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COMPOSITION DEPENDENCE OF THE M, TEMPERATURE IN THE β'NiAl COMPOUND

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Martensitic transformation start (M_s) temperatures have been measured in binary NiAl sintered alloys (36 - 38 at% Al) using an electrical resistivity method. The composition dependence of the M_s temperature has been investigated by a statistical approach employing the Bragg-Williams approximation. The results obtained are as follows: (1) In these alloys, the linear relationship between M_s temperature and aluminum content, having a slope of about 160K/at% Al, was observed. The M_s temperature is about 30K below the corresponding Al temperature. (2) There are no differences in the composition dependence of the M_s temperature between the sintered and cast alloys. (3) The composition dependence of the M_s temperature is found to have a good correlation with that of T_c. (4) The interaction parameter V_{NiAl} between Ni and Al atoms in the martensite phase could be estimated at about 12.7 kJ/mol. (5) The composition dependence of the M_s temperature is closely related to the interaction parameters in the parent and martensite phase and the temperature dependence of the difference in the Gibbs free energy of constituent elements between the Al (fcc) and the A2 (bcc) crystal structure.

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Keywords: intermetallic compound, nickel aluminum, sintered alloy, martensitic transformation, martensite start temperature, electrical resistivity

I. Introduction

In our previous paper[1], we investigated morphological and mechanical properties and shape memory effect of Martensitic transformation of sintered alloys of NiAl metallic compound (β), which contained 36 - 38 % of Al. We estimated A_f temperature from the temperature of the shape recovery completion, and found that it strongly depended on composition (about 160K/at% Al). This

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tendency was also found for the M_s temperature (temperature for the beginning of transformation).[7-4] Thus, this is quite a general feature for the Martensitic transformation of NiAl.

The lower the concentration of β' NiAl, the higher the Martensitic transformation temperature. This was interpreted in terms of the stability of the B2 phase which is 3/2 electron compounds or of resistance forces due to shear deformation of Martensitic transformation.[5,6]

However these discussions are qualitative and there is no quantitative analysis based on the band electron structure or thermodynamics approach. In the present work, we investigated relationships between M_s temperature and composition of NiAl sintered alloys and compared them with those of cast alloys. Further, we studied a main controlling factor for the M_s temperature using the Bragg-Williams approximation of statistical thermodynamics.

II. Experiment

We used the same NiAl sintered alloys as we used previously.[7] Al contents of our samples were between 36 - 56 at% with every 0.5 at% step. Samples for electrical resistance measurement were thermally treated (1273-86.4 ks), made in wire rods of 1mm x 1mm x 25mm, heated at 1,573 K maintaining 7.2 ks, and rapidly quenched into an ice salt water.

We measured electrical resistance of samples which had perfect Martensite structures by quenching, using the four probe method.

The samples were heated and cooled in an argon atmosphere using an image furnace. The potential difference between the both ends with 50 mA steady current and the electro motive force of the thermocouple were input in the X-Y recorder and we obtained resistance temperature curves from there.

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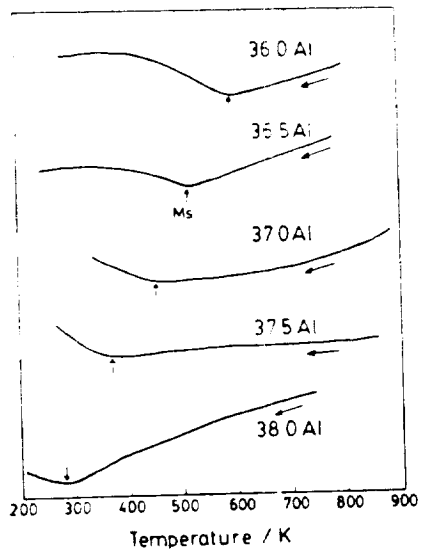

Figure 1

III. Experimental Results and Discussion

1. Electric Resistance - Temperature Curve

In order to investigate the starting temperature of Martensitic transformation, we measured electric resistance during the cooling process. The relation between electric resistance and temperature is shown in Fig. 1. The resistance decreases as temperature decreases and then it again increases when temperature becomes lower than a certain value. Such local minima correspond to a M_s temperature and the minima tend to become lower as the Al concentration increases.

