Thermal Expansion Coefficient of Fe-Ni(*fcc*) Alloys*

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Synopsis

The thermal expansion coefficient, α, was measured over the range from 800°C to room temperature for Fe-Ni(*fcc*) alloys. The results obtained are as follows: (1) On the temperature vs. α curve, a peak appears at the Curie temperature, T_c, in the composition range above 42% of Ni but none in the range of 42–30% of Ni. (2) T_c of the alloys with more than 42% of Ni is present in the γ phase at a temperature higher than the upper limit for $(\alpha+\gamma)$ mixture phase in the equilibrium diagram. (3) the value of α_P obtained from α by eliminating the magnetic contribution shows a minimum in the Invar range as in the case of α. This may suggest that the interatomic cohesive force must be considered in addition to the magnetic effect in making clear the origin of Invar property.

I. Introduction

Most of the investigations on Invar properties have been concentrated on the sudden decrease in saturation magnetic moment in the Invar range, with a general trend to explain this phenomenon in connection with the ferromagnetism in γ phase[1]. Particularly in experimental investigations, most of them have been directed to see the nature of ferromagnetism in the *fcc* alloy with $(\mathbf{s}+\mathbf{d})$ electrons low in number by preparation of those specimens of Fe-Ni alloys either processed into powder or added by a third element, such as Co, Mn, Cr or others, thereby to keep away martensitic transformation. All of these are based on the concept that if martensitic transformation in $\alpha \rightleftarrows \gamma$ phases can be kept away from Invar range, quasi-stable γ phase can be held stationary as well as in the other range richer Ni concentration.

In the equilibrium diagram of Fe-Ni alloys[2] shown in Fig. 1, a mixture phase of $(\alpha+\gamma)$ exists in the range of $10\sim70\%$ of Ni at room temperature. However, in the practical quasi-equilibrium diagram, the alloys containing more than 30% of Ni are in γ phase at room temperature, as is evidently observable in X-ray after they have been cooled from a high temperature. This is apparently because of an extremely slow diffusion of atoms in the alloys of this system. Therefore, even if the phase boundary of martensitic transformation is held back in the concentration less than that of Invar by addition of third elements or by other means, the alloys

* The **1473rd** report of the Research Institute for Iron, Steel and Other Metals. Published in the J. Japan Inst. Metals, **34** (1970), 228 (in Japanese).

(1) S. Chikazumi and T. Mizoguchi, Solid State Physics, **3** (1968), 67 (in Japanese).

(2) M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, Inc. (1958).

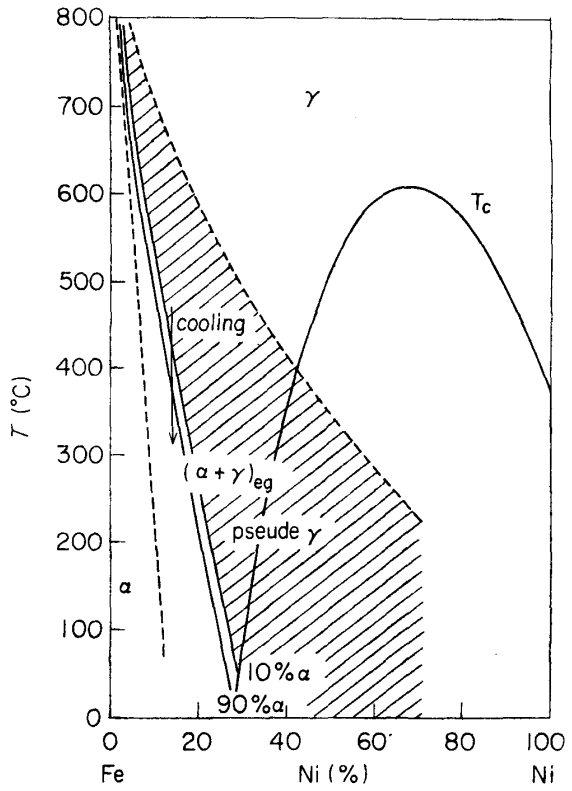


Fig. 1. Phase diagram of Fe-Ni system. The region of the thermal unequilibrium γ phase is shown by the oblique line (pseudo γ phase) (see reference (2)).

will still remain constitutionally in unequilibrium γ phase. Such difference in crystal structure between the unequilibrium γ phase mentioned above and the stable γ phase in the higher concentration of Ni has been generally neglected in the investigations of Invar properties so far reported.

