, Ⅲ and Ⅳ respectively, as shown in Fig. 2. While Al atoms occupy site Ⅰ, Fe atoms occupy sites Ⅰ, Ⅱ, Ⅲ and Ⅳ. The DO_3 structure can change into B2 structure above 540 ℃. In Fe_3Al superlattice, sites Ⅲ and Ⅳ are occupied only by Al atoms, while the remaining Fe and Al atoms occupy sites Ⅰ and Ⅱ in a random manner[9]. The lattice parameter of DO_3 structure (indicated as a') is twice of that of the B2 lattice, and the volume of its unit cell is now eight times of the B2 lattice. The molecular formula of DO_3 can be shown as $Al^{I}Fe^{II}Fe^{III}Fe^{IV}$, where superscript Ⅰ, Ⅱ, Ⅲ and Ⅳ, are sites Ⅰ, Ⅱ, Ⅲ and Ⅳ respectively.

Secondly, DO_3 superlattice structure is considered for the Fe-28Al alloy with a comparison with the stoichiometric composition of Fe_3Al. While Fe atoms occupy sites Ⅲ and Ⅳ and Al atoms occupy site Ⅰ, which are similar to that in DO_3 superlattice mode at the stoichiometric composition of Fe_3Al, site Ⅱ is partly occupied by Al atoms and Fe atoms[9, 10]. According to Yu's theory "equal cell mode", its equimolecular formula can be shown as $Al^{I}Al^{II}_{0.12}Fe^{II}_{0.88}Fe^{III}Fe^{IV}$, where site Ⅱ is occupied by equiatoms of 88% Fe atoms and 12% Al atoms. Its lattice constant, a', is 2.896 0 Å, which was measured by X-ray diffraction method. The valence electron and bond strength of DO_3-ordered Fe-28Al alloy in each bond being not ignored at room temperature were mathematically calculated by computer simulation of Fe and Al hybrid atomic

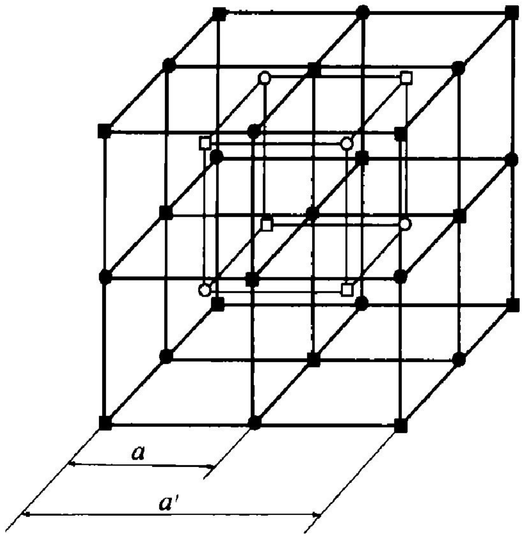

Fig. 2 DO3-type superlattice, consisting of four nonequivalent interpenetrating face-centered cubic sublattices
(Sites: ○—Ⅰ; □—Ⅱ; ■—Ⅲ; ●—Ⅳ)

states based on the valence electron theory [6,8,12]. The results are shown in Table 2. In Table 2, I_α is the number of equivalence bonds, n is the number of valence electrons, D_n is the experimental space of each valence bond, and E is the bond strength in each bond. The calculating procedure is simply described below.

1) Determining space of valence bond D_n

The experimental space of the valence bond is the distance between the two atoms that form the bond. Ignoring the bonds whose distance is more than $\sqrt{3}\,a'$ (the atoms react with each other very weakly in those bonds), there are 14 kinds of bonds being not ignored, as listed in Table 2. I_α is calculated by

