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A MAGNETIC AFTEREFFECT IN DILUTE h.c.p. Co-C ALLOYS*

J. R. KEISER† and M. WUTTIG‡

A magnetic disaccommodation in dilute h.c.p. Co-C alloys has been observed around 90°C. The thermally activated process giving rise to the disaccommodation is characterized by an activation energy of 26 kcal mole⁻¹ and an attack frequency on the order of 10⁺¹³ sec⁻¹. An application of the selection rules shows that the disaccommodation cannot be caused by the redistribution of tetrahedral or octahedral interstitials or any nearest neighbor interstitial pairs as long as the defects interact linearly with the internal magnetic field.

TRAINAGE MAGNETIQUE DANS LES ALLIAGES DILUES h.c. Co-C

Une désaccommodation magnétique a été observée dans les alliages dilués h.c. Co-C au voisinage de 90°C. Le processus activé thermiquement produisant la désaccommodation est caractérisé par une énergie d'activation de 26 kcal mole⁻¹ et une fréquence d'attaque de l'ordre de 10⁺¹³ sec⁻¹. L'application des règles de sélection montre que la désaccommodation ne peut être due à la redistribution des interstitiels tétraédriques ou octaédriques ou de n'importe quelle paire d'interstitiels premiers voisins, car les défauts interagissent linéairement avec le champ magnétique interne.

EINE MAGNETISCHE NACHWIRKUNG IN VERDÜNNTEN HEXAGONALEN Co-C-LEGIERUNGEN

Bei etwa 90°C wurde eine magnetische Desakkommodation in verdünnten hexagonalen Co-C-Legierungen beobachtet. Der die Desakkommodation verursachende, thermisch aktivierte Prozeß hat eine Aktivierungsenergie von 26 kcal Mol⁻¹ und eine Sprungfrequenz von der Größenordnung 10⁺¹³ sec⁻¹. Eine Anwendung der Auswahlregel zeigt, daß die Desakkommodation nicht durch die Neuverteilung tetraedrischer oder oktaedrischer Zwischengitteratome oder irgendwelcher Zwischengitteratompaare auf benachbarten Plätzen verursacht werden kann, solange die Defekte mit dem inneren magnetischen Feld linear wechselwirken.

INTRODUCTION

A variety of magnetic aftereffects due to the diffusion controlled redistribution of defects with respect to the direction of the local spontaneous magnetization has been observed for b.c.c. and f.c.c. metals and alloys. Typical examples are given in Table I. No such aftereffects have been reported for h.c.p. structures,

TABLE I. Magnetic after effects due to the redistribution of different defects in f.c.c. and b.c.c. metals and alloys

Defect type	Metal, alloy	
	b.c.c.	f.c.c.
Self interstitial	Fe ⁽¹⁾	Ni ⁽²⁾
Interstitial	Fe-C ⁽³⁾	
Interstitial pair		Ni-C ⁽⁴⁾
Substitutional pair	Fe-Si ⁽⁵⁾	Co-Ti ⁽⁶⁾
Interstitial-substitutional pair	Fe-Si-C ⁽⁷⁾	Fe-Ni-C ⁽⁸⁾

although internal friction maxima corresponding to the reorientation of substitutional-interstitial clusters are known.⁽⁹⁻¹²⁾ It is thus of interest to perform disaccommodation studies on h.c.p. cobalt base alloys. For the present study Co-C alloys were chosen because samples were readily available.

SAMPLES AND EXPERIMENTAL TECHNIQUE

The samples were kindly provided by Mah and were thus comparable to those used in his study.⁽¹³⁾ The samples had been prepared by heating nominally

99.99% Johnson and Matthey cobalt in a carbonaceous atmosphere at 1050°C for several hours. Polycrystalline specimens thus obtained had been zone refined to produce f.c.c. single crystals which upon cooling transformed into h.c.p. single crystals. The h.c.p. single and (f.c.c. + h.c.p.) polycrystalline samples used in this study contained 0.37 wt. %[‡] and 0.26 wt. %[§] carbon respectively.