Of several interpretations[3]~[7] on the abnormal volume expansion of Invar alloys, that of Kondorsky and Sedov[4] will be taken up as typical one. In their investigation on Invar alloys, they have found that the spontaneous magnetization at 0°K, $(\sigma_s)_T=0$, decreases with increasing pressure, and have proposed that the magnetic exchange energy of the nearest neighbouring Fe-Fe ions, J_{FeFe}, is negative, and changes with the magnetic moment σ_s of antiferromagnetic Fe ions, which are latent in the alloys, eventually causing a large volume expansion.

Their interpretation, however, is solely concerned with the abnormalities caused by ferromagnetism and latent *"antiferromagnetism"*, and apparently has neglected the physical properties of unequilibrium γ phase. In view of the matter of interest in what way the physical properties of unequilbirium γ phase relate to the large volume expansion in Invar alloys, the present authors have investigated

(3) H. Masumoto, Sci. Rep. Tohoku Imp. Univ., **23** (1934), 265.
(4) E.I. Kondorsky and V.L. Sedov, J. Appl. Phys., **31S** (1960), 331.
(5) R.J. Weiss, Proc. Phys. Soc. (London), **82** (1963), 281.
(6) A. Katsuki and K. Terao, J. Phys. Soc. Japan, **26** (1969), 1109.
(7) S.K. Sidorov and A.V. Doroschenko, Phys. Stat. Sol., **16** (1966), 737.

the thermal expansion coefficient which is regarded intrinsically related to Invar properties.

Thermal expansion coefficients of Fe-Ni alloys have been measured by many investigators including Guillaume[8], Chevenard[9], Scott[10], Lohr and Hopkins[11], and other contemporary workers. White[12] recently carried out experiments on various Invar alloys as well as on Fe, Ni, Co, Cr, and Mn with regard to their thermal expansion coefficients at low temperatures (600°~3°K), and found that Invar alloys and antiferromagnetic Cr and Mn have negative expansion coefficients at 30°K and below. However, his experimental results are yet unsuitable for making clear the physical properties of unequilibrium γ phase, so, in the present investigation, the thermal expansion coefficients of Fe-Ni (*fcc*) alloys were measured again over the range from high temperatures down to room temperature, thereon to obtain their temperature dependence, composition dependence, and spontaneous volume magnetostriction.

II. Specimens and measurements

1. Specimens

Specimens were prepared with electrolytic Fe and electrolytic Ni, the results of chemical analyses of which are shown in Table 1. These metals were mixed to a total of 1 kg and melted in a high frequency electric furnace; the cast ingot was forged, rolled and faced to a finished flat rectangular bar, 120 mm in length, 12 mm in width, and 1.3~1.5 mm in thickness, which was then annealed in vacuum at 1000°C for 10 hr and cooled. Results of chemical analyses of the specimens on Ni and their dimensional specifications are shown in Table 2.

Table 1. Chemical analysis of metals used in wt%

Material	Fe	Si	C	S	P	Cu	Mn	Ni
Elect. Fe	rest	0.0038	0.0047	0.0046	0.0018	0.0002	0.0071	—
Elect. Ni	0.012	0.007	—	—	—	0.008	0.003	rest

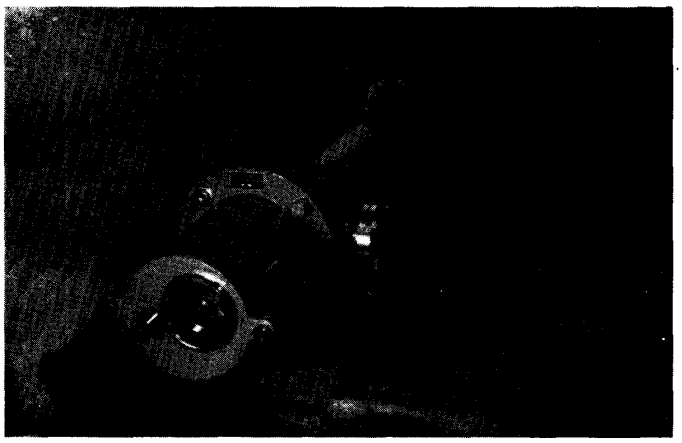
2. Measurements

In the present experiments, a new differential dilatometer improved by Sasaki and Yamaguchi[13] was used. The outside view of the present measuring apparatus and its head parts are shown in Phots. 1 and 2, respectively. As the standard specimen, a quartz bar, 5 mm in diameter, 120 mm in length, and $\alpha=$

