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Stacking fault probability and stacking fault energy in CoNi alloys①

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[Abstract] The stacking fault probability of CoNi alloys with different contents of Ni was measured by X-ray diffraction methods. The results show that the stacking fault decreases with increasing Ni content and with increasing temperature. The thermodynamical calculation has found an equation that can express the stacking fault energy γ of CoNi at temperature T. The phase equilibrium temperature depends on the composition of the certain alloy. The relationship between stacking fault energy γ and stacking fault probability P_{sf} is determined.

[Key words] stacking fault energy; stacking fault probability; martensitic transformation; CoNi alloy
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1 INTRODUCTION

The study of $\gamma \rightarrow \varepsilon$ transformation in the alloys with low stacking fault energy (SFE) has found that the stacking fault plays an important role during the transformation[1]. The slip of Shockley partial dislocations on alternative {111} planes leads to the stacking faults, which act as the nucleus of ε martensite. So the measurement and calculation of stacking fault energy and related stacking fault probability in the alloy is important for the study of martensitic transformation. Recently, the magnetic induced strain has been found in an CoNi single crystal[3]. The related mechanism is being investigated. It has been already found that $\gamma \rightarrow \varepsilon$ transformation in CoNi alloys is realized through stacking fault[4, 5]. A detailed knowledge of stacking fault energy is essential not only for the study of the related mechanism but also for improving the properties of material dependent on SFE. In this paper the stacking fault probability in 5 CoNi alloys with different contents of Ni is measured by the X-ray methods. The method has been effectively practiced during the study of FeMnSi based alloys[6~8]. The chemical free energy of the alloys is calculated and temperature dependence of SFE is deduced.

2 RELATIONSHIP BETWEEN STACKING FAULT ENERGY AND STACKING FAULT PROBABILITY

The stacking fault energy γ is inversely proportional to stacking fault probability P_{sf} i. e. $\gamma \propto 1/P_{sf}$ as shown in the following equation developed by Noskova and Pavlov[9]:

$$\gamma = \frac{Ga_o^2 d\rho}{24\pi P_{sf}} \quad (1)$$

where G is the shear modulus, a_o is the lattice parameter, d is the lattice space of determined crystal plane and ρ refers to the density of dislocation. The error of calculating SFE with Eqn. (1) is quite large due to the difficulty of measuring ρ precisely. Reed and Schramm[10] established another equation:

$$\gamma = \frac{K_{111}\omega_o G_{111} a_o}{\sqrt{3}\pi} A^{-0.37} \frac{\langle \varepsilon_{50}^2 \rangle}{P_{sf}} \quad (2)$$

where K_{111} ω_o is a proportional constant taken as 6.6, G_{111} is the shear modulus on the (111) stacking fault plane with $G_{111} = (C_{44} + C_{11} - C_{12})/3$, ($C_{11}$, C_{12}, C_{44} are the elastic stiffness constants); A is Zener's anisotropy constant with $A = 2C_{44}/(C_{11} - C_{12})$, and $\langle \varepsilon_{50}^2 \rangle$ is the mean square strain. It is also impossible to calculate SFE of CoNi from Eqn. (2) due to lacking of related data of C_{ij}. But both Eqns. (1) and (2) show that γ is inversely proportional to P_{sf} when the dislocation density and shear modulus keeps constant and can be expressed as

$$\gamma = C/P_{sf} \quad (3)$$

where C is a proportional constant.

