Thermally activated dislocation glide in magnetic FeNi–invar alloys

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Abstract. The theory of thermally activated motion of dislocations yields a cusp in the graph of activation free enthalpy ΔG versus temperature when applied to FeNi–invar alloys. This is attributed to a magnetic induced hardening of FeNi. A theory of thermal activation is developed taking into account the magnetic hardening and the results are compared with CRSS and yield stress measurements of FeNi and FeNiMn alloys.

1. Introduction

The plastic deformation of metals by dislocation glide is controlled by various processes, such as viscous drag [1], diffusion of interstitials [2], the effect of inertia [3], quantum vibration [4] and thermally activated motion of dislocations.

This paper deals with a theoretical model of thermal activation for a magnetic material and its comparison with experiment.

The theory of thermal activation analysis [5, 6] has been applied to various metals and alloys yielding information on the obstacle and the glide process, qualitatively as well as quantitatively. At first, thermal activation was expressed in terms of activation energy [5]; however, today it is generally accepted for the analysis of tensile test experiments to use the free enthalpy, which is the corresponding thermodynamic function for experiments at constant τ, T [6]. A comprehensive evaluation of the theory was given by Surek and co-workers [7]. This evaluation will be referred to as *standard activation analysis*.

Although thermal activation analysis has been successfully applied to many metals and alloys, it was shown to fail in the case of FeNi–invar alloys [8]. These ferromagnetic FCC alloys ($c_{Ni} \simeq 35\%$) are characterized by a very small thermal expansion coefficient [9] below the Curie temperature (approximately 500 K). The small thermal expansion is widely accepted to be of magnetic origin, as shown by the correlation between magnetic ordering (i.e. Curie temperature) and size of thermal expansion coefficient.

Beside the archetypal FeNi system various other alloys reveal invar properties [10], e.g. the well-known Fe_3Pt [11] or YMn_2, which was reported [12] to have the largest volume magnetostriction discovered so far.

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Although invar alloys in general and especially FeNi alloys have been widely investigated, e.g. by magnetization measurements [13, 14], neutron scattering [15, 16], Mössbauer measurements [17, 18] and others [19], very few investigations have dealt with the plastic deformation of FeNi [20–25] and the corresponding dislocation structure [26–28]. The critical resolved shear stress (CRSS) $\tau_0(T)$ of FeNi–invar shows a sharp increase somewhat below the Curie temperature, T_c, yielding a high CRSS at low temperature. The dependence of τ_0 on temperature as well as the Ni concentration is not in accordance with theories of solid solution hardening [29], and this is widely accepted to be due to a magnetically induced hardening [20–25]. The magnetic origin of this hardening was stringently demonstrated by an investigation of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys, where the magnetic hardening can be adjusted independently from solid solution hardening via the manganese content, x [24, 25] (cf figure 2, later).

For the archetypal FeNi–invar alloy the free activation enthalpy ΔG was calculated according to standard thermodynamic activation analysis [8, 20] yielding a sharp peak in $\Delta G(T)$ at $T \lesssim T_c$ with anomalously high figures for ΔG. This unexpected finding, accomplished by means of standard activation analysis, was attributed to the extraordinary properties of FeNi–invar. It was supposed to be a magnetic effect because of the correlation between the $\Delta G(T)$ peak and the Curie temperature.

Up to now magnetic effects have not been considered in the theory of thermal activation. Thus, the theory may not be applicable in the case of FeNi, where plastic deformation is controlled by magnetic hardening. This investigation is aimed at developing a model which takes account for magnetic effects, and to apply it to tensile test measurements of FeNi–invar alloys. Besides the calculation of the magnetic contribution to ΔG, our approach provides a generalized method to deal with additional effects in the field of activation analysis.

2. Thermodynamic activation analysis

In this section an equation will be derived to calculate ΔG from tensile test measurements. This equation will reveal the same structure as the results of [7] except some very small but important modifications.