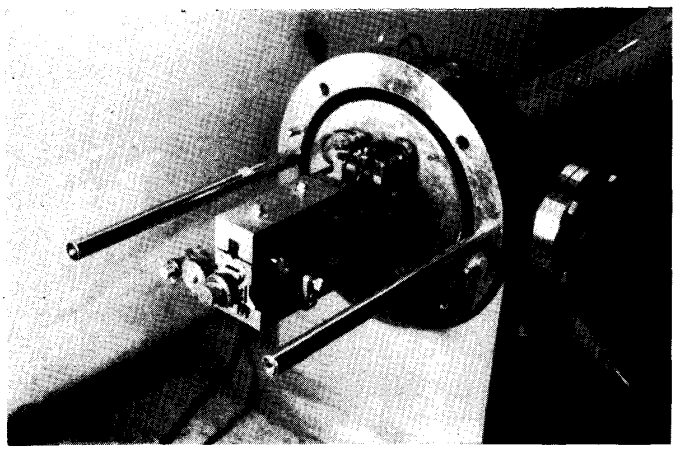
(8) Ch. Ed. Guillaume, C.R. Acad. Sci. Paris, **124** (1897).
(9) P. Chevenard, Rev. de Met., **11** (1914), 841.
(10) H. Scott, Trans. Am. Soc. Steel Treat., **13** (1928), 829.
(11) J. Lohr and C.H. Hopkins, Trans. AIME, **135** (1939), 535.
(12) G.K. White, Proc. Phys. Soc., **86** (1965), 159.
(13) E. Sasaki and H. Yamaguchi, Technical Science Report, Research Institute for Iron Steel and Other Metals, Tohoku Univ., **1** (1969), 23.

Table 2. Chemical analysis, mean dimension and density for Fe-Ni ($f\,c\,c$) alloys

Speci. No.	Chemi. analy. Ni(%)	Mean dimension (cm)			Density ρ (g/cm^3)
		Length l	Width b	Thickness t	
P-1	99.98	12.000	1.1989	0.1351	8.904
P-2	89.60	11.995	1.1990	0.1480	8.757
P-3	78.50	11.995	1.2007	0.1495	8.600
P-4	70.02	11.995	1.1989	0.1484	8.476
P-5	60.70	11.988	1.1860	0.1483	8.334
P-6	49.96	11.990	1.1995	0.1477	8.205
P-7	44.43	12.000	1.1997	0.1277	8.165
P-8	39.62	11.992	1.1990	0.1493	8.142
P-9	35.70	11.992	1.1987	0.1258	8.138
P-10	29.82	11.990	1.1983	0.1492	8.165



Phot. 1. Outside view of measuring apparatus.



Phot. 2. View of measuring head.

0.58×10^{-6} [14] (room temperature to 1000°C), was adopted. Specimens were heated in vacuum at 800°C for 10 min, then cooled at a rate of 10°~15°C/hr, and their dimensional changes were measured. The density of each specimen measured by weighing in water is shown in Table 2.

III. Results of measurements and discussions

1. Dependence of thermal expansion coefficient on temperature and composition

Thermal expansion coefficient, α of each specimen was measured during cooling from 800°C to room temperature. The results are shown in Figs. 2 and 3. As clear in the figures, α of Ni shows a sharp peak around Curie temperature T_c. This peak becomes gradually low as Fe is added to Ni, and, above about 75% of Ni, the peak changes into a valley. The mode of change in sign of this anomaly well corresponds to that in sign in T_c with pressure, dT_c/d_p [15]. In the α-T curve of