3 THERMODYNAMICAL CONSIDERATION OF CRITICAL DRIVING FORCE FOR fcc $\gamma \rightarrow$ hcp ε MARTENSITIC TRANSFORMATION IN CoNi ALLOYS

According to the model of substitutional solution, the Gibbs energy of the α (α= hcp, fcc) phase in CoNi alloys can be expressed as

$$G_m^{\alpha} = x_{Co}{}^0G_{Co}^{\alpha} + x_{Ni}{}^0G_{Ni}^{\alpha} + RT(x_{Co}\ln x_{Co} + x_{Ni}\ln x_{Ni}) + {}^EG_m^{\alpha} + \Delta G_m^{mg} \quad (4)$$

where x_i is the molar fraction of the element i, ${}^0G_i^{\alpha}$ is the molar Gibbs energy of element i with the struc-

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ture of the phase α in an hypothetical nonmagnetic state, ${}^{E}G_{m}^{\alpha}$ is the excess Gibbs energy of the phase α, and ΔG_{m}^{mg} is the magnetic contribution of Gibbs energy for α phase.

The excess Gibbs energy ${}^{E}G_{m}^{\alpha}$ is modeled by using the regular solution approximation, i. e. ${}^{E}G_{m}^{\alpha} = x_{Co}x_{Ni}L_{Co,Ni}^{\alpha}$, where $L_{Co,Ni}^{\alpha}$ is defined as a parameter of the regular solution. The expression for the magnetic contribution to the Gibbs energy ΔG_{m}^{mg} was described by Guillermet[11]. As the curie temperature of CoNi alloys is much higher than the γ ⟷ ε transformation temperature, the related parameters of both phases for calculating ΔG_{m}^{mg} were assumed to be equal. Thus the term ΔG_{m}^{mg} was neglected[11]. When ${}^{0}G_{i}^{\alpha}$, ${}^{E}G_{m}^{\alpha}$ for the α (α= hcp, fcc) phase is known, the molar Gibbs energy of fcc(γ) and hcp(ε) phase for CoNi alloys can be calculated. The difference of Gibbs energy of fcc(γ) and hcp(ε) phase is regarded as the driving force for fcc(γ) → hcp(ε) martensitic transformation and can be expressed as

$$\Delta G_{c}^{\gamma\rightarrow\varepsilon} = G_{m}^{\varepsilon} - G_{m}^{\gamma} \quad (5)$$

Guillermet[11] has systematically calculated the phase of Co-Ni system and provided the data of ${}^{0}G_{i}^{\alpha}$, ${}^{E}G_{m}^{\alpha}$ as follows (SI units):

$${}^{0}G_{Co}^{fcc} - H^{ser} = 737.832 + 132.750762T - 25.086T\ln T - 2.654738\times10^{-3}T^{2} - 1.7348T\times10^{-3}T^{3} + 7252.9T^{-1} + G_{mag}$$

$${}^{0}G_{Co}^{hcp} - H^{ser} = 310.241 + 133.36601T - 25.086T\ln T - 2.654738\times10^{-3}T^{2} - 1.7348T\times10^{-3}T^{3} + 7252.9T^{-1} + G_{mag}$$

$${}^{0}G_{Ni}^{fcc} - H^{ser} = -5179.159 + 117.854T - 22.096T\ln T - 4.8407\times10^{-3}T^{2} + G_{mag}$$

$${}^{0}G_{Ni}^{hcp} - H^{ser} = -4133.159 + 119.109T - 22.096T\ln T - 4.8407\times10^{-3}T^{2} + G_{mag}$$

$${}^{E}G_{m}^{fcc} = (-800 + 1.2629T)x_{Co}x_{Ni}$$

$${}^{E}G_{m}^{hcp} = -(1620 - 0.385T)x_{Co}x_{Ni}$$

From Eqns. (4) and (5) the expression of chemical driving force for fcc(γ) → hcp(ε) martensitc transformation and the phase equilibrium ($G_{m}^{\varepsilon} = G_{m}^{\gamma}$) temperature T_0 can be calculated. Table 1 lists the expression of $\Delta G_{c}^{\gamma\rightarrow\varepsilon}(T)$ with Ni content among 28% ~ 33% and phase equilibrium temperature T_0.