The basic interaction in our model is the magnetoelastic coupling, which is particularly large in the case of invar alloys. In the vicinity of a dislocation the magnetization, M, is locally altered due to the dislocation strain field acting via the magnetoelastic coupling. This change in magnetization, ΔM, within a small volume, V (not the activation volume), around the dislocation is equivalent to a change in the magnetic moment, $\Delta m = V\Delta M$. When exposed to a magnetic field, h, the change in m yields a change in magnetic energy:

$$\Delta E = -h\Delta m. \tag{1}$$

Principally this energy, ΔE, represents the barrier which has to be surmounted by the dislocation during thermal activation. The details of the microscopic magnetic barrier are very complex [24, 25]. However, the phenomenological theory of thermal activation depends on neither the origin nor on microscopic details of the barrier or interaction. Our approach to thermodynamic activation analysis is to extend the standard model [6, 7]. Thus, the emphasis of the following evaluation is on the extension of this model.
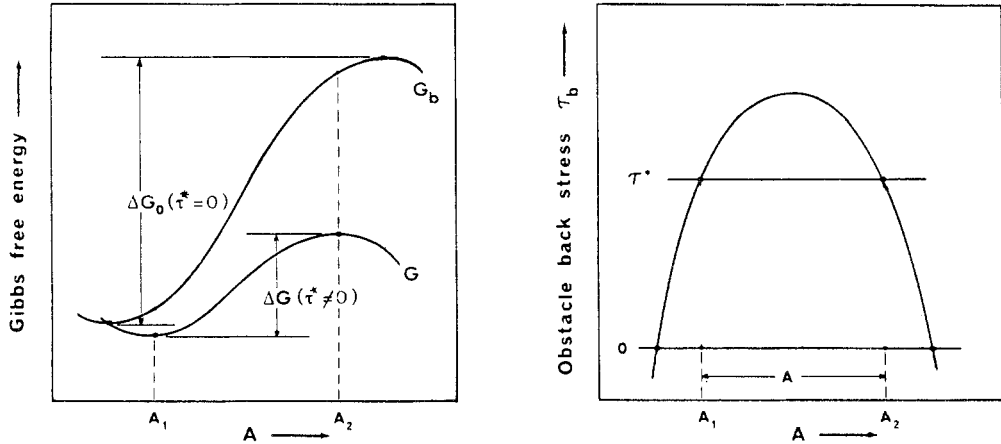
Figure 1. Gibbs free energy and obstacle back stress of a rigid obstacle, from [7].

We take account for a magnetic alloy by supplementing the free enthalpy, usually given by

$$G = U + PV - TS \tag{2a}$$

with a magnetic term yielding

$$G = U + PV - TS - hm. \tag{2b}$$

Here, U is the internal energy, P the pressure, V the volume, T the temperature, S the entropy, h the magnetic field, m the magnetic moment; μ_0 is omitted throughout this paper.

Therefore we have three independent variables, namely p, T and (additionally) the magnetic field h. We assume the field h to consist of an externally applied magnetic field h_a and an internal mean field h_i:

$$h = h_a + h_i. \tag{3}$$

Exchange interactions between magnetic moments are represented by h_i, which is assumed to be proportional to the magnetization, M, in the mean field approximation.

The starting point of the thermodynamic activation analysis is the rigid obstacle (figure 1), characterized by the obstacle back stress τ_B. The free enthalpy of activation is [7]

$$\Delta G = b \int_{A_1}^{A_2} \tau_B \, dA - b\tau^*(A_2 - A_1) \tag{4}$$

where $\tau^* = \tau_a - \tau_i$ is the effective stress, τ_a is the applied stress, τ_i the internal stress, b the Burgers vector, $A_2 - A_1$ the area swept out by dislocation during activation. ΔG is the change in free enthalpy produced by moving the dislocation from the equilibrium position A_1 to the activated position A_2. The obstacle back stress $\tau_B(A, T)$ is usually assumed to be a product of a function $g(A)$ and the shear modulus $\mu(T)$. To allow for magnetic hardening, the obstacle back stress must be dependent on magnetic variables, too. Experimental results [20–25] clearly reveal the influence of magnetic ordering on the CRSS (i.e. in the mean field approximation, a dependence on h_i). The dependence of