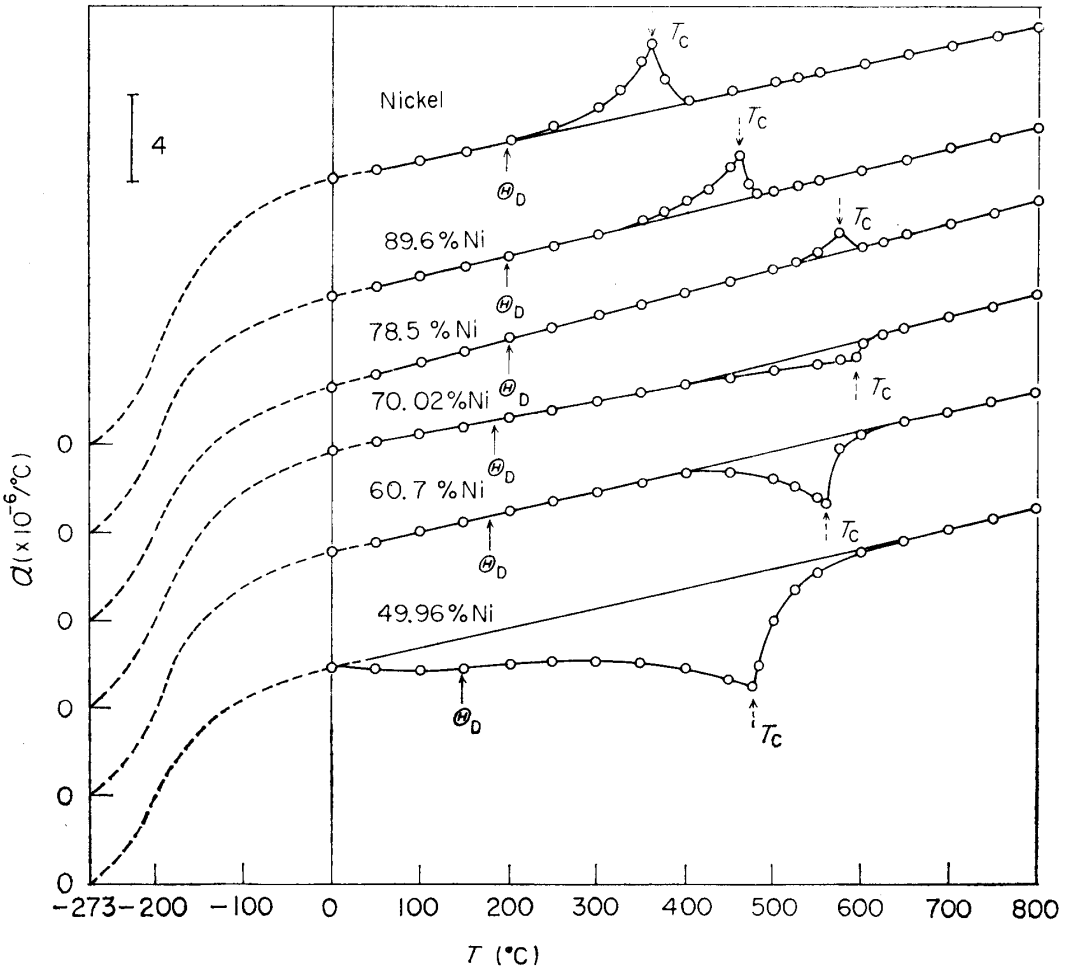


Fig. 2. Temperature dependence of thermal expansion coefficient α of Fe-Ni alloys. Θ_D: Debye temperature.

(14) J. Strong, *Modern Laboratory Practice*, Blackie and Son Ltd. (1950).
(15) J.S. Kouvel and R.H. Wilson, J. Appl. Phys., **32** (1961), 435.