2. M_s (A_f) Transformation Temperature - Composition Curve

A plot of M_s temperature against composition is displayed in Fig. 2. For comparison purposes, we included in Fig. 2 data of cast alloys from Au et al.[2], Sinlalek et al.[3], Chakravorty et al.[4], and Litvinov et al.[5]. Further Nenno and

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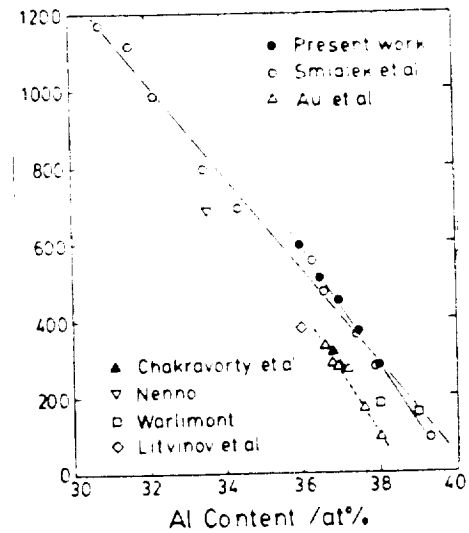

Figure 2

Warlimont's results reported in ref. (3) was also included in Fig. 2. M_s temperature decreases nearly linearly against the Al concentration, as other cast alloys (From now one we call this negative composition dependence of M_s temperature). Our results well agree with those of Smialek et al. Also, the slope of M_s temperature against composition fits to that of high Al content (35 at% Al or more) side obtained by Smialek et al. and to that of Au et al. (about -169 K/at% Al), and is about -160 K/at% Al. When the Al concentration is low, the deposition of Ni_3Al phase is not retarded. In this case Al concentration in the parent phase increases and M_s temperature decreases. The chain line in Fig. 2 which represents Smialek et al's results has a smaller slope. This may be interpreted by such a non-retardation effect. In sum, as far as the M_s temperature is concerned, there is no difference of composition dependence between sintered and cast alloys.

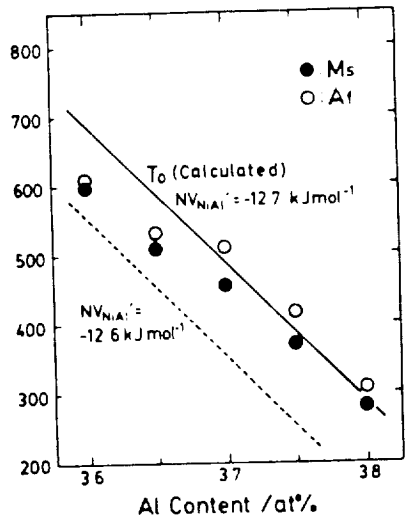

Figure 3

On the other hand, electric resistance of sintered alloys did not vary much and could not determine the A_s temperature uniquely. In our previous paper, we estimated the A_f from the temperature at which deformation at room temperature vanishes due to the heating. Both A_f and M_s temperatures are plotted against Al composition in Fig. 3. The A_f temperature is about 50 K higher than M_s temperature. For cast alloys it is well known that the electric resistance clearly changes at the transformation temperature during the heating process, and that no hysteresis is observed for the electric resistance during the heating and cooling processes.[3,5] The above facts suggest that sintered alloys are less easily transformed from the Martensitic phase to the parent phase than cast alloys.

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3. Previous Views

Typical 3/2 electron compounds which show the Martensitic transformation include CuZn, AuZn, and AuCd. Slopes of the M_s temperature against composition are -80K/at% Zn,[7] 18K/at% Zn,[8] -20K/at% Cd,[9] and -25K/at% Cd,[10] respectively. There is no β phase of noble metals which have as large slopes as NiAl (-150K/at% Al). Most practical NiTi[11] has a slope of about 95K/at% Ti. Thus, NiAl is very specific in this respect. Now we briefly review previous views for the composition dependence of M_s temperature. Ball[7] pointed out two points.