The disaccommodation technique applied in this investigation is quite similar to the well known anelastic techniques for the study of point defects. The difference is that in ferromagnetic solids the normally uniform distribution of defects among crystallographically equivalent sites is intrinsically perturbed within a ferromagnetic domain while it takes an externally applied stress to perturb the defect population in nonferromagnetic solids. In order to be able to observe the establishment of the perturbed state of the defect population, the domain structure must be altered. This is usually done by demagnetizing the sample. The decrease of the initial permeability, the disaccommodation, occurring after the demagnetization, signals the redistribution of the defect population. It is equivalent to the decrease of the elastic modulus during an aperiodic anelastic experiment. Further details of the disaccommodation phenomenon can be found in suitable monographs.⁽¹⁴⁾

‡ Chemical analysis performed by C. C. Kavin Co., Maywood, Illinois.

§ The mass of the polycrystalline sample available was too small for chemical analysis. Therefore, its carbon content was estimated on the basis of the observed ratio of the disaccommodation amplitudes of the single and polycrystalline samples.

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Details on the experimental technique can be found elsewhere.⁽¹⁵⁾

EXPERIMENTAL RESULTS

Figure 1 gives a survey of the disaccommodations observed in the temperature range -20 to $+120^\circ\text{C}$ which constituted the temperature limits of the apparatus. In this figure, the temperature dependence of the normalized difference of the initial permeabilities measured at 1 and 5 min after demagnetization is plotted for a polycrystalline and a single crystalline specimen. The data were normalized with respect to the height of the maximum at around 90°C to facilitate a direct comparison of the two sets of data independent of the carbon content in the h.c.p. phase. It should be noted that no disaccommodation was observed in the above mentioned temperature range in a decarburized polycrystalline sample.

In order to characterize the relaxation process giving rise to the maximum⁽¹⁵⁾ in Fig. 1, isothermal disaccommodation measurements of 20 hr duration were performed on a h.c.p. Co-C single crystal. The time limit of the isothermal runs was determined by the time at which the rate of disaccommodation had decreased to 0.1 per cent of its initial value. Plots of the logarithm of the reluctivity vs. time showed that the disaccommodation should be decomposed into two relaxations. Therefore, the data were analysed in terms of the expression,^(16,17)

$$\begin{aligned} [r(\infty) - r(t)]/[r(\infty) - r(0)] &= \sum_{i=1}^2 \frac{a_i}{\sqrt{\pi}} \\ &\times \int_{-\infty}^{+\infty} \exp(-x^2) \exp\left(-\frac{t}{\tau_i} \exp(-\beta_i x)\right) dx. \end{aligned}$$

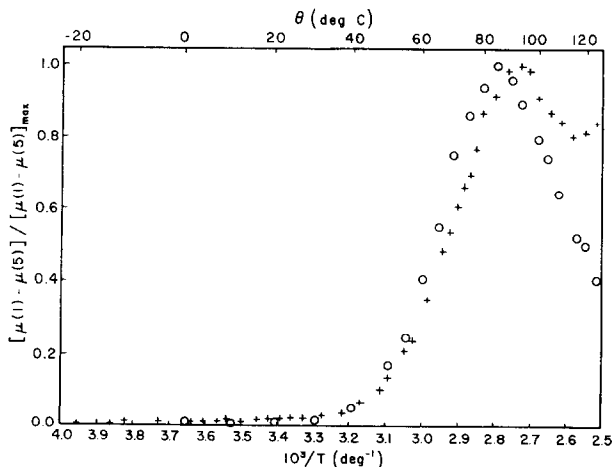


FIG. 1. Normalized difference of the initial permeability measured at 1 and 5 min after demagnetization vs. temperature: + + + + polycrystalline (f.c.c. and h.c.p.), o o o o single crystalline h.c.p., Co-0.37 wt. % C alloy.

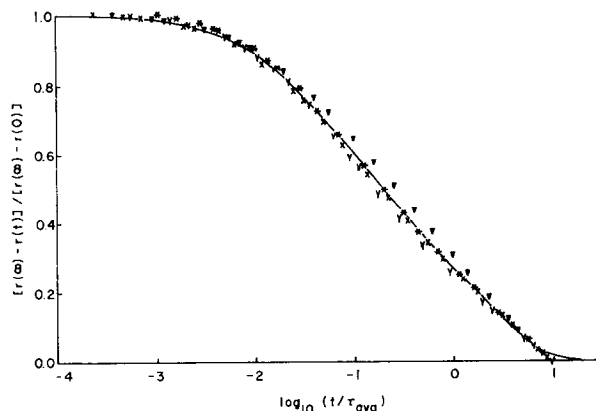


FIG. 2. Isothermal disaccommodation of a h.c.p. Co-0.37 wt. % alloy. Solid line-calculated master curve. $\times \times \times$ 70°C ; $\nabla \nabla \nabla$ 75°C ; yyy 75°C ; $***$ 80°C .

r = reluctivity = (initial permeability) $^{-1}$;
 a_i = normalized amplitude of i th relaxation,
 $\sum a_i = 1$;
 τ_i = mean relaxation time of i th relaxation;
 β_i = half width of Gaussian distribution of i th relaxation.