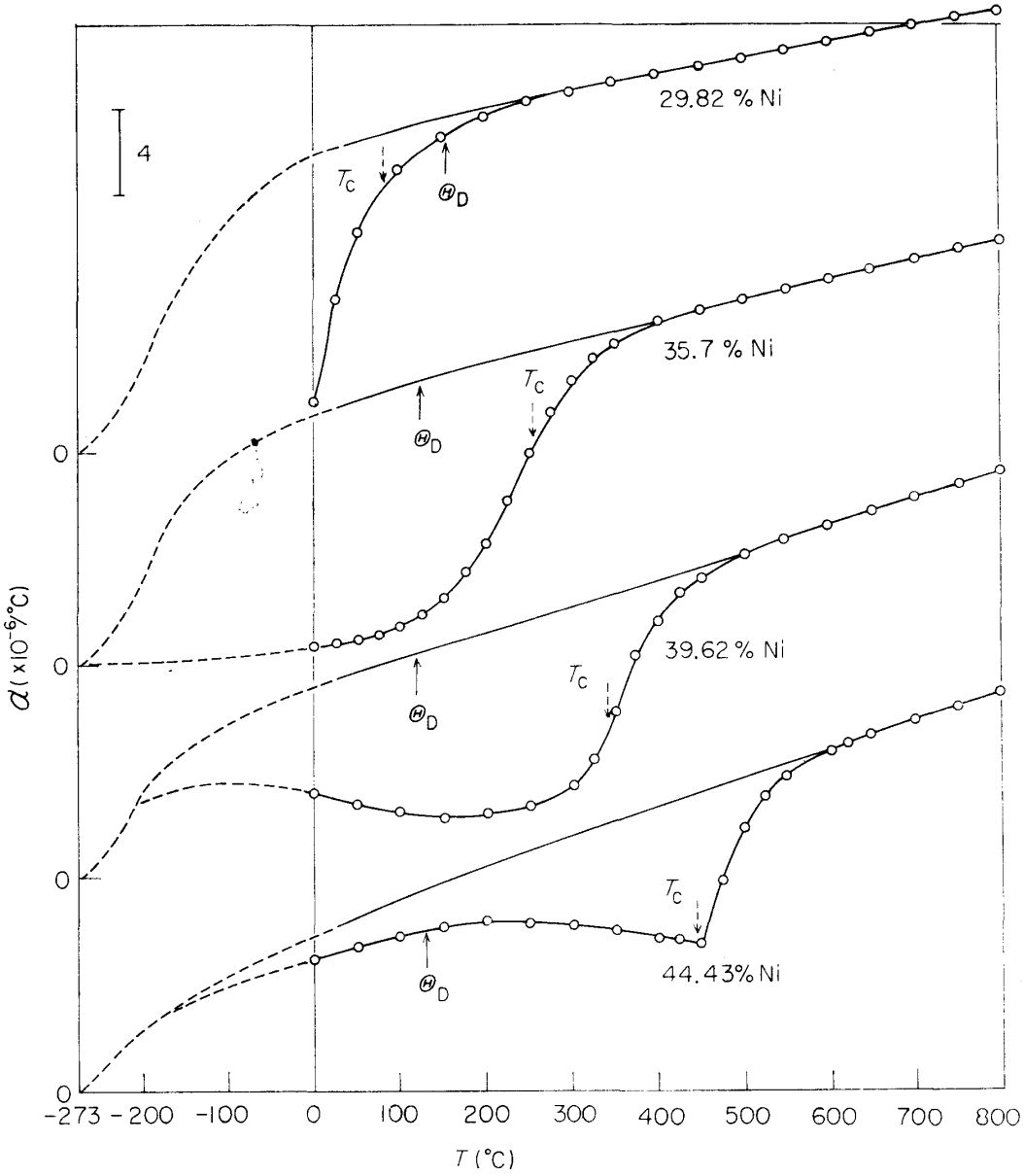


Fig. 3. Temperature dependence of thermal expansion coefficient α of Fe-Ni(*fcc*) alloys. Θ_D: Debye temperature.

44.43% of Ni, a very sharp spike-like fall is observed in the valley of α, while in the experiment by Scott[10] there appeared no such spike-like fall in the curve of 44.8% of Ni. The cause of the difference between the above two still remains uncertain. When Ni-content is lowered to about 40%, the curve shows no deep valley but follows a smooth line, T_c becoming obscure. A comparative examination of these results with the equilibrium diagram in Fig. 1 shows that, when T_c of the alloys is higher than the upper limit of temperature for the mixture phase of $(\alpha+\gamma)$ in equilibrium state, there appears in the α-T curve of the alloys a sharp form of peak or valley. This feature may suggest its close relationship to the substantial stability of crystal structure.

Composition dependences of α of Fe-Ni(*fcc*) alloys at various temperatures are shown in Fig. 4. As clear in the figure, at 0°C, α shows around 35% of Ni a minimum of $\alpha=0.8\times10^{-6}$/°C. As T increases, α gradually becomes large and the composition showing its minimum at that temperature shifts to the side richer in Ni. This signifies that α in the Invar range suddenly increases from around T_c. and its composition dependence at each temperature is very complex apparently because of the difference in the way of contribution of spontaneous volume magnetostriction at each temperature. It should be noted that, at $T=600°$ and 800°C, all Fe-Ni alloys are nonferromagnetic but there is a minimum in the composition dependence of α at around 50% of Ni.