(1) For β phase electron compounds which develop at the valence electron concentration (e/a) of 3/2, the stability of the β phase decreases as the e/a value becomes smaller, according to the Jone's theory.[12] This suggests that M_s temperature increases. CuZn, AgCd, and AuCd mentioned above support this view.

(2) From stoichiometric composition, as the Al concentration decreases, the regularity force between Ni and Al atoms becomes weaker. As a result, the shearing resistance required for the Martensitic transformation becomes small and the M_s temperature increases.

However, there is β phase compounds such as 2 dim AuZn whose M_s temperature increases as the e/a value increases. Further, precise investigations of M_s temperature and e/a for CuZn,[13,14] AuZn,[8] and AuCd[15] by adding the third component to alloys revealed no correlation between the two. Therefore, it is unlikely that the e/a value is a dominant factor determining the composition dependence of M_s temperature. This may also apply to the NiAl phase.

Low frequency thermal vibrations are dominant at low temperatures and the

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amplitude of the smaller elastic modulus becomes large. Therefore, as the Al concentration decreases in NiAl compounds, the shear rigidity becomes lower or an anisotropy of elastic modulus increases, and the M_s temperature increases. To date a relation between the elastic modulus and composition dependence has not been known. Enami et al.[7] found that for NiAl whose Al content was 50 at%, the $C' = (C_{11} - C_{12})/2$ value associated with $\{110\} < 110 >$ shear resistance decreases when the temperature is lowered to M_s temperature from the high temperature side, and that the anisotropy of elastic modulus $A = C_{44}/C'$ was about 9 which is as large as that for CuZn.[7] Further, the elastic anisotropy increases as the concentration of Zn or Cd decreases. These facts support contributions mentioned in (2) of the composition dependence of M_s temperature. However, Ball's view can not give any quantitative understanding of the sharp change of the transformation temperature for NiAl.

4. Relation between M_s Temperature and T_0

The Martensitic transformation is governed by a balance between enthalpic chemical free energy and the elastic non-chemical energy. As suggested by the shape memory characteristics, the transformation is reversible, and the super cooling effect is small enough to be neglected compared to the non-thermal elastic effect. Therefore, a temperature, T_0, at which the chemical free energy of the Martensitic phase is equal to that of the parent phase is very close to M_s temperature.

One of the reasons that we had difficulties determining M_f and A_s temperatures experimentally is that these are lower than A_f and M_s temperatures for NiAl sintered alloys. The order of these temperatures is

$$(M_f, A_s) < M_s < A_f \quad (1)$$

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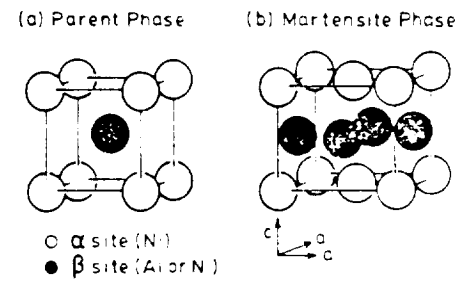

Figure 4

This indicates that the Martensitic transformation of NiAl is the thermal elastic type Martensitic transformation of the second kind.[4] For this case, the following condition is known[4]

$$M_s < T_0 < A_f. \quad (2)$$

Further, because M_s and A_f are very close for NiAl compounds (Fig. 3), T_0 is approximated by $(M_s - A_f)/2$

Thus, the composition dependence of M_s temperature of NiAl is very similar to that of T_0. In other words, composition dependence of elastic anisotropy or shear rigidity may be secondary effects to the transformation. In the next section we examine the validity of these deduction.