Careful sampling of the space spanned by the six parameters a_1 , a_2 , τ_1 , τ_2 , β_1 and β_2 revealed only one minimum of the variance. The quality of the fit thus achieved can be seen from Fig. 2 showing a normalized plot of the reluctivity as a function of normalized time. The time normalization was performed with respect to the average relaxation time.

$$\tau_{av} = \frac{\sum a_i \tau_i}{\sum a_i}$$

The solid line in Fig. 2 represents the disaccommodation master curve calculated by using the values of the parameters a_i , τ_i and β_i obtained from a least square fit and averaged over all runs performed. An Arrhenius plot of the relaxation times τ_1 and τ_2 is shown in Fig. 3. The error bars give the 95 per cent confidence limits as obtained from the least square analysis* and the lines represent least square fits to the data points. While the Arrhenius plot for τ_2 is of acceptable quality, the same for τ_1 is not. The reasons for this lack of quality are currently not understood.

The temperature dependence of the mean relaxation times of the defect redistribution is given by

$$\tau_1 = 1.9 \times 10^{-14 \pm 21} \exp[-(26.7 \pm 37.8) \text{ kcal mole}^{-1}/RT] \text{ sec}$$

and

$$\tau_2 = 1.5 \times 10^{-12 \pm 3} \exp[-(25.9 \pm 5.5) \text{ kcal mole}^{-1}/RT] \text{ sec}$$

* These confidence limits were calculated from a linearized expression for the sum of the least squares. Hence, they will deviate slightly but most likely not significantly from their true values.⁽¹⁸⁾

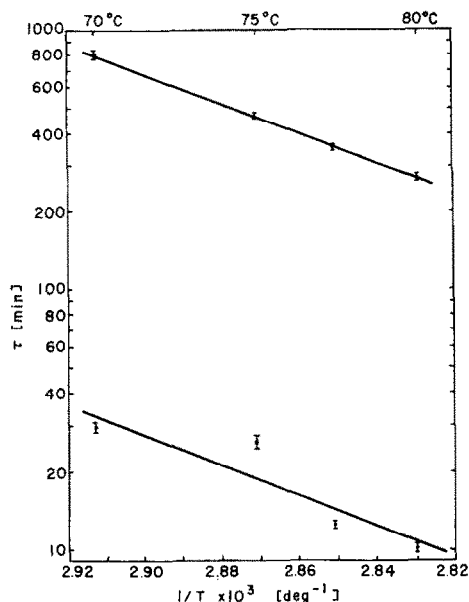


Fig. 3. Arrhenius plots for carbon redistribution in h.c.p. cobalt: upper line, τ_2 ; lower line, τ_1 .

and the two half widths are

$$\beta_1 = 2.2 \pm 0.1$$

and

$$\beta_2 = 0.0.$$

Again, the error limits represent 95 per cent confidence limits as obtained from the least square analysis. No error limit could be obtained for β_2 in this way although it is estimated to be of the same order of magnitude as that of β_1 . This former parameter had to be varied stepwise and could not be directly included in the least square iteration analysis as the convergence for near zero exponentials is known to be very poor.⁽¹⁹⁾ The value $\beta_2 = 0$, is remarkable, although the reasons for such an unusually narrow distribution of relaxation times are presently unknown.