the shear modulus, μ, on magnetic ordering is evident from measurements of shear modulus versus temperature [30]. We assume g as well as μ to be also a function of h. We write the obstacle back stress in a magnetic alloy as follows:

$$\tau_B(A, T, h) = g(A, h)\mu(h, T). \tag{5}$$

During the activation process the dislocation moves at constant effective stress τ^* from position A_1 to A_2 (see figure 1) yielding a change in enthalpy, H, and entropy, S, (in the standard model):

$$\Delta G = \Delta H_{\tau^*} - T\,\Delta S_{\tau^*}. \tag{6}$$

(Remark: the index at S and H shows which stress is constant.) In a magnetic alloy, the dislocation movement additionally yields a change in the magnetic moment, m:

$$\Delta G = \Delta H_{\tau^*} - T\,\Delta S_{\tau^*} - h\,\Delta m. \tag{7}$$

The change of magnetic moment, i.e. the change of magnetization within a small volume in the vicinity of the dislocation, is supposed to be the origin of the invar hardening; the interaction between dislocation and magnetization is provided by the magnetoelastic coupling. Details of this interaction were tackled on a phenomenological scale [21–23] and on a microscopic scale [24, 25]. However, neither the details of the magnetization change nor its size have any influence on the activation analysis.

First, the change in entropy, ΔS, during activation is calculated. The total differential of the free enthalpy in terms of T, τ^* and h is:

$$d\Delta G = -\Delta S_{\tau^*}\,dT - b(A_2 - A_1)\,d\tau^* - \Delta m\,dh \tag{8}$$

yielding

$$\Delta S_{\tau^*,h} = -(\partial \Delta G/\partial T)_{\tau^*,h}$$

$$= -b\tau_B(A_2, T, h)(\partial A_2/\partial T)_{\tau^*,h} + b\tau_B(A_1, T, h)(\partial A_1/\partial T)_{\tau^*,h}$$

$$+ b\tau^*[\partial(A_2 - A_1)/\partial T]_{\tau^*,h} - b\int_{A_1}^{A_2}[\partial \tau_B(A, T, h)/\partial T]_h\,dA$$

$$= -b\int_{A_1}^{A_2}[\partial \tau_B(A, T, h)/\partial T]_h\,dA. \tag{9}$$

Equation 9 is transformed by means of equation (5):

$$\Delta S_{\tau^*,h} = -[b/\mu(T, h)](\partial \mu/\partial T)_h \int_{A_1}^{A_2} \tau_B(A, T, h)\,dA$$

$$= -[1/\mu(T, h)](\partial \mu/\partial T)_h[\Delta G + b(A_2 - A_1)\tau^*]. \tag{10}$$

Together with equation (7) we get the free enthalpy of activation:

$$\Delta G = \frac{\Delta H_{\tau^*} - h\Delta m + b(A_2 - A_1)\tau^*(T/\mu)(\partial \mu/\partial T)_h}{1 - (T/\mu)(\partial \mu/\partial T)_h}. \tag{11}$$

Equation (11) resembles equation (18) of reference [7] except for the term $h\Delta m$ and the constant h regarding the derivation of the shear modulus μ, both features characterizing the magnetic obstacle.

We have calculated the free activation enthalpy ΔG as a function of the effective stress, τ^*. Now, τ^* cannot be experimentally determined but τ_a can. To derive $\Delta G(\tau_a, h, T)$ we evaluate the total differential $\Delta G = \Delta G(\tau^*, T, h)$ and substitute τ^*.

The effective stress $\tau^* = \tau_a - \tau_i$ is assumed to be temperature dependent via the internal stress and additionally dependent on the magnetic field h, i.e. $\tau^* = \tau^*(\tau_a, T, h)$. With τ^* we get ΔG in terms of τ_a, h, t:

$$d\Delta G = (\partial\Delta G/\partial T)_{\tau^*,h}\, dT + (\partial\Delta G/\partial\tau^*)_{T,h}\, d\tau^* + (\partial\Delta G/\partial h)_{T,\tau^*}\, dh \tag{12}$$

yielding, at constant τ_a, h:

$$\Delta S_{\tau_a,h} = -(\partial\Delta G/\partial T)_{\tau^*,h} - (\partial\Delta G/\partial\tau^*)_{T,h}(\partial\tau^*/\partial T)_{\tau_a,h}. \tag{13}$$