5. Free Energy

Enami et al.[6] found that the Martensitic transformation obeys the Bain's deformation. The highest regular structures of the parent and Martensite phases are shown in Fig. 4. Ni(A) atoms predominantly occupy at the α sites and Al(B) atoms mainly sit at the β sites in the parent β2 structure. However, in the Martensite phase each site for M_s separate layers of the L1$_0$ structure which stack alternatively in the C axial direction

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Here we calculate free energies of both crystals in the Bragg-Williams approximation. Let N be the number of all atoms, $[A/\alpha]$ be the number of A atoms at the α sites. Then

$$\begin{aligned} &\alpha \text{ [illegible] } A \text{ [illegible] } A/\alpha \text{ [illegible]} \\ &[A/\alpha] = N(1-X_B)(1-S)/2 \\ &[A/\beta] = N(1-X_B)(1-S)/2 \\ &[B/\alpha] = NX_B(1-S)/2 \\ &[B/\beta] = NX_B(1-S)/2 \end{aligned} \tag{3}$$

where X_B is a mole fraction for B atom ($0 < X_B < 1/2$). S represents the long-range regularity which is the same for both the parent and Martensite phases. S is independent of composition and $S = 1$ and $S = 0$ for the perfect regularity and perfect irregularity, respectively. In the Bragg-Williams approximation, the number of atom pairs is proportional to a product of atomic concentrations which compose pairs. Thus, the binding energy for an A-A atom pair is v_{AA} and then the internal energy of the B2 crystal structure at 0 K is given by[21]

$$\begin{aligned} E(B2)/N = {} & Z_b v_{AA}(1-X_B)/2 - Z_b v_{BB} X_B/2 \\ & + Z_b V_{AB} X_B[1-(1-S^2)X_B] \end{aligned} \tag{4}$$

where Z_b represents the number of the nearest neighbor atoms and is 8 for A2 (bcc) crystals. V_{AB} is an interaction parameter, a thermodynamic factor, and is equal to $v_{AB} - (v_{AA} - v_{BB})/2$. Similarly, the internal energy for the 2 dimensional $L1_0$ structure may be expressed by

$$\begin{aligned} E(L1_0)/N = {} & Z_f v_{AA}'(1-X_B)/2 + Z_f v_{BB}' X_B/2 \\ & + Z_f V_{AB}' X_B[1-(1-S^2/3)X_B] \end{aligned} \tag{5}$$

where Z_f represents the number of the nearest neighbor atoms and is 12 for the Al (fcc) crystals. The thermodynamic factors for the $L1_0$ structure are represented by the prime ( ). The total number of atomic arrangements is given by

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$$W = [N/2]![N/2]![A/\alpha]!^{-1}[A/\beta]!^{-1}$$
$$[B/\alpha]!^{-1}[B/\beta]!^{-1} \tag{6}$$

and thus the entropy of configuration, Φ, may be written by

$$\begin{aligned}\Phi &= k \ln W \\ &= -kN[X_B(1-S)\ln\{X_B(1+S)\} \\ &\quad +\{1-X_B(1+S)\}\ln\{1-X_B(1+S)\} \\ &\quad +X_B(1-S)\ln\{X_B(1-S)\} \\ &\quad +\{1-X_B(1-S)\}\ln\{1-X_B(1-S)\}]/2\end{aligned} \tag{7}$$

This agrees with the entropy of configuration for the $L1_0$ structure formed from the B2 structure.[7] This suggests that in the Bragg-Williams approximation the entropy of configuration may not contribute to T_0 where two structures have the same free energies.

The free energies of the parent and Martensite phases at temperature T(K) may be written by

$$F(B2) = E(B2) - T\Phi + f(B2) \tag{8a}$$

$$F(L1_0) = E(L1_0) - T\Phi + f(L1_0) \tag{8b}$$

where f(B2) and $f(L1_0)$ are specific heats for B2 and $L1_0$ structures, respectively. They are represented by

$$f(B2) = f_A(A2)(1-X_B) + f_B(A2)X_B \tag{9a}$$

$$f(L1_0) = f_A(A1)(1-X_B) + f_B(A1)X_B \tag{9b}$$

where f(A1) and f(A2) are specific heats for fcc and bcc structures of pure metal A. Further, let $F_i(A1)$ and $F_i(A2)$ be free energies for A1 and A2 crystals of atom type i (A or B). Then, F_i may be expressed by