DISCUSSION

Because of the size difference of the cobalt and carbon ions it is generally believed that carbon enters the cobalt lattice interstitially. Therefore, the fact that a disaccommodation can only be observed in cobalt samples containing carbon indicates that the elementary process giving rise to the observed disaccommodation consists of a redistribution of carbon interstitials with respect to the direction of the spontaneous magnetization. The values of the pre-exponential factors derived from the Arrhenius plot support this conclusion. Furthermore, both the poly (f.c.c. + h.c.p.) and single-crystalline h.c.p. samples display the maximum of the difference of the initial

permeabilities at 90° shown in Fig. 1, whereas only the polycrystalline (f.c.c. + h.c.p.) sample seems to exhibit another maximum located at higher temperatures. The maximum of this high temperature peak would be expected around 180°C according to Mah's data⁽¹³⁾ and would be associated with the f.c.c. phase. It follows that the maximum in Fig. 1 is associated with a diffusion controlled redistribution of carbon interstitials in h.c.p. cobalt. The activation energy of about 26 kcal/mole is then characteristic for this redistribution process. In comparing this figure with the reported values for the activation energy for carbon diffusion in f.c.c. cobalt, 38 kcal mole⁻¹,⁽²⁰⁾ one might be tempted to conclude that carbon diffuses easier in the h.c.p. than in the f.c.c. phase of cobalt. However, a comparison of the activation energies of carbon diffusion in f.c.c. cobalt with the activation energy of carbon redistribution in h.c.p. cobalt is only valid if the mode of redistribution is known.

The following paragraphs contain a brief discussion of possible modes of interstitial redistribution although it is realized that the experimental evidence presented in this work is insufficient to establish any one mode with any degree of certainty. The main reason for pursuing this discussion nevertheless is the apparent lack of an anelastic analogue. Although the absence of a pronounced internal friction peak in dilute h.c.p. Co-C alloys might merely indicate that the strain tensor of the defect involved is so small that no stress relaxation can be observed, this possibility will be ignored.

Possible modes of redistribution of defects may be obtained from the selection rules as shown by Nowick and Heller⁽²¹⁾ as long as it can be assumed that the defects interact linearly with stress, electric and magnetic fields. These selection rules indicate, in effect, which combination of field components is capable of redistributing the defects. One set of selection rules to be considered applies to defect redistribution under stress in h.c.p. polycrystals; it is given implicitly in Ref. 21. The disaccommodation is caused by a defect redistribution mode that can be excited by the magnetic field attendant to the spontaneous magnetization. As the direction of the spontaneous magnetization in cobalt is directed normal to the basal plane, it follows that the selection rules for defect redistribution under the influence of a magnetic field in the $\langle 001 \rangle$ direction are applicable. Those rules may be obtained⁽²²⁾ from the character and correlation tables published by Wilson.⁽²³⁾ Table 2 contains the anelastic and magnetic selection rules for the h.c.p. host lattice, crystal group, D_{6h} (6/mmm).

Further discussion will be restricted to defects of

TABLE 2. Selection rules for the anelastic relaxations in hexagonal close packed polycrystals and disaccommodations in single crystals of the same type

Type of relaxation	Defect symmetry						
	Hexagonal		Trigonal		Orthor.	Monocl.	Tricl.
	Upper	Lower	Upper	Lower			
Anelasticity in polycrystals	No	No	No	No	Yes	Yes	Yes
Disaccommodation	No	Yes	No	Yes	No	Yes*	Yes

* Only defects with a mirror plane perpendicular to the *c*-axis.

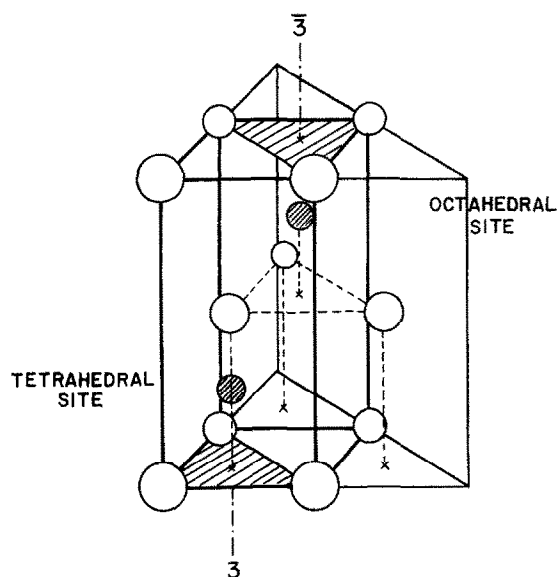


FIG. 4. Interstitial sites in the h.c.p. structure.