The second term of equation (13) can be evaluated assuming τ_i to be proportional to $\mu(T, h)$ [1, 6, 7]. Together with equation (10), we get

$$\Delta S_{\tau_a,h} = \Delta S_{\tau^*,h} - b(A_2 - A_1)(\tau_i/\mu)(\partial\mu/\partial T)_h$$

$$= -(1/\mu)(\partial\mu/\partial T)_h[\Delta G + b(A_2 - A_1)\tau_a]. \tag{14}$$

Equation (14) yields the free activation enthalpy in terms of τ_a, T and h:

$$\Delta G = \frac{\Delta H_{\tau_a} - h\Delta m + b(A_2 - A_1)\tau_a(T/\mu)(\partial\mu/\partial T)_h}{1 - (T/\mu)(\partial\mu/\partial T)_h}. \tag{15}$$

All quantities in equation (15) except ΔH_{τ_a} and $h\Delta m$ can be determined by experiment, at least theoretically.

In the calculation shown above one single dislocation in front of an individual obstacle has been considered on a microscopic scale. Both ΔH_{τ_a} and $h\Delta m$ have to be determined by a macroscopic model and a statistical treatment, respectively. In the following, the macroscopic strain rate $\dot\varepsilon$ produced by an ensemble of dislocations is related to the average free enthalpy of activation.

Usually, for the strain rate an Arrhenius-type equation is assumed to be applicable [1, 5–7]:

$$\dot\varepsilon = \dot\varepsilon_0 \exp(-\Delta G/kT). \tag{16}$$

It is generally accepted that the dependence of $\dot\varepsilon_0$ on τ_a, h, T is small or even negligible, thus $\dot\varepsilon_0$ is assumed to be constant for the differentiation with respect to τ_a, h, T. Equation (16) yields

$$(\partial\Delta G/\partial T)_{\dot\varepsilon,h} = -k\ln(\dot\varepsilon/\dot\varepsilon_0) = \Delta G/T. \tag{17}$$

Thus

$$\Delta H_{\tau_a} - h\,\Delta m = T(\partial\Delta G/\partial T)_{\dot\varepsilon,h} - T(\partial\Delta G/\partial T)_{\tau_a,h}. \tag{18}$$

Equation (18) can be evaluated by means of the total differential of $\Delta G(\tau_a, T, h)$ and $\tau_a(\dot\varepsilon, h, T)$, respectively.

The dependence of the applied stress on the magnetic field h characterizes the magnetic obstacles. Combined with equation (18) the total differentials of ΔG and τ_a yield

$$\Delta H_{\tau_a} - h\,\Delta m = T(\partial\Delta G/\partial\tau_a)_{h,T}(\partial\tau_a/\partial T)_{\dot\varepsilon,h}. \tag{19}$$

Now, equation (15) can be transformed yielding the free activation enthalpy in terms of τ_a, $\dot\varepsilon$ and T:

$$\Delta G = \frac{-TV(\partial\tau_a/\partial T)_{\dot\varepsilon,h} + V\tau_a(T/\mu)(\partial\mu/\partial T)_h}{1 - (T/\mu)(\partial\mu/\partial T)_h}. \tag{20}$$

This equation completely resembles the result of the standard activation analysis [6, 7], except the constant h for the differentials, which is the essential difference in thermal activation regarding the effect of magnetic hardening.

3. Experimental determination of activation parameters

The free enthalpy of activation shall be determined for $Fe_{65}Ni_{35}$ in zero applied field ($h = h_i$) by means of equation (20). The total differential of $\tau_a(\dot\varepsilon, h, T)$ at constant $\dot\varepsilon$ and h yields

$$(\partial\tau_a/\partial T)_{\dot\varepsilon,h} = (\partial\tau_a/\partial T)_{\dot\varepsilon} - (\partial\tau_a/\partial h)_{T,\dot\varepsilon}(dh/dT). \tag{21}$$

