Effects of annealing processes on the Curie temperature of Fe-Ni Invar alloys

Effects of annealing processes on the Curie temperature of Fe–Ni Invar alloys

M R Gallas and J A H da Jornada

Instituto de Física, Universidade Federal do Rio Grande do Sul, 91500 Porto Alegre, Brazil

Abstract. The Curie temperature (T_c) of the iron–nickel Invar alloy with composition 30.6 at.% Ni was studied as a function of the annealing time at different temperatures. An increase in T_c of more than 20 °C was observed with annealing at temperatures as low as 340 °C. The change in T_c with time was similar to that observed in metallic glasses, and was interpreted as an atomic rearrangement, with a change in the chemical short-range order. The activation energy for the process was estimated to be about 1.5 eV, indicating movement of quenched-in vacancies as the main relaxation mechanism.

1. Introduction

The Fe–Ni system has been studied for over a hundred years. It is a very rich and interesting system, mainly in the Invar range (between 30 and 45 at.% Ni, with FCC structure), where anomalous behaviour is observed in some physical properties, like large magnetostriction, extremely low thermal expansion, etc. (Nakamura 1976). In spite of much experimental and theoretical effort, the Invar problem is not yet completely understood.

Although recent studies (Wassermann 1987) highlighted the 2γ-states model of Weiss as describing the root of the Invar problem, structural inhomogeneities on Fe–Ni alloys could play a dominant role (Kakehashi 1988, Komura *et al* 1985). Structural changes involving phase separation and ordering take place below $\sim$ 500 °C, where diffusion is very limited, in such a way that there is hardly a state of equilibrium. In Fe–Ni alloys found in meteorites, a state closer to the thermodynamic equilibrium can be observed, because the cooling rates are very slow: about 1 K in 10^6 years.

Special techniques have been used to enhance diffusion at rather low temperatures in Fe–Ni Invar alloys, in order to allow the system to attain a state more close to the thermodynamic equilibrium in reasonable times. Examples of such special techniques are: electron irradiation (Rechenberg 1973, Reuter *et al* 1989a), neutron irradiation (Morita *et al* 1983), ultrafine particles (Kaito *et al* 1989, Franco and Rechenberg 1985), and more recently, ion implantation (Gallas *et al* 1990). These works show a tendency to a phase separation and ordering, similar to that found in Fe–Ni meteorites (Scorzelli and Danon 1985, Jago *et al* 1982).

Evidence of atomic inhomogeneity in the Invar alloy $Fe_{65}Ni_{35}$ is found from Mössbauer measurements (Rancourt *et al* 1987). In a recent work (Gallas *et al* 1989),

an increase was observed in the linewidth of the Mössbauer spectra of $Fe_{70}Ni_{30}$ alloys annealed at high pressure. This increase is related to an atomic rearrangement and, in this case, probably to an increase in the short-range order, which agree with other works (Makarov and Puzey 1974).

These structural rearrangements are also reported to result in changes in the Curie temperature in Fe–Ni alloys of different compositions for samples irradiated with neutrons and electrons, with compositions between 30 and 50 at.% Ni. Morita *et al* (1983,1984) observed a rise in T_c which was attributed to a phase separation. For Fe–Ni-based amorphous alloys subjected to thermal treatments, increases in T_c up to 35 °C were also observed at rather low temperatures, these being interpreted as a result of a local rearrangement of atoms (Liebermann *et al* 1977). On the other hand, recent theoretical calculations for Fe–Ni alloys (Kakehashi 1988) show important changes in magnetic properties due to local environment effects.

The change in T_c with composition for Fe–Ni alloys is particularly large near 30 at.% Ni, where it changes from about 320 °C at 35 at.% Ni to nearly 0 °C at about 29 at.% Ni, presumably because of a strong competition between ferromagnetism (related to a positive exchange interaction between Fe–Ni and Ni–Ni pairs) and antiferromagnetism (favoured by a negative exchange interaction between Fe–Fe pairs) (Lawrence and Rossiter 1986). It is interesting to note that the theoretical work of Kakehashi (1988) finds that coupling between two neighbouring Fe atoms can be either ferromagnetic or antiferromagnetic, depending on the number of the Fe nearest neighbours surrounding it. Therefore, in this region T_c is expected to be very sensitive to structural changes like short-range order or clustering. Another important aspect is that, in this region, the Curie temperature is low enough (~ 150 °C) for its measurement not to introduce annealing effects.