4 TEMPERATURE AND STACKING FAULT ENERGY

For the γ → ε transformation, Olson and Cohen[5] proposed that an intrinsic stacking fault acts as an hcp embryo. The fault energy γ expressed perunit area of fault (in the fault plane), for a fault with n planes in thickness can be written as

$$\gamma = n\rho_{A}(\Delta G_{c}^{\gamma\rightarrow\varepsilon} + E^{str}) + 2\sigma(n) \quad (6)$$

where ρ_{A} is the density of atoms in a close packed plane in moles per unit area, E^{str} is strain energy and $\sigma(n)$ is the surface energy per unit area of the particle/matrix interface, dependent on the fault thickness (e.g. for two planes in thickness, n= 2).

Due to the small volume change during γ → ε transformation, strain energy E^{str} is negligible (less than 0.1% of the stacking fault energy[5]). It can be concluded from Table 1 that $\Delta G_{c}^{\gamma\rightarrow\varepsilon}$ can be expressed as $-M + NT$, where M, N are constants related to the alloys with different contents of Ni. As $T_0 = M/N$, $\Delta G_{c}^{\gamma\rightarrow\varepsilon} = N(T - T_0)$. When Ni content is in certain range, N is close to 0.459 J·mol^{-1}·K^{-1}, according to the measurement of Hitzenberger[12], the surface energy in CoNi alloy $\sigma = 7.5\times10^{-3}$ J·m^{-2}. For the fcc phase a_0= 0.357 nm, it can be calculated $\rho_{A} = 3.01\times10^{-5}$ mol·m^{-2}. Supposing n= 2, it can be drawn from Eqn. (6):

$$\gamma/(J\cdot m^{-2}) = [0.028(T - T_0) + 15]\times10^{-3} \quad (7)$$

It is concluded that the stacking fault energy increases as temperature rises. With the node method, Erricsson[13] found that the stacking fault energy in Co-Ni alloy can be written as $\gamma/(J\cdot m^{-2}) = [0.03\cdot(T - T_0) + 15]\times10^{-3}$, quite similar to our result.

Table 1 Expression of $\Delta G_{c}^{\gamma\rightarrow\varepsilon}(T)$ of CoNi alloys and phase equilibrium temperature T_0

x(Ni)/%	$\Delta G_{c}^{\gamma\rightarrow\varepsilon}(T)$/(J·mol^{-1})	T_0/K
28	−180.34+ 0.4601T	392.0
29	−169.13+ 0.4593T	368.2
30	−157.76+ 0.4590T	343.7
31	−146.23+ 0.4589T	318.7
32	−134.53+ 0.4592T	293.0
33	−122.66+ 0.4598T	266.8

5 EXPERIMENTAL METHODS AND PROCEDURE

Five kinds of alloys with different contents of Ni (i. e. Co-28% Ni, Co-30% Ni, Co-31% Ni, Co-32% Ni, Co-33% Ni, in mole fraction) were prepared by using metal elements Co and Ni with the purity of more than 99.5%. After melting in vacuum induction furnace and homogenization at 1373 K, the ingots were hot rolled into 2 mm thick plates at 1073 K. The specimens with required dimensions

were cut and quenched from 973 K into ice water. Before testing, all specimens were grinding and electrical polishing in order to remove the oxidization layer or stress-induced martensites.

The stacking probabilities of the samples were measured by the methods of peak shift. According to Warren's X-ray diffraction theory[14], the diffraction peak shift is due to deformation faulting in fcc crystal. So the deformation fault probability P_{sf} can be determined by measured peak shift.

The peak displacement is expressed in the following form:

$$\Delta(2\theta_{111}) = \frac{90\sqrt{3}P_{sf}\tan\theta_{111}}{\pi^2}(+1/4) \quad (8)$$

$$\Delta(2\theta_{200}) = \frac{90\sqrt{3}P_{sf}\tan\theta_{200}}{\pi^2}(-1/2) \quad (9)$$

In order to improve accuracy, the pair of 111-200 was measured to avoid the disturbance of other factors, the calculating equation is

$$\Delta(2\theta_{200}-2\theta_{111}) = -\frac{90\sqrt{3}P_{sf}}{\pi^2}\left(\frac{\tan\theta_{200}}{2}+\frac{\tan\theta_{111}}{4}\right)$$

The detailed measurement procedure was presented by He et al[8].