In an analogous manner, $(\partial\mu/\partial T)_h$ is derived:

$$(\partial\mu/\partial T)_h = (d\mu/dT) - (\partial\mu/\partial h)_T(dh/dT). \tag{22}$$

The difference from the standard case is shown by the second terms in (20) and (21), respectively. In zero applied field ($h_a = 0$) the field dependence of τ_a can be transformed assuming $h = h_i \sim M$ (mean field approximation). Thus, (21) yields

$$(\partial\tau_a/\partial T)_{\dot\varepsilon,h} = (\partial\tau_a/\partial T)_{\dot\varepsilon} - (\partial\tau_a/\partial M)_{T,\dot\varepsilon}\, dM/dT. \tag{23}$$

In the case of $h_a = 0$ the difference between our extended activation analysis and the standard activation analysis vanishes for $T > T_c$ as well as for $T \to 0$: the internal field $h_i \sim M$ is constant above T_c (equal to 0) and for $T \to 0$, thus $dh_i/dT \sim dM/dT$ is zero, the second terms of equations (21)–(23) are zero and (20) transforms to the usual result (cf [6, 7]). On the other hand the difference is large for $T \lesssim T_c$, because $dh_i/dT \sim dM/dT$ is particularly large in this temperature range (cf figure 2 later).

The quantities $(\partial\tau_a/\partial T)_{\dot\varepsilon}$, $d\mu/dT$ and dM/dT can be measured as usual or compiled from literature. However, both terms $(\partial\tau_a/\partial M)_{T,\dot\varepsilon}$ and $(\partial\mu/\partial M)_T$ are not easy to determine by experiment, because an external magnetic field h_a of some 1000 Tesla, which would be strong enough to change the magnetization in a magnetic domain and allow its influence on τ_a and μ to be determined, is not available. (Remark: a change of the global magnetization is not relevant, because it corresponds to a change in the position of the domain walls only and not to the magnetization change of the domains.)

The influence of $(\partial\tau_a/\partial M)_{T,\dot\varepsilon}$ was estimated indirectly: the magnetization of the domains of specific alloys at a given temperature cannot be changed by external means to measure $d\tau_a/dM$; instead we measured the applied stress τ_a of alloys having similar compositions but different magnetizations M. This task was performed with the ternary $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys, where normal solid solution hardening was shown to be nearly
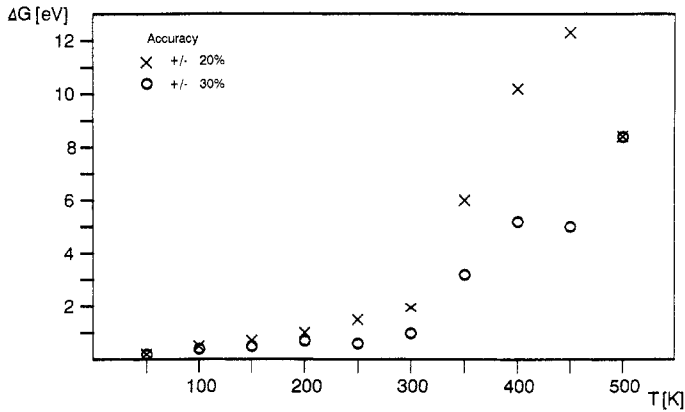
Figure 2. (○), Free activation enthalpy of $Fe_{65}Ni_{35}$, taking into account magnetic hardening according to equation (20); (×), calculation neglecting magnetic effects is shown for comparison.
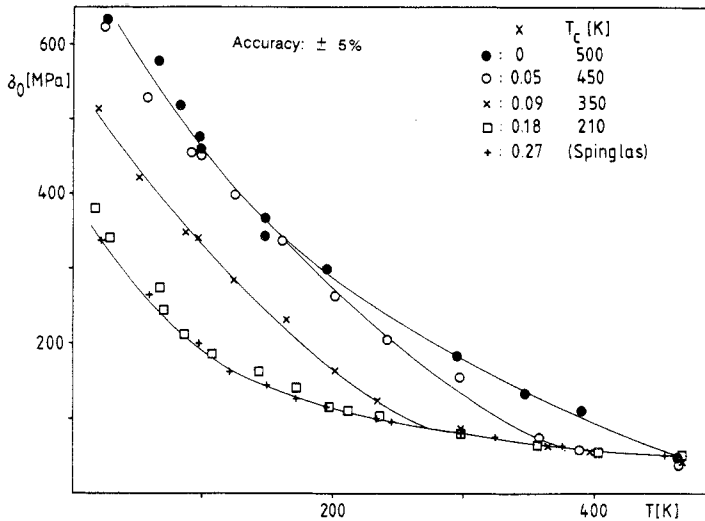
Figure 3. Yield stress of $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ alloys from [24, 25]; Curie temperatures from [33]. (Curves are drawn as a guide to the eye.)