In the present work we report a systematic study of the Curie temperature as a function of annealing time and temperature in a Fe–Ni alloy with composition 30.6 at.% Ni.

2. Experimental procedure

The measurements of the Curie temperature were obtained from the drop in the magnetic AC susceptibility, by means of a Hartshorn bridge (Brodbeck *et al* 1978). A typical experimental curve obtained with this method is shown in figure 1. T_c is determined from the intersection point between a linear extrapolation of the steepest part of the curve and the background, as is usual (Shirakawa *et al* 1981). Although this method is not very precise for determining the true T_c, it is a simple, very reproducible and accurate way of measuring changes in T_c.

As mentioned before, the sample used in the present work had a composition of 30.6 at.% Ni, with a purity better than 99.9 at.% (major impurities were Si and Mn with less than 0.01 at.% of each). Samples were sawed and burnished to an irregular cylindrical shape with height approximately 7 mm and diameter approximately 1 mm, and encapsulated in small quartz tubes with Ar atmosphere. These tubes could easily be placed inside the coil to measure T_c. The encapsuled samples were annealed at 1000 °C for 1 h.

The series of isothermal and isochronal anneals were made in a furnace with thermal stability of ± 0.5 °C. The anneals were performed in a temperature range from 250 to 800 °C and the time varied basically from 1 to ~ 110 h for the lower temperatures and from 1 to ~ 22 h for higher temperatures.
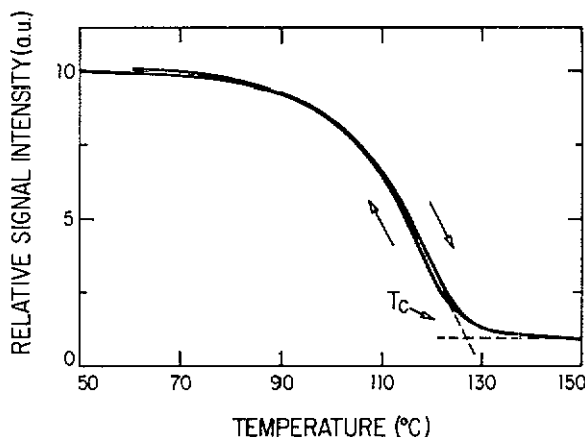
Figure 1. Typical experimental curve obtained by the method used to determine T_{c}.

The thermal treatment and T_{c} measurements were always done with the sample inside the small quartz capsule already mentioned, in order to prevent contamination and to avoid change in the stoichiometry due to possible sublimation during annealing at high temperatures. To measure the quenching rate of the sample, a thermocouple was placed in a similar configuration, giving a rate of approximately 400 °C s^{-1}.

The steps followed for each isothermal treatment were: annealing for 1 hour at 1000 °C; quenching in water; T_{c} measurement; annealing for the desired time t_1 at a certain temperature; quenching in water; T_{c} measurement; annealing for the time t_2 at the same temperature (the time was cumulative: the total annealing time was therefore $t_1 + t_2$); quenching in water; T_{c} measurement. For isochronal treatments the same basic steps were followed.

3. Results and discussion

Our results are summarized in figures 2, 3 and 4 below, where the change in Curie temperature (ΔT_{c}) relative to the as-prepared sample is shown for different conditions. Figure 2 shows the change in T_{c} for isochronal annealing, first increasing the annealing temperature up to 800 °C and then decreasing it down to room temperature.

It should be observed in figure 2 that with the annealing temperature increasing, there is no change in T_{c} for temperatures below about 350 °C. Above this value, T_{c} increases very rapidly with temperature, but this increase saturates at about 400 °C, and then T_{c} starts to decrease, reaching the same initial value for temperatures above 700 °C. With annealing temperature decreasing from 750 °C, it was observed that T_{c} starts to increase below 700 °C reaching a maximum value around 440 °C. The behaviour of ΔT_{c}, for increasing and decreasing annealing temperature, is nearly the same for temperatures down to about 440 °C, but from this value down to room temperature, no more changes in T_{c} are observed.