$$I_\alpha = I_m \cdot I_s \cdot I_k \qquad (1)$$

Table 2 Valence electron and bond strength in DO3 Fe-28Al superlattice

Bond	I_α	n	D_n	$E/(\mathrm{kJ\cdot mol^{-1}})$
Fe^{III}-A^{II}	8.00	0.489 8	2.508	19.222 0
Fe^{IV}-A^{II}	8.00	0.469 6	2.508	18.683 0
A^{II}-A^{III}	1.44	0.187 5	2.896	4.562 0
Al^{I}-Al^{I}	12.00	0.187 5	2.896	5.798 0
Al^{II}-Al^{II}	0.72	0.187 5	2.896	3.589 0
Fe^{II}-Al^{II}	1.44	0.133 4	2.896	3.616 3
Fe^{III}-Al^{II}	0.96	0.489 8	2.508	15.332 2
Fe^{IV}-Al^{II}	0.96	0.469 6	2.508	14.699 9
Fe^{II}-Fe^{II}	5.28	0.094 9	2.896	3.643 0
Fe^{II}-Fe^{III}	7.04	0.348 4	2.508	15.234 3
Fe^{II}-Fe^{IV}	7.04	0.334 0	2.508	15.234 3
Fe^{III}-Fe^{III}	12.00	0.002 1	4.096	0.555 5
Fe^{III}-Fe^{IV}	12.00	0.099 0	2.896	3.748 9
Fe^{IV}-Fe^{IV}	12.00	0.001 9	4.096	0.051 6

where I_m is the number of reference atoms included in the lattice cell, I_s is the duplicity factor of bonds related to the symmetrical atom sites, and I_k is the duplicity factor of the bonds related to the atoms that form a bond.

2) Establishing lg γ equation[6]

$$D_n^{uv} = R_u(I) + R_v(I) - \beta \lg \pi \qquad (2)$$

where D_n^{uv} is the bond distance between u, v atoms, $R_u(I)$ and $R_v(I)$ are the half-distance of the bond between u, v atoms, and constant β is 0.71. The theoretic bond distance $\overline{D_n}$ being not ignored is calculated by Eqn. (2), and order

$$\gamma_\alpha = \frac{n_\alpha}{n_{Fe^{II}-Al^{I}}} \qquad (3)$$

Then the following formula can be obtained from Eqns. (1)−(3):

$$\lg \gamma_{Al^{I}-Fe^{III}} = \frac{[D_{nFe^{II}-Al^{I}} - D_{nAl^{I}-Fe^{III}}] + [R_{Fe^{III}}(\mathrm{I}) - R_{Fe^{II}}(\mathrm{I})]}{0.71}$$

$$\lg \gamma_{Al^{I}-Fe^{IV}} = \frac{[D_{nFe^{II}-Al^{I}} - D_{nAl^{I}-Fe^{IV}}] + [R_{Fe^{IV}}(\mathrm{I}) - R_{Fe^{II}}(\mathrm{I})]}{0.71}$$

$$\vdots$$

$$\lg \gamma_{Fe^{IV}-Fe^{IV}} = \frac{[D_{nFe^{II}-Al^{I}} - D_{nFe^{IV}-Fe^{IV}}] + [2R_{Fe^{II}}(\mathrm{I}) - R_{Al^{I}}(\mathrm{I})]}{0.71} \qquad (4)$$

3) Establishing the equation for number of valence electrons

According to the equastructure of DO3-ordered Fe-28Al alloy, the number of valence electrons in the lattice cell is

$$\sum n = n_{Al^{I}} + 0.12 n_{Al^{II}} + 0.88 n_{Fe^{II}} + n_{Fe^{III}} + n_{Fe^{IV}} \qquad (5)$$

On the other hand, the number of valence electrons in all bonds being not ignored is

$$\sum n = n_{Fe^{II}-Al^{I}} \sum I_\alpha \gamma_\alpha \qquad (6)$$

From Eqns. (5) and (6), Eqn. (7) is then obtained:

$$n_{Fe^{II}-Al^{I}} = \frac{n_{Al^{I}} + 0.12 n_{Al^{II}} + 0.88 n_{Fe^{II}} + n_{Fe^{III}} + n_{Fe^{IV}}}{\sum I_\alpha \gamma_\alpha}$$

As

$$|\Delta D_n| = \begin{vmatrix} D_{nFe^{II}-Al^{I}} - \overline{D}_{nFe^{II}-Al^{I}} \\ D_{nAl^{I}-Fe^{III}} - \overline{D}_{nAl^{I}-Fe^{III}} \\ \vdots \\ D_{nFe^{IV}-Fe^{IV}} - \overline{D}_{nFe^{IV}-Fe^{IV}} \end{vmatrix} \leqslant 0.005\,\mathrm{nm} \qquad (7)$$

Theoretic bond distance $\overline{D_n}$ is consistent with experimental bond distance D_n and then the calculated hybrid atomic states are what atoms exist actually. Calculating the data in the hybrid table of Fe and Al atoms[12, 13] by computer and analyzing the calculated results, we can determine that Al^{I}, Al^{II}, Fe^{II},

Fe^{III}, and Fe^{IV} are 5, 3, 16, 15 and 16 hybrid states, respectively.