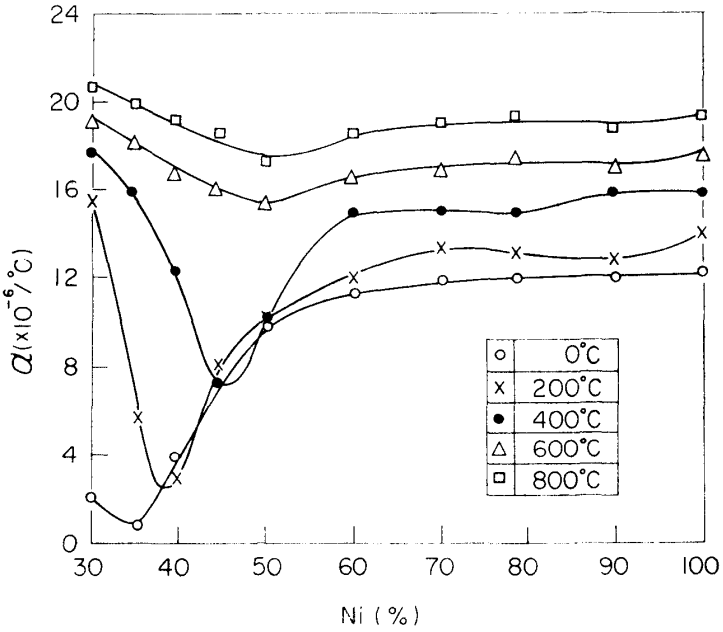


Fig. 4. Thermal expansion coefficient α vs. Ni content curves at various temperatures for Fe-Ni(*fcc*) alloys.

2. Thermal expansion coefficient at paramagnetic state

As the factors contributing to thermal expansion coefficient at the paramagnetic state, α_p, two kinds are considered, that is, the contribution of lattice and that of conduction electron. Wallace[16] recently carried out a theoretical calculation of thermal expansion coefficient of solid, and has shown that in the range of $0.75\,\Theta_D<T$ (Θ_D: Debye temperature) α_p changes almost linearly with T, and later gradually decreases toward zero. Accordingly, in the present work, the α_p-T curve for each specimen was obtained by extrapolation of the curves at high temperatures. The results are shown in thin and dotted lines together with experimental values in Figs. 2 and 3. The trends of Θ_D shown in the figures are those obtained from Young's and shear moduli by Tanji, Moriya and Shirakawa[17].

(16) D.C. Wallace, Phys. Rev., **176** (1968), 827.

(17) Y. Tanji, H. Moriya and Y. Shirakawa, J. Phys. Soc. Lecture Draft (4p D21, Oct. 1968), 21.

The ferromagnetic part of thermal expansion coefficient, α_f, can be obtained as the difference between α_p and the observed value α_{ex} as follows:

$$\alpha_f = \alpha_p - \alpha_{ex} \tag{1}$$

Thus, α_f obtained from Figs. 2 and 3 is shown in Fig. 5 as the function of Ni concentration. As clear in the figure, at T=0°C, α_f shows its maximum around 30% of Ni. As T becomes high, the maximum of α_f linearly shifts toward a range richer in Ni, because T_c rises and w_s lowers.

α_p is shown in Fig. 6 as the function of Ni concentration. As clear in the

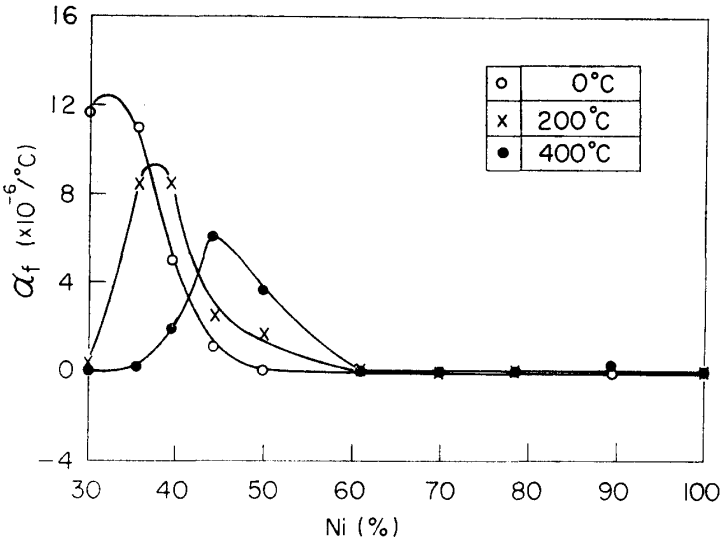


Fig. 5. Magnetic contribution of thermal expansion coefficient α_f vs. Ni content curves at various temperatures for Fe-Ni(*fcc*) alloys.