independent of the manganese content x but the magnetic hardening varies with M via x [24, 25]. Thus, alloys with different x-values have only different yield stresses due to different magnetic properties. The normal solid solution hardening is nearly constant, because the concentration of solute atoms is independent of x (i.e. $c = c_{Ni} + c_{Mn} = 35\%$) and the size parameters of Ni and Mn determining solid solution hardening are similar, as revealed by lattice parameter measurements [31]. This is, of course, a rough estimation, but may be sufficient for a principal validation of the theory. The term $d\mu/dM$ could be calculated by a similar method, however, the influence on equation (20) is small. Thus, we neglected $d\mu/dM$ for this rough estimation.

The free activation enthalpy of $Fe_{65}Ni_{35}$ derived by means of equation (20) is shown in Figure 2 (figures calculated according to standard activation analysis are shown for comparison). For figure 3 (c.f. equations (20), (21)) we used $(\partial\tau_a/\partial T)_\dot{\varepsilon}$ data from [24, 25]. The temperature dependence of the magnetization M for $Fe_{65}Ni_{35}$ was taken

from [13, 14]. The dependence of M on τ_a for $Fe_{65}Ni_{35}$ was calculated from $Fe_{65}(Ni_{1-x}Mn_x)_{35}$ data by combining $(\partial\sigma/\partial x)_T$ taken from figure 3 and $(\partial M/\partial x)_T$ from [32, 33] yielding $(\partial\tau_a/\partial M)_T$ at $x = 0$. (Remark: results at $x > 0$, although determined as well, are not relevant for ΔG of $Fe_{65}Ni_{35}$).

4. Discussion

Three ranges of temperature can be distinguished in figure 2. Firstly, for $T \ll T_c$, both extended as well as standard theory yields similar figures for ΔG because $dM/dT = 0$. For $T \lesssim T_c$ the cusp in ΔG is removed in our theory, i.e. the difference from standard activation analysis is particularly large in this area because dM/dT is large (the magnetic obstacles are strongly temperature dependent—not proportional to $\mu(T)$—which is not accounted for by the standard model). Finally, for $T > T_c$ both theories yield very high figures for ΔG. In particular, in the range just below T_c the accuracy of ΔG derived from experimental data by means of the extended theory is reduced, because ΔG is the difference of two values of the same order of magnitude (cf equations (20), (23)). We conclude from figure 2 that the anomaly in the free enthalpy of activation ΔG, i.e. the cusp at $T < T_c$ calculated by means of standard activation analysis, is caused by neglecting the magnetic effects. The theory derived in section 2 removes this anomaly (details in the $\Delta G(T)$ curve at $T < T_c$ shall not be assessed due to the limited accuracy—see above). Thus, the results of our theory support the idea of magnetic-induced hardening of invar.

Although the cusp in ΔG vanishes according to the extended theory (cf figure 2), the figures for ΔG are still high for $T > T_c$. The very large activation enthalpy at $T > T_c$ and $M = 0$ cannot be explained by means of equation (20).