4) Calculating bond energy

After hybrid atomic states in the cell are determined, the bond energy of each valence bond can be calculated by

$$E_{\alpha}=\frac{b\cdot f\cdot n}{D_n} \qquad (8)$$

where b is the factor related to the shield effect of the electron on the nuclon charge, and f is the factor related to the bonding ability of the atoms and can be calculated by

$$\left.\begin{aligned} f &= \sqrt{\alpha}+\sqrt{3\beta}+\sqrt{5\gamma} \\ \alpha &= \frac{[l\tau+(l'\tau'-l\tau)C_{\tau\sigma}]}{n} \\ \beta &= \frac{[m+9m'-m)C_{\tau\sigma}]}{n_{\tau\sigma}} \\ \gamma &= \frac{[n+(n'-n)C_{\tau\sigma}]}{n_{\tau\sigma}} \end{aligned}\right\} \qquad (9)$$

Inserting the data[13, 15] of the atoms at four sublattice sites into Eqns. (8) and (9) could lead to the calculation of each valence bond energy. Table 2 shows that there are six strong bonds in the ⟨111⟩ direction, such as Al^{I}-Fe^{III}, Al^{I}-Fe^{IV}, Al^{I}-Fe^{III}, Al^{I}-Fe^{IV}, Fe^{II}-Fe^{III}, and Fe^{II}-Fe^{IV}, and their total bond energy is about 98.407 5 kJ/mol. The bonds are weak in the ⟨100⟩ direction: Al^{II}-Al^{II}, Fe^{II}-Fe^{II}, Al^{I}-Fe^{II}, Fe^{III}-Fe^{III}, and Fe^{IV}-Fe^{IV}, and their total bond energy is only 29.660 4 kJ/mol, about one-third of the energy in the ⟨111⟩ direction, as listed in Table 3. The higher the bond energy, the stronger the bonding ability between atoms and then the higher the cleavage strength on the bond. It is obvious that the alloy would fracture on {100} planes, which is consistent with the result made by SUN et al[2], who confirmed {100} cleavage fracture in DO_3 Fe_3Al by using the X-ray back-reflection Laue method.

Thirdly, the DO_3 superlattice mode is considered for the Fe-28Al-1.5V alloy. The Fe sites of II, III and IV are easily exchanged by V atoms because the nature of the V element is similar to that of Fe, such as atom size or atomic number, and Fe atoms are lacking while Al atoms are rich in DO_3 Fe-28Al-1.5V alloy. When V atoms occupy Fe sites of II, III and IV, respectively, the valence electrons bond strengths are calculated by computer simulation of Fe, Al, and V hybrid atomic states[9-11], as listed in Table 3 and Table 4. Table 4 shows that although the V addition could increase the bond strength in both ⟨100⟩ and ⟨111⟩ direction, the bond strength in the ⟨100⟩ direction for Fe-28Al-1.5V alloy is still weaker than that in the ⟨111⟩ direction, meaning that the cleavage would still take place on {100} planes. The increase in bond strength in the ⟨100⟩ direction after the V addition could lead to increase in cleavage strength on {100} planes and then increased in fracture strength of the Fe-28Al-1.5V alloy, so the mechanism of change in cleavage strength could explain the tensile results why the V addition could

Table 3 Effect of V on valence electron and bond strength in alloys

Bond	Fe-28Al		Fe-28Al-1.5V	
	n_{α}	E_{α}/(kJ•mol^{-1})	n_{α}	E_{α}/(kJ•mol^{-1})
Al^{I}-Fe^{II}	0.133 4	4.596 1	0.139 2	4.731 0
Al^{I}-Fe^{III}	0.489 8	19.222 0	0.469 7	18.686 5
Al^{I}-Fe^{IV}	0.469 6	18.683 0	0.469 7	18.686 5
Al^{I}-Al^{II}	0.187 5	4.562 0	0.187 6	4.564 4
Al^{II}-Al^{II}	0.187 5	5.798 0	0.187 6	5.801 8
Al^{II}-Al^{II}	0.187 5	3.589 5	0.187 6	3.591 4
Al^{II}-Fe^{II}	0.133 4	3.616 3	0.139 2	3.722 4
Al^{II}-Fe^{III}	0.489 8	15.332 2	0.469 7	14.703 0
Al^{II}-Fe^{IV}	0.469 6	14.699 9	0.469 7	14.703 0
Fe^{II}-Fe^{III}	0.094 9	3.643 0	0.103 3	3.858 8
Fe^{II}-Fe^{IV}	0.348 4	15.234 3	0.348 5	15.238 2
Fe^{III}-Fe^{III}	0.344 0	15.234 3	0.348 5	15.238 2
Fe^{II}-Fe^{II}	0.002 1	0.055 5	0.001 9	0.051 6
Fe^{III}-Fe^{IV}	0.099 0	3.748 9	0.094 9	3.643 0
Fe^{IV}-Fe^{IV}	0.001 9	0.051 6	0.001 9	0.051 6
V-Al^{I}			0.871 5	30.995 0
V-A^{II}			0.871 5	30.995 0
V-Fe^{II}			0.646 7	25.278 5
V-Fe^{III}			0.176 2	6.045 3
V-Fe^{IV}			0.003 6	0.087 4
V-V			0.006 7	0.144 9