interstitial type only as any substitutional-interstitial combination may be discounted on the basis of the 99.99 per cent purity of the cobalt used for the sample preparation. The traditional tetrahedral and octahedral interstitial sites are shown in Fig. 4. As can be seen from this figure, the two sites have the symmetries $C_{3v}(3m)$ and $D_{3h}(\bar{3}m)$ respectively and thus belong to the upper subclass of trigonal symmetry. From Table 2, it follows then that neither of these defects can give rise to a disaccommodation. This also means that no simple carbon interstitial type defect can be found which can cause disaccommodation without an anelastic analog in cobalt polycrystals. Nearest neighbor $\langle 001 \rangle$ dimers (tetrahedral-tetrahedral and octahedral-octahedral pairs) belong to the upper hexagonal class of symmetry $D_{3h}(3/m\bar{m} = \bar{6}m)$. Therefore, an inspection of Table 2 shows that these two types of nearest neighbor dimers are ineligible too.

The symmetry element characterizing $\langle 110 \rangle$ dimers (tetrahedral-octahedral pair) is a mirror plane oriented parallel to the *c*-axis. Hence, they are of monoclinic symmetry and it follows from Table 2 that they cannot give rise to a disaccommodation if only the redistribution with respect to the intrinsic magnetic field is considered. It would appear from Table 2, however, that $\langle 110 \rangle$ dimers can interact with the magnetostrictive field attending the magnetic field. In the special case of h.c.p. cobalt, though, the demagnetization leaves the magnetostrictive field unaltered. Therefore, $\langle 110 \rangle$ dimers do not constitute an eligible defect either.

So far, it was implicitly assumed that the concentrations of defects of given types remained constant in the course of the experiment, i.e. defect "reaction" modes were ignored. In a h.c.p. structure such modes can only be excited by stresses.⁽²³⁾ It has already been pointed out, however, that the intrinsic magnetostrictive field cannot be changed. Thus, defect reactions are not a possible cause of the observed disaccommodation.

It thus can be seen that within the limits of a linear theory neither the traditional mono- nor nearest neighbor diinterstitials can give rise to an elastic or magnetic redistribution mode in h.c.p. cobalt. It is equally clear that neither of the remaining possible defect relaxation modes can be associated with the observed disaccommodation with any degree of certainty.

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REFERENCES

1. P. MOSER, Thesis, University of Grenoble (1965).
2. P. PERETTO, Thesis, University of Grenoble (1967).
3. J. L. SNOEK, *Physica* **5**, 668 (1938).
4. M. WUTTIG and H. K. BIRNBAUM, *Appl. Phys. Lett.* **7**, 320 (1965).
5. P. BRISSONNEAU and P. MOSER, *J. phys. Soc. Japan* **17**, 333 (1962).
6. H. B. AARON, M. WUTTIG and H. K. BIRNBAUM, *Acta Met.* **16**, 269 (1968).
7. W. HAMPE and D. WIDMAN, *Z. angew. Phys.* **12**, 360 (1963).
8. E. ADLER and C. RADELOFF, *J. appl. Phys.* **40**, 1526 (1969).
9. J. N. PRATT, W. J. BRATINA and B. CHALMERS, *Acta Met.* **2**, 203 (1954).
10. D. GUPTA and S. WEINIG, *Acta Met.* **10**, 292 (1962).
11. D. R. MILLER, *Trans. Am. Inst. Min. Engrs* **224**, 275 (1962).
12. E. BISOGNI, G. MAH and C. WERT, *J. less-common Metals* **7**, 197 (1964).
13. G. MAH and C. WERT, *Trans. Am. Inst. Min. Engrs* **242**, 1211 (1968).
14. S. CHIKAZUMI, *Physics of Magnetism*. John Wiley (1964).
15. M. WUTTIG and H. K. BIRNBAUM, *J. phys. Chem. Solids* **27**, 225 (1966).
16. A. S. NOWICK and B. S. BERRY, *IBM J. Res.* **5**, 297 (1961).
17. E. T. YEN and M. WUTTIG, *J. phys. Chem. Solids* **30**, 2269 (1969).
18. N. R. DRAPER and H. SMITH, *Applied Regression Theory*. John Wiley (1967).
19. R. H. MOORE, Ph.D. Thesis, Oklahoma State University (1962).
20. T. HEHENKAMP, *Acta Met.* **14**, 887 (1966).
21. A. S. NOWICK and W. R. HELLER, *Adv. Phys.* **14**, 101 (1965).
22. A. S. NOWICK, private communication.
23. E. B. WILSON, J. C. DECUS and P. C. CROSS, *Molecular Vibrations*. McGraw-Hill (1955).