This behaviour of T_{c} with annealing treatments is similar to the change in the residual resistivity in certain alloys, due to the change in short-range order (Dahmani *et al* 1985). It can be understood qualitatively on the basis of two competing mechanisms: on the one hand, an increase in temperature favours diffusion, thus allowing the system to attain a state closer to the thermodynamic equilibrium, and on the other, decreasing
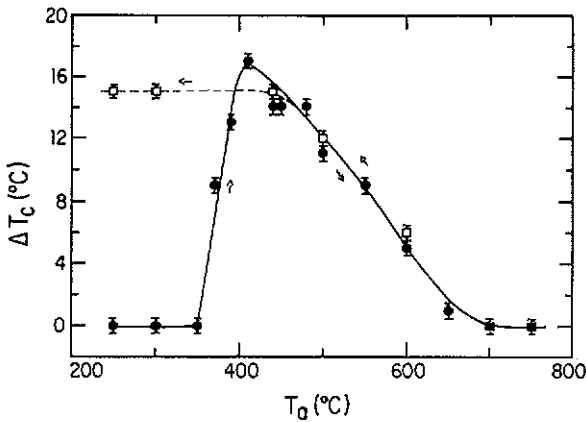
Figure 2. Results for the change in T_c, for isochronal annealing of 2 h at each temperature. The curves are only guides for the eye. Full curve, increasing annealing temperature, starting with an as-prepared sample; broken curve, decreasing annealing temperature, starting with the sample quenched from 750 °C.

temperature would favour the phenomena responsible for the increase in T_c. On the basis of the facts discussed in the introduction, this change in T_c is probably related to atomic rearrangements like short-range ordering, clustering or a spinodal decomposition.

It is interesting to remark that the change observed in T_c is not due to possible stress relaxation effects. First, because this change is rather high and second, because our experiments in heavily cold worked samples showed only a minor change in the steepness of the susceptibility against temperature curve (figure 1). Also, we made a search for evidence of more drastic atomic rearrangements like long-range order by means of x-ray diffraction, using Co Kα radiation to increase the atomic scattering factor difference for Fe and Ni, in such a way as to enhance the contrast between them. We have negative results, indicating that the scale of the atomic rearrangements should be rather small.

Moreover, measurements of hardness with microindentation were also performed. After an annealing treatment of 4 h at 360 °C, with the sample encapsuled in an Ar atmosphere, we obtain an increase in hardness of about 8%. This increase indicates that some atomic rearrangement like clustering had probably occurred, because this kind of rearrangement leads to an increase in hardness.

Another important point to note is that the diffusion coefficient in Fe–Ni alloys at these low temperatures is extremely small. Below about 350 °C diffusion would be so limited as to make the system practically frozen in. Based on published studies for diffusion activation energy for Fe–Ni alloys, we can make an estimate of the diffusion length at low temperatures. Extrapolating the data of Ustad and Sørum (1973) for our case, of an alloy with 30.6 at.% Ni subjected to an annealing treatment of 350 °C for 1 h, one obtains a value of 0.04 Å. This very short diffusion length (about 100 times smaller than the lattice parameter) could not produce important atomic rearrangements, thus a significant change in T_c is not expected. Therefore, this kind of diffusion process is probably not responsible for the changes observed at low temperatures and another process like quenched-in defects, especially vacancies should be taken in account.

In figure 3 the change in T_c for annealing of samples at different temperatures and
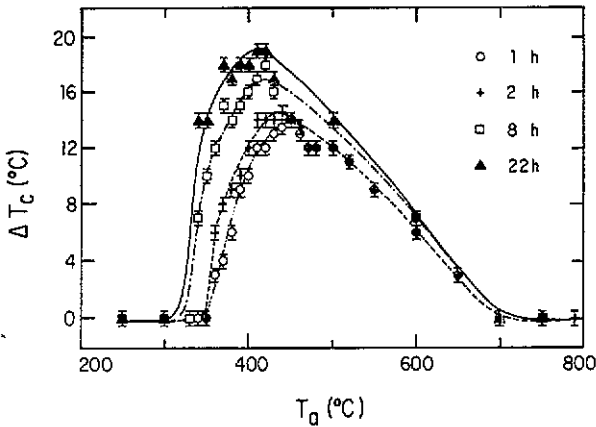
Figure 3. Change in T_c plotted as a function of the annealing temperature, for different annealing times. Before each annealing at different temperatures, the sample was homogenized at 1000 °C, to assure the same initial conditions. The curves are only guides for the eye.