Table 4 Bond strength (E) in DO_3-ordered structure with or without V (kJ•mol^{-1})

Alloy	Direction	E_{Al-Fe}	E_{Fe-Fe}	E_{Al-Al}	E_{Al-V}	E_{V-V}	E_{Fe-V}	E_{Total}
Fe-28Al	⟨111⟩	67.937 1	30.468 6					98.4057
	⟨100⟩	8.212 4	7.499 0	13.949 0				29.660 4
Fe-28Al-1.5V	⟨111⟩	66.779	19.097 0		61.990 0		25.278 5	173.144 5
	⟨100⟩	8.453 4	18.984 4	13.957 6		0.144 9	6.132 7	47.673 0

improve mechanical properties of the DO_3-ordered Fe_3Al alloy and changed the fracture mode from cleavage failure to intergranular mixing failure.

4 CONCLUSIONS

1) The addition of V changes DO_3-ordered Fe_3Al fracture mode from transgranular cleavage to transgranular cleavage-intergranular mixed type, which is related to high cleavage strength of Fe_3Al containing V.

2) The theoretical analysis about the cleavage strength for DO_3-ordered Fe_3Al alloys with or without V addition confirms the results for the Fe_3Al alloy fracture on {100} planes.

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REFERENCES

[1] Mckamey C G, Devan J H, Tortorelli P F, et al. A review of recent developments in Fe_3Al-based alloys[J]. J Mater Res, 1991(6): 1779.

[2] SUN Yang-shan, GUO Jun, ZHANG Li-ning, et al. Effects of Ce and Cr on room temperature mechanical properties of Fe_3Al[J]. Acta Metall Sinica, 1991, 27(4): 255.

[3] Knibloe J R, Wright R N. Elevated temperature behavior of Fe_3Al with chromium addition[J]. Mater Sci Eng A, 1992, 153: 382.

[4] LOU Bai-yang, ZHANG X B, LIU Mao-sen, et al. Effects of Mn on fracture behavior of DO_3 Fe_3Al-based intermetallic alloy[J]. J Mater Sic, 1998, 33: 1481.

[5] LOU Bai-yang, LIU Mao-sen, CHANG Xiao-bing, et al. Influence of Mn addition on the ordering of DO_3 Fe-28% Al intermetallics[J]. J Mater Sci, 1999, 34: 4039.

[6] Marcinkowski M J, Taylor M E, Kayser F X. Relationship between atomic ordering and fracture in Fe-Al alloy [J]. J Mater Sci, 1975, 10: 406.

[7] YU Rui-huang. Experienced electronic theory of the solid and molecule[J]. Chinese Sci Bull, 1978, 23(4): 271.

[8] LOU Bai-yang, LIU Mao-sen, MAO Zhi-yuan. The effect of Mn addition on the cleavage strength in DO_3 Fe-28Al alloy[J]. J Mater Sci Letters, 1998, 17: 1945.

[9] Taylor A, Jones R M. Constitution and magnetic properties of iron-rich iron-aluminum alloys[J]. J Phys Chem Solids, 1958(6): 16.

[10] ZHANG Jie-ming, ZHANG Rui-lin, YU Rui-huang, et al. Electron theory study of order-disorder transformations in Fe-Al alloys[J]. Acta Metall Sinica, 1994, 30 (5) : A204.

[11] XU Rui-huang, ZHANG Rui-lin, YU Rui-huang. Study of joining energy between metal compounds[J]. Chinese Science, 1988, 3 (3): 323.

[12] YU Rui-huang. Experienced electronic theory of the solid and molecule-electron model[J]. Chinese Sci Bull, 1981, 26: 206.

[13] LOU Bai-yang. Mechanical behaviors of Fe_3Al with V addition[J]. The Chinese Journal of Nonferrous Metals. 2000, 10(S1): 36. (in Chinese)

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