Up to now, this problem has not been investigated in detail, however, some clues do exist [24]. For FeNi polycrystals the influence of carbon impurities on the activation volume and activation enthalpy was investigated [20]. Generally, the activation volume V increases with increasing carbon concentration c_C, yielding an increase in ΔG (cf equation (20)). An influence of c_C on V, as measured by strain rate changes, may indicate an influence of c_C on the dislocation velocity. Such a dependence of carbon atoms on the dislocation velocity is well known [2]. The influence of interstitials on measurements of V was detailed in reference [34]. The stress changes induced by strain rate changes during activation volume measurements can be lower than expected or even negative due to the diffusion of interstitials. Appreciable effects may even occur at concentrations below 0.1 at.% [35]. An activation analysis, which accounts for diffusion effects in FeNi, was outlined [24] but has not yet been elaborated upon. The tensile test measurements were accomplished with alloys containing approximately 0.1 at.% carbon. Thus it is concluded that carbon impurities may cause the large free enthalpy of activation at $T > T_c$.

References

[1] Kocks U F, Argon A S and Ashby M F 1975 *Prog. Mater. Sci.* **19**

[2] Cottrell A H and Jawson M A 1949 *Proc. R. Soc.* A **199** 104
[3] Granato A V, Lücke K, Schlipf J and Teutonico L J 1964 *J. Appl. Phys.* **35** 2732
[4] Conrad H and Wiedersich H 1960 *Acta Metall.* **8** 128
[5] Gibbs G B 1967 *Phil. Mag.* **16** 97
[6] Schoeck G 1965 *Phys. Status Solidi* **8** 499
[7] Surek T, Luton M J and Jonas J J 1973 *Phil. Mag.* **27** 425
[8] Gudladt H J 1979 *Diploma Thesis* Technische Universität Braunschweig, FRG
[9] Guillaume Ch E 1904 in *Les Application des Aciers au Nickel* (Paris: Gauthier Villar)
[10] Shimizu M 1980 *J. Magn. Magn. Mater.* **20** 47 (and references therein)
[11] Nakamura Y, Sumiyama K and Shiga M 1979 *J. Magn. Magn. Mater.* **12** 127
[12] Nakamura Y 1983 *J. Magn. Magn. Mater.* **31–34** 829
[13] Crangle J and Hallam G C 1963 *Proc. R. Soc.* A **272** 119
[14] Cochrane R W and Graham G M 1970 *Can. J. Phys.* **48** 264
[15] Werner S A 1970 *J. Appl. Phys.* **41** 1363
[16] Ishakawa Y, Onodera S and Tajima K 1979 *J. Magn. Magn. Mater.* **10** 183
[17] Shiga M and Nakamura Y 1984 *J. Magn. Magn. Mater.* **40** 319
[18] Müller J B and Hesse J 1983 *Z. Phys.* B **54** 35, 43
[19] Nakamura Y 1976 *IEEE Trans. Mag.* **12** 278
[20] Bolling G F and Richman R H 1969 *Phil. Mag.* **19** 247
[21] Echigoya J, Hayashi S, Nakamichi T and Yamamoto M 1971 *J. Phys. Soc. Japan* **30** 289
[22] Echigoya J, Hayashi S and Yamamoto M 1972 *Phys. Status Solidi* a **14** 463
[23] Flor H, Gudladt H J and Schwink Ch 1980 *Acta Metall.* **28** 1611
[24] Retat I 1986 *PhD Thesis* Technische Universität Braunschweig, FRG
[25] Retat I 1987 *Phys. Status Solidi* a **99** 121
[26] Echigoya J and Hayashi S 1979 *Phys. Status Solidi* a **55** 279
[27] Echigoya J, Hayashi S and Yamamoto M 1975 *Phys. Status Solidi* a **30** 521
[28] Retat I, Steffens Th and Schwink Ch 1985 *Phys. Status Solidi* a **92** 507
[29] Labusch R 1972 *Acta Metall.* **20** 917
[30] Hausch G and Warlimont H 1973 *Acta Metall.* **21** 401
[31] Hayase M, Shiga M and Nakamura Y 1971 *J. Phys. Soc. Japan* **30** 729
[32] Nakamura Y, Hayase M, Shiga M, Miyamoto Y and Kawai N 1971 *J. Phys. Soc. Japan* **30** 720
[33] Shiga M 1967 *J. Phys. Soc. Japan* **22** 539
[34] Mulford R A and Kocks U F 1979 *Acta Metall.* **27** 1125
[35] Lothe J and Hirth J P 1982 *Dislocation Theory* (Chichester: Wiley)