times is shown. It can be seen that for longer annealing times the ΔT_c maximum is increased, and also that the peak in ΔT_c occurs at lower temperatures. This behaviour fits in with the mechanism discussed before. If we allow longer annealing times, the system is certainly closer to thermodynamic equilibrium; thus the peak in ΔT_c shifts further towards lower temperatures, where the driving force for the physical process responsible for the increase in ΔT_c is higher.

Morita *et al* (1984) showed that the effects of electron irradiation in Fe–Ni Invar alloys, which also increase ΔT_c, disappear on annealing at a temperature between 427 and 527 °C. In that work, the temperature of 427 °C was considered to be the temperature above which atoms 'begin to diffuse'. Their results are compatible with ours, as around 400 °C ΔT_c starts to decrease if we further increase the annealing temperature. They also observed a change in T_c of about 80 °C for Fe–Ni alloys with different compositions, irradiated with electrons at 200 °C. In this case the temperature is lower, but the irradiation is sufficient to enhance diffusion in a short time, allowing a large amount of atomic motion that is reflected in a strong variation in T_c. In our case, a prohibitively large time would be necessary to get a reasonable diffusion at 200 °C. It is important to remark that in his theoretical work Kakehashi (1988) found an increase in T_c of about 180 °C for $Fe_{65}Ni_{35}$, when the short-range order parameter changed from the random distribution case to a situation of minimum likelihood of Ni–Ni nearest neighbours.

Finally, it is interesting to note that Fe–Ni-based amorphous alloys of a composition near that studied here exhibit a similar change in T_c upon annealing (Liebermann *et al* 1977). However, the change observed was about 35 °C, which is 15 °C above the value we found. In the case of amorphous alloys, the annealing process is considered to produce two main effects: a change in the chemical short-range order and a topological change in the structure, whereas in the case of an alloy in the crystalline state, the only change possible is in the chemical order. However, a higher value in ΔT_c for the amorphous state is reasonable, not only because of topological changes but also because the more defective structure certainly favours more rapid diffusion.

We now consider the time dependence of ΔT_c for different temperatures: the results are presented in figure 4. Due to a limited range in time, it was not possible
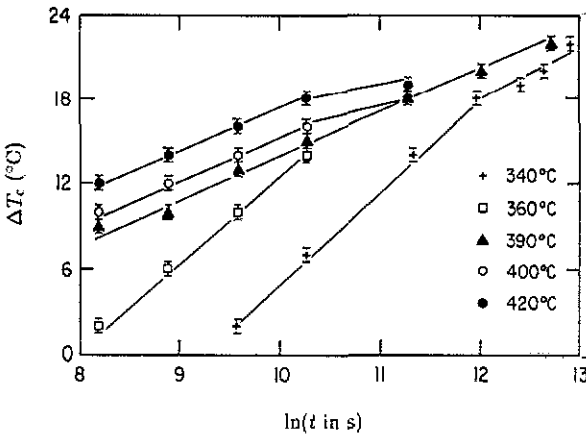
Figure 4. Change in T_c as a function of the logarithm of the annealing time, in seconds. The curves are for different isothermal treatments, each one starting with an as-prepared sample.

to make a detailed analysis of the best function describing all the cases. However it was very clear that a single exponential decay yielded a very poor description of the experimental data. We tried more specific functions used to study relaxation phenomena, like stretched exponentials (Palmer *et al* 1984) or t^n (Huse 1986), but none produced a good description for all cases. Some properties in solids have been shown to relax according to a logarithmic time dependence, whose slope can change for different time regions (Gibbs *et al* 1983). In fact, Riveiro and Hernando (1985) and Oseroff *et al* (1982) observed a $\ln t$ dependence for some magnetic properties in amorphous alloys and in spin glasses, respectively. So, in figure 4 we present our result of ΔT_c as a function of $\ln t$, and as can be seen, at least for the 390 °C case, a single straight line can well describe the results in this time range (up to 110 h). However, for the other cases it is necessary to consider a changing of slope over this time range, as in the case of the amorphous alloys already mentioned. For the lowest annealing temperature studied, namely 340 °C, we observed that the first four hours of annealing produced no change in T_c, but later on T_c increases in the same way as the curves for higher temperatures, indicating a kind of incubation period. This fact points to a nucleation mechanism, and is thus in agreement with the idea of clustering and phase separation.