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$$F_i(A1) = Z_i N v_0 (2 - f_i) A1 \tag{10a}$$

$$F_i(A2) = Z_i N v_0 (2 - f_i) A2 \tag{10b}$$

The temperature at which two free energies of eq. (6) become equal is a solution of the following equation:

$$\begin{aligned}&[F_A(A2) - F_A(A1)](1 - X_B) - [F_B(A2) - F_B(A1)]X_B \\ &= Z_i N V_{AB} X_B [1 - (1 - S^2/3) X_B] \\ &\quad - Z_b N V_{AB} X_B [1 - (1 - S^2) X_B]\end{aligned} \tag{11}$$

6. Computation and Estimation of NV_{NiAl}

The change of free energy for the A1 to A2 transformation may be approximated by

$$F_{Ni}(A2) - F_{Ni}(A1) = a_{Ni} - b_{Ni} T \tag{12a}$$

$$F_{Al}(A2) - F_{Al}(A1) = a_{Al} - b_{Al} T \tag{12b}$$

Kaufman et al.[2] used the following values:* a_{Ni} = 5564.72 J/mol, b = 1.046 J/molK, a_{Al} = 10083.4 J/mol, b = 4.8116 J/molK.

* In order to avoid magnetic effects, we used a_{Ni} and b values for higher temperatures (> 1000 K)

The value of S was approximated to be 1 since the NiAl phase is a stable metal component just below the melting point. NV_{NiAl} was calculated to be about -16.4 kJ/mol using heat of formation for NiAl at 298 K. NV_{NiAl} may be slightly larger at 0 K than -16.5 kJ/mol, but the difference may be negligible in our approximation.

There has been no data of V_{NiAl} for the $L1_0$ type of NiAl, but we can evaluate

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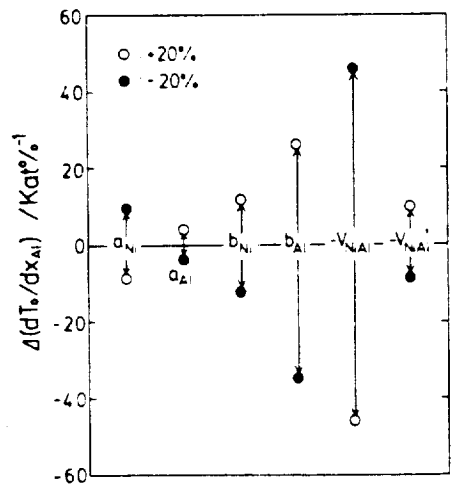

Figure 5

If b_{Ni} is equal to b_{Al}, the slope of T_s concentration curve increases by about 100k/at% Al. From these analysis the significant composition dependence of M_s temperature of NiAl are governed by not only e/a values, but also various effects are accumulated.

In the present work, we used the Bragg-Williams approximation in calculating the free energy for NiAl inter metal compounds, and also neglected effects of variation of axial ratios for $L1_0$ on the free energy. Yet our analysis showed that the theory semi-quantitatively agrees with the observed composition dependence of M_s (T_s). The following may be cited as two reasons that statistical thermodynamics succeeds to interprete Martensitic transformation of NiAl:

(1) In the thermal elastic type Martensitic transformation which is closely related to the shape memory effect, a contribution of non chemical energy to the transformation temperature is much smaller than that of chemical energy.

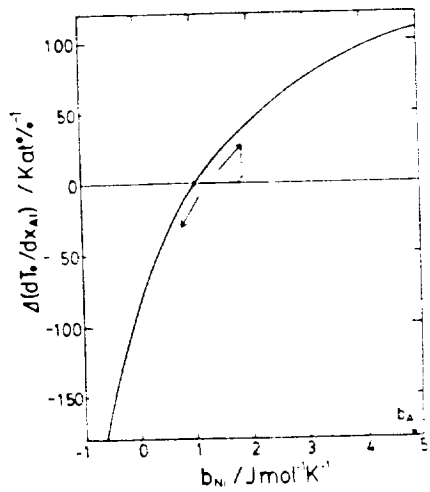

Figure 6

(2) The Martensite phase has a simple periodically laminated structure of 3RL1).