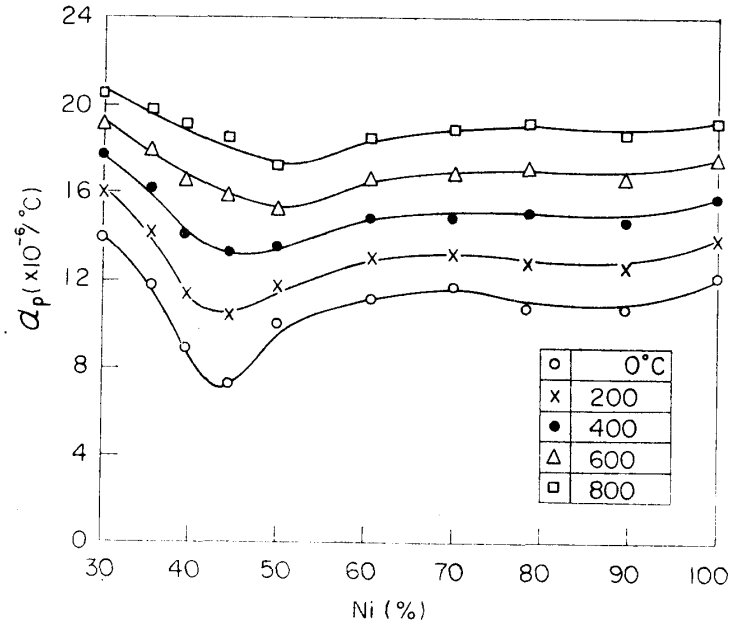


Fig. 6. Paramagnetic contribution of thermal expansion coefficient α_p vs. Ni content curves at various temperatures for Fe-Ni(*fcc*) alloys.

figure, α_p shows its minimum in the Invar range like the composition dependence of α_{ex} shown in Fig. 4. The form of the minimum becomes more conspicuous at lower temperatures. At $T=0$°C, the minimum of α_p appears at 42% of Ni with about 7.6×10^{-6}/°C. As T becomes high, the minimum shifts linearly toward a range richer in Ni, increasing its value monotonously. The fact that α_p shows in its composition dependence a minimum alike in the case of α_{ex} may signify that the interatomic cohesive force of the alloys in the range showing α_p-minimum is distinctly different from that in other ranges of composition. This may suggest that Invar properties cannot be explained by the magnetic effect alone. Also, this is considered to have a close relationship to the constitution of unequilibrium γ phase as described previously, though details still remain unknown. This experimental indication of α_p-minimum in the composition of alloy may be the first attempt.

3. Spontaneous volume magnetostriction

Change in volume caused by the emergence of spontaneous magnetization, w_s, can be expressed by the following equation:

$$\omega_s = \int_0^\infty 3\alpha_f \cdot dT = \int_0^\infty 3(\alpha_p - \alpha_{ex}) \cdot dT \qquad (2)$$

The α_p-T curves in the range of high temperatures were obtained, as shown in Figs. 2 and 3, by linear extrapolation from α_p above T_c. In the range of low temperatures, however, the α_p-T curves of the alloys were obtained analogous to the α_p-T curve of Ni that has been obtained by Nix and McNair[18] with the formula of Grüneisen. For 35.7, 39.62 and 44.43% Ni-Fe alloys α_{ex} at low temperatures was obtained by extrapolation on the basis of the results that have been obtained by Scott on the alloys similar to the present specimens. Thus, the area defined by Eq. (2), w_s, was obtained from Figs. 2 and 3, and the results** are shown in Fig. 7 as the function of Ni concentration. As clear in the figure, w_s is -5.0×10^{-4} at Ni: 0 around 75% of Ni, and as the Ni concentration further decreases, w_s sharply increases as much as to 142.3×10^{-4} at 35.7% of Ni. According to the results of the calculation made by Fujimori[19],[20] on the molecular field theory for magnetic material, w_s is proportional to the change in T_c with pressure, and can be expressed by the following equation:

$$\omega_s = -\frac{3}{4}R \cdot \frac{\rho \cdot N}{M} \cdot \frac{dT_c}{dp} \qquad (3)$$

where k, ρ, M and N are respectively Boltzmann's constant, density, atomic

(18) F.C. Nix and D. McNair, Phys. Rev., **60** (1941), 597.
(19) H. Fujimori, J. Phys. Soc. Japan, **21** (1966), 1860.
(20) H. Saitô and H. Fujimori, J. Japan Inst. Metals, **7** (1968), 263.
** The calculation miss was found in w_s of the alloys shown in J. Japan Inst. Metals, **34** (1970), 228. So, the values of w_s were correctively recalculated as shown in Fig. 7.