In slow kinetic processes a function of the type $\exp(t/\tau)^\beta$, where τ is the relaxation time and $\beta > 1$ (the Johnson–Mehl–Avrami law) is commonly used to study crystallization kinetics in crystalline solids (Cahn 1970). We also tried to use this equation to fit our results, but we found a value of $\beta \sim 0.24$, which is in the range of the so-called stretched exponential relaxation process. This value of β usually describes structural relaxation in amorphous materials.

Although the facts discussed above suggest a rather complex relaxation process, it is possible to make a rough estimate of an activation energy (E_a), by assuming a scaling in time in such a way that the time dependence of ΔT_c is given only by the number of atomic jumps η produced during a time t, and assuming ΔT_c to be proportional to $\ln t$ as suggested by our experimental results and by the work of Gibbs *et al* (1983):

$$\Delta T_c(t, T) \equiv \Delta T_c(\eta) \propto \ln(\eta).$$

It is reasonable to assume that the number of jumps η is activated according to an Arrhenius law

$$\eta \propto t \exp(-E_a/kT).$$

Then, if $\Delta T_c(t, T) = \Delta T_c(t', T')$ we obtain

$$t \exp(-E_a/kT) = t' \exp(-E_a/kT').$$

Using the data of figure 4 and the above equation, we can calculate E_a. This calculation was done for all sets of curves that have approximately the same slope and an average value was then obtained, yielding $E_a = 1.5 \pm 0.4$ eV. Although we did not obtain a very good fit with the Johnson–Mehl–Avrami law, we also made a rough estimate of an activation energy for the process, using $\nu = 1/\tau = 10^{12}$ Hz, as is usual for this kind of process. It yields a value of 1.05 ± 0.25 eV, comparable with the value obtained above. From the experimental work of Ustad and Sørum (1973), the activation energy for diffusion in Fe–Ni with 30 at.% Ni is about 3.0 eV. As this energy is the sum of the vacancy formation and migration energies, we conclude that our value of 1.5 eV, which agrees roughly with the vacancy migration energy of about 1.2 eV for pure Ni reported by Cheng and Ellis (1989), corresponds effectively to the migration energy for vacancies, which should be in excess.

4. Conclusions

In this work we investigated the effect of thermal treatments on the Fe–Ni Invar alloy of composition 30.6 at.% Ni. In this region the magnetic properties change very strongly with atomic concentration, these being very sensitive to atomic rearrangements. Annealing treatments, even at relatively low temperatures like 340 °C, increase the Curie temperature of these alloys, this being interpreted as being due to a rearrangement of atoms on a very small scale, with a change in the chemical short-range order, probably clustering, a phenomena observed in other studies (Rechenberg 1973, Scorzelli and Danon 1985, Rancourt *et al* 1987, Kakehashi 1988, Russell and Garner 1990). It is an anomalous behaviour since the normal diffusion coefficient at these temperatures is very low. These results suggest that quenched-in vacancies are responsible for the enhancement of diffusion at lower temperatures and that they are the main mechanism of the relaxation process, therefore favouring the structural changes that are responsible for the increase in T_c.

Another point that reinforces our conclusion is that the dependence of ΔT_c with time is very similar to that observed in Fe–Ni-based amorphous alloys, which is interpreted as a change in the chemical short-range order and in the topological order. It is very difficult to separate these two effects in amorphous alloys. We believe that our results can contribute to the separation of these two effects, since the effects observed in this work are only due to the change in chemical-order and we showed that the relaxation kinetics is also very similar to that of amorphous and metallic glasses. This similarity is in fact surprising, because the structures of the amorphous and crystalline alloys are completely different.