IV. Conclusion

Martensitic transformation start (M_s) temperatures have been measured in binary NiAl sintered alloys (36 - 38 at% Al) using an electrical resistivity method. The composition dependence of the M_s temperature has been investigated by a statistical approach employing the Bragg-Williams approximation. The results obtained are as follows:

(1) In these alloys, the linear relationship between M_s temperature and aluminum content, having a slope of about 100K/at% Al, was observed. The M_s temperature is about 30K below the corresponding Al temperature.

(2) There are no differences in the composition dependence of the M_s temperature between the sintered and cast alloys.

(3) The composition dependence of the M_s temperature is found to have a good correlation with that of T_0.

(4) The interaction parameter V'_{NiAl} between Ni and Al atoms in the martensite phase could be estimated at about 12.7 kJ/mol.

(5) The composition dependence of the M_s temperature is closely related to the interaction parameters in the parent and martensite phase and the temperature dependence of the difference in the Gibbs free energy of constituent elements between the A1 (fcc) and the A2 (bcc) crystal structure.

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References

1) S. Odnai, O. Noguchi, and M. Ueno: Nippon Kinzoku Gakkaishi, 31 (1967), 900.

2) Y. K. Au and C. M. Wayman: Scr. Metall., 6 (1972), 1209

3) J. L. Smialek and R. F. Hehemann: Metall. Trans., 4 (1973), 1571.

4) S. Chakravorty and C. M. Wayman: Metall. Trans., 7A (1976), 47.

5) A. Ball: Met. Sci. J., (1967), 47.

6) V. S. Litvinov, L. P. Zelenin and R. H. Shklyar: Fiz. Metal. Metalloved., 24 (1967), 137.

7) H. Pops and T. B. Massalski: Trans. Met. Soc. AIME., 230 (1964), 1662.

8) N. Ridley and H. Pops: Metall. Trans., 1(1970), 2867.

9) D. de Masson: Trans. Met. Soc. AIME, 218 (1960), 94.

10) N. Nakanishi and C. M. Wayman: Trans. Met. Soc. AIME, 227(1963), 300.

11) T. Funakubo: Keijo Kioku Gokin(Shape Memory Alloys), Sangyo Tosho, (1984).

12) H. Jones: Proc. Phys. Soc., 49 (1937), 250.

13) H. Pops: Trans. Met. Soc. AIME, 236 (1966), 1532.

14) H. Pops and N. Ridley: Metall. Trans., 1 (1970), 2653.

15) M. E. Brookes and R. W. Smith: Met. Sci. J., 2 (1968), 161.

16) K. Enami, J. Hsunuma, A. Nagasawa and S. Nenno: Ser. Metall. 10 (1976), 679.

17) D. Lazarus: Phys. Rev., 74 (1948), 1726; 76(1949), 545.

18) G. M. McManus: Phys. Rev., 129 (1963), 2004.

19) S. Zirinsky: Acta Metall., 4 (1956), 164.

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OF POOR QUALITY

20) K. Enami, S. Nenno and K. Shimizu: Trans. JIM, 14 (1973), 161

21) Y. Takagi: Proc. Phys. Math. Soc. JPN., 23 (1941), 44.

22) L. Kaufman: CLAPHAD, 1 (1977), 26

23) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelley: Selected Values of the Thermodynamic Properties of Binary Alloys, Am. Soc. Metals Park, (1973), 192.

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16. Abstract

Martensitic transformation start (M_s) temps. were measured for Ni-Al sintered alloys contg. 36-38 at.% Al by using an elec. resistivity method. The compn. dependence was investigated by using a statistical approach involving the Bragg-Williams approxn. A linear relation exists between M_s temp and Al content and has a slope of 160 K/at % Al. There are no differences in compn. dependence of the Ms temp. between the sintered and cast alloys. The interaction parameter between Ni and Al atoms in the martensitic phase is estd. at -12.7 kJ/mol. The compn. dependence is closely related to the interaction parameters in the parent and martensitic phases and temp. dependence of the difference in the Gibbs free energy of constituent elements between the fcc. Al and bcc. A2 crystal structure.

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