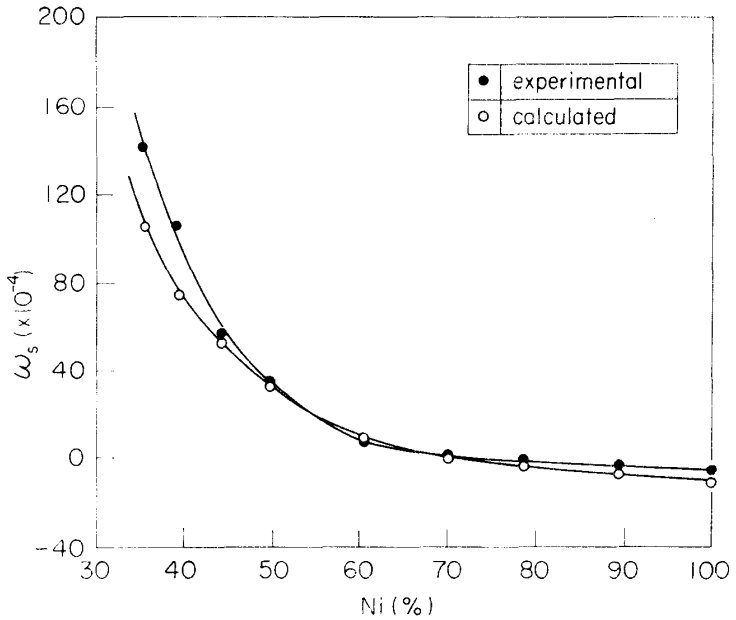


Fig. 7. Spontaneous volume magnetostriction w_s vs. Ni content curves of Fe-Ni (*fcc*) alloys.
* Calculated from Fujimori's formula[19] divided by 3.

volume, and Avogadoro's number.

w_s was calculated by using dT_c/dp measured by Patrick[21] in Eq. (3). The results appear for Ni with -31×10^{-4} and for 35.7% Ni-Fe with 217×10^{-4}. These values are 6 to 2 times as large as the observed values. Such a difference cannot be regarded to have resulted from error in the measurement of dT_c/dp or w_s. As above mentioned, Eq. (3) has been obtained on the molecular field theory with the magnetic exchange force taken into consideration and, therefore, without the consideration of that strength of interatomic cohesive force which needs a sufficient consideration as previously mentioned, though the feature of its contribution has not yet been specified. In the present experiment, the right member of Eq. (3) was multiplied by A, a coefficient referable to the interatomic cohesive force, which was settled as $A=1/6$ to accord with the observed value of w_s of Ni, and therewith Eq. (3) was recalculated. The results are shown in Fig. 7 together with the observed values. As clear in the figure, both of the values fairly agree with each other in the range of composition rich in Ni, but from around 44% of Ni they show a difference, which becomes more distinct toward the side richer in Fe. The extrapolations of α_p and of α_{ex} for 35.7, 39.62 and 44.43%Ni-Fe in the range of low temperatures have been practiced on a rough assumption, and, therefore, the results may include some errors and remain insufficient in explaining these differences intrinsically. However, it is probable that w_s in this range includes various contributions such as from the latent *"antiferromagnetism"* proposed by Kondorsky and Sedov, and others, in addition to a change in volume caused by ferromagnetic spontaneous magnetostriction. The mechanism of the emergence of

(21) L. Patrick, Phys. Rev., **93** (1954), 384.

w_s of the alloys will be reported later[22].

Summary

Thermal expansion coefficients of Fe-Ni (fcc) alloys were measured in the range from 800°C to room temperature. The results are as follows:

(1) An anomaly appears in the curve of thermal expansion coefficient α vs. temperature T. α in the range of composition above 42% of Ni shows a sharp peak or valley at Curie temperature T_c but no such form of anomaly in the range of 40–30% of Ni.

(2) T_c of the alloys containing more than 42% of Ni is in the range of γ phase over the upper limit of T for the mixture phase of $(\alpha+\gamma)$ in the equilibrium diagram.

(3) The paramagnetic thermal expansion coefficient below T_c, α_p, has been obtained by means of extrapolation of the α-T curves above T_c.

(4) This α_p shows a composition dependence similar to that of the observed value and has its minimum in the Invar range. This property, found for the first time, may suggest that it is necessary for a through explanation of Invar properties to consider other effects than the magnetic one.

Acknowledgements

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(22) Y. Tanji, J. Phys. Soc. Japan, (to be published).