We would also like to point out that other properties of the Fe–Ni alloys could in some way be very sensitive to their low-temperature thermal history. Our measurements of the Curie temperature, mainly the results presented in figure 2, show that

depending on the thermal treatment of the same alloy, T_c could be rather different. It would be interesting to measure other properties like magnetic anisotropy, volume magnetostriction, saturation magnetization, etc. It would also be very interesting to make a systematic study by neutron diffraction, as this could indicate the real nature of the structural changes observed in this work.

Finally, we would emphasize the need for theoretical work to make the proper quantitative connection between the local chemical order and the magnetic properties, mainly the Curie temperature, for Invar alloys, which would permit the use of a simple technique for quantitative studies of the kinetics of phase separation and ordering.

Acknowledgments

References

Brodbeck C M, Bukrey R R and Hoeksema J T 1978 *Rev. Sci. Instrum.* **49** 1279
Cahn R W 1970 *Physical Metallurgy* (Amsterdam: North-Holland)
Cheng H P and Ellis D E 1989 *Phys. Rev.* B **39** 12469
Dahmani C E, Cadeville M C and Pierron-Bohnes V 1985 *Acta Metall.* **33** 369
Franco H and Rechenberg H R 1985 *J. Phys. F: Met. Phys.* **15** 719
Gallas M R, Amaral L and Jornada J A H 1990 submitted
Gallas M R, Amaral L, Vasquez A and Jornada J A H 1989 *High Pressure Science and Technology: Proc. 11th AIRAPT Conf. (Kiev 1987)* vol 1 (Kiev: Naukova Dumka) p 299
Gibbs M R J, Evetts J E and Leake J A 1983 *J. Mater. Sci.* **18** 278
Huse D A 1986 *Phys. Rev.* B **34** 7845
Jago R A, Clark P E and Rossiter P L 1982 *Phys. Status Solidi* a **74** 247
Kaito C, Saito Y and Fujita K 1989 *Jap. J. Appl. Phys.* **28** L694
Kakehashi Y 1988 *Phys. Rev.* B **38** 474
Komura S, Takeda T and Endoh Y 1985 *J. Magn. Magn. Mater.* **50** 69
Lawrence P J and Rossiter P L 1986 *J. Phys. F: Met. Phys.* **16** 543
Liebermann H H, Graham Jr. C D and Flanders P J 1977 *IEEE Trans. Magn.* **MAG-13** 1541
Makarov V A and Puzey I M 1974 *Fiz. Metal. Metalloved.* **38** 161
Morita H, Tanji Y, Hiroyoshi H and Nakagawa Y 1983 *J. Magn. Magn. Mater.* **31-34** 107
Morita H, Chamberod A and Steinemann S 1984 *J. Phys. F : Met. Phys.* **14** 3053
Nakamura Y 1976 *IEEE Trans. Magn.* **MAG-12** 278
Oseroff S, Mesa M, Tovar M and Arce R 1982 *J. Appl. Phys.* **53** 2208
Palmer R G, Stein D L, Abrahams E and Anderson P W 1984 *Phys. Rev. Lett.* **53** 958
Rancourt D G, Smit H H A and Thiel R C 1987 *J. Magn. Magn. Mater.* **66** 121
Rechenberg H 1973 *PhD Thesis* Université de Grenoble
Reuter K B, Williams D B and Goldstein J I 1989a *Metall. Trans.* A **20** 711
——— 1989b *Metall. Trans.* A **20** 719
Riveiro J M and Hernando A 1985 *Phys. Rev.* B **32** 5102
Russell K C and Garner F A 1990 *Metall. Trans.* A **21** 1073
Scorzelli R B and Danon J 1985 *Phys. Scr.* **32** 143
Shirakawa K, Kaneko T, Nose M, Ohnuma S Fujimori H and Masumoto T 1981 *J. Appl. Phys.* **52** 1829
Ustad T and Sørum H 1973 *Phys. Status Solidi* a **20** 285
Wassermann E F 1987 *Festkörperprobleme (Advances in Solid State Physics)* vol 27 ed P Grosse (Braunschweig: Vieweg) p 85