6 RESULTS AND DISCUSSION

6.1 Effect of alloying composition on stacking probability P_{sf}

Table 2 lists the measured P_{sf} of the alloys at room temperature (T = 298 K) by peak shift method. The stacking fault energy γ calculated from Eqn. (7) is also presented. From Table 2, it can be seen the stacking probability decreases with increasing Ni content, while stacking fault energy increases. It is consistent with the relationship between stacking fault energy γ and stacking fault probability P_{sf}($\gamma = C/P_{sf}$). In the alloys with low stacking fault energy, ε martensite forms through the nucleation of stacking fault. The lower the stacking fault energy, the higher the stacking fault probability, the easier for the nucleation of martensite, and vice versa. So it explains that the $\gamma \rightarrow \varepsilon$ transformation temperature in CoNi alloys decreases with increasing Ni content. The constant C value in $\gamma = C/P_{sf}$ can be worked out from the measured values of P_{sf} and calculated values of γ, that is $C = 2.13\times10^{-5}$ J·m^{-2}.

Table 2 Stacking fault probability P_{sf} and stacking fault energy γ of CoNi alloys

x(Ni)/%	$P_{sf}/10^{-3}$	$\gamma/(10^{-3}$ J·m$^{-2})$
28	1.85	12.4
30	1.66	13.7
31	1.51	14.4
32	1.31	15.1
33	1.22	15.9

6.2 Temperature and stacking fault probability

The stacking fault probability of the sample with 33% Ni was measured at room temperature (298 K), 373, 473 and 573 K. The experimental results (listed in Table 3) show that the stacking fault probability decreases with increasing temperature. According to the equation $\gamma = C/P_{sf}$, the value of the stacking fault energy γ_m is presented in Table 3. It can also be calculated from Eqn. (6) and the calculated result γ_c is also listed in Table 3. The two results agree with each other quite well.

During heating, the stacking fault energy increases with increasing temperature and the Shockley partial dislocations contract. The reverse transformation starts when the temperature reaches the reverse transformation temperature T_s. During cooling, the stacking fault energy decreases, and the driving force for $\gamma \rightarrow \varepsilon$ transformation increases gradually. Shockley partial dislocations extend wider and wider and stacking faults overlap, and ε martensite forms at temperature lower than M_s.

Table 3 Stacking fault probability P_{sf} and stacking fault energy γ of Co-33Ni at various temperature

Temperature /K	P_{sf} $/10^{-3}$	γ_m $/(10^{-3}$ J·m$^{-2})$	γ_c $/(10^{-3}$ J·m$^{-2})$
298	1.22	17.4	15.9
373	1.10	19.4	18.0
473	1.04	20.5	20.8
573	0.77	27.7	23.6
683	0.60	35.5	26.7

7 CONCLUSIONS

1) The thermodynamical calculation has found that the stacking fault energy γ of CoNi at temperature T is expressed as $\gamma/(\text{J}\cdot\text{m}^{-2}) = [0.028(T - T_0) + 15]\times10^{-3}$, where T_0 refers to phase equilibrium temperature and depends on the composition of the certain alloy.

2) X-ray diffraction results show that the stacking fault probability decreases with increasing Ni content, the relation of stacking fault energy γ and stacking fault probability P_{sf} is expressed as $\gamma/(\text{J}\cdot\text{m}^{-2}) = 2.13\times10^{-5}/P_{sf}$.

3) The stacking fault probability decreases with increase of temperature. The value of stacking fault energy from the equation, $\gamma/(\text{J}\cdot\text{m}^{-2}) = 2.13\times10^{-5}/P_{sf}$, is close to the one from the equation:

$$\gamma/(\text{J}\cdot\text{m}^{-2}) = [0.028(T - T_0) + 15]\times10^{-3}.$$

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