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Long-range order kinetics in $\text{Ni}_3\text{Al}_{0.4}\text{Fe}_{0.6}$

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Abstract. Isothermal relaxations of the electrical resistance of $\text{Ni}_3\text{Al}_{0.4}\text{Fe}_{0.6}$ resulting from the long-range order (LRO) evolution were measured between 743 and 833 K, i.e. within the $L1_2$ -ordered γ' -phase domain. Both ordering and disordering kinetics were measured.

The LRO relaxations were generally much faster than in the previously studied Ni_3Al . The experimental curves fitted single exponentials; however, the Arrhenius plot of the resulting relaxation times yielded different values of the activation energy below and above 800 K, which is a Curie point of the alloy. Moreover, the estimated activation energies of long-range ordering and disordering within the ferromagnetic phase differed from each other.

The results were discussed in terms of the magnetic order effect on atomic ordering and of the model of vacancy diffusion in $L1_2$ structures proposed by Schoijet and Girifalco.

1. Introduction

Homogeneous long-range ordering is a diffusion-controlled process and thus any study of its kinetics involves the problems of atomic diffusion in ordered–disordered structures. The topic has recently been considered by Bakker [1] and it is now well known that generally long-range order (LRO) slows diffusion processes, degree of LRO and the ordering energy (i.e. T_C) quantitatively determining the phenomenon [2]. Despite the extensive theoretical and recent computer simulation material there has been, however, no systematic experimental study of the kinetics of diffusion-controlled processes as a function of the above parameters.

The present work contributes to a research project aiming to study LRO kinetics in the system $\text{Ni}_3\text{Al}_{1-x}\text{Fe}_x$ which has recently been started off by the examination of pure Ni_3Al [3].

The data on the ternary system Ni–Al–Fe have been reviewed by Rivlin and Raynor [4] while the particular section Ni_3Al – Ni_3Fe has been considered by Masahashi *et al* [5], who proposed the phase diagram shown in figure 1. Although the phase boundary $\gamma'-(\gamma + \gamma')$ has not been well established for iron contents higher than 8 at.%, it is reasonable to suppose, also on the basis of other investigations [6], that the γ' region spreads up to 25 at.% Fe at least below 770 K. The phase diagram of $\text{Ni}_3\text{Al}_{1-x}\text{Fe}_x$ shows that one has a LRO system with the critical order–disorder temperature varying continuously from 1720 K for Ni_3Al [7] to 770 K for Ni_3Fe . Moreover, studies performed

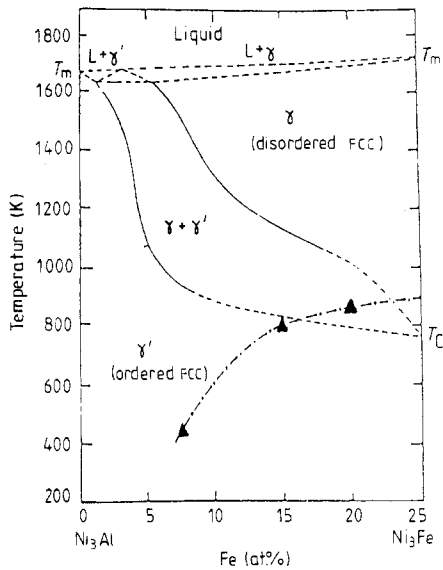


Figure 1. The Ni₃Al–Ni₃Fe section of the phase diagram of the Ni–Al–Fe system [5]: —, line joining the Curie points (▲) evaluated in [11].

by means of the Mössbauer effect and atom-probe field-ion microscopy [8–10] indicated that; when iron atoms are added to Ni₃Al, they occupy preferentially the sites on the Al sublattice. The Ni₃Al_{1-x}Fe_x alloys may thus be considered as quasi-binary Ni₃M alloys, M being an ‘average atom’ (Al, Fe), whose properties control the ordering energy and the value of T_C . The alloys containing more than 5 at.% Fe are ferromagnets at 300 K. Recently Efthimiadis *et al* [11] have evaluated the Curie points for $x = 0.3, 0.6$ and 0.8 as 450 K, 800 K and 850 K, respectively (figure 1). From the point of view of LRO kinetics investigations this means that the effect of magnetic order on atomic ordering has to be taken into account.

In the subsequent sections the results of the resistometric study of LRO kinetics in Ni₃Al_{0.4}Fe_{0.6} (15 at.% Fe) are presented. Most of the change in T_C takes place between 0 and 15 at.% Fe (figure 1). On the other hand, while LRO relaxed in a paramagnetic phase in the case of Ni₃Al, now the Curie point is located within the temperature domain of the measurements. The examined alloy may thus be considered as a counterpart of Ni₃Al in the discussed quasi-binary section and it will be interesting to compare the results obtained for both alloys.

2. Experimental method

The appropriate mixture of 99.999% Al, 99.99% Ni and 99.99% Fe was cast in a high-frequency furnace under Ar and, as in the case of Ni₃Al [3], rapidly solidified in a quartz capillary tube. The needle-like ingot 25 mm long and 1 mm in diameter was homogenised for 24 h at 1273 K, i.e. within the γ -phase region, in a vacuum quartz ampoule and water quenched. An x-ray diffraction test revealed a disordered A1-type structure with the lattice parameter of 0.35594 ± 0.00005 nm, the result being in good agreement with the data on Ni–Al–Fe of a similar composition in the literature [5, 10].

According to the goal of the investigations the sample was then aged for 1 week at 773 K so that homogeneity of the γ' -phase was attained and the measured LRO kinetics

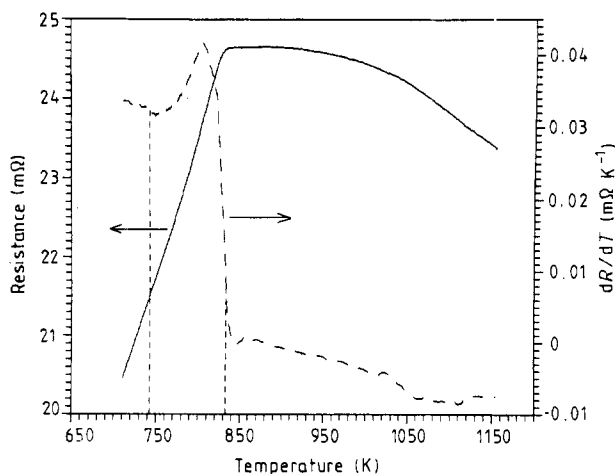


Figure 2. Temperature dependence of the electrical resistance of $Ni_3Al_{0.4}Fe_{0.6}$ annealed at 773 K (—), and the resulting derivative dR/dT (---); ---, limits of the temperature range of the LRO kinetics investigation.

were controlled, at least predominantly, by volume diffusion in a long-range ordered structure. Fulfilment of such requirements was additionally ascertained by scanning electron microscopy examination of a similar alloy solidified at the same conditions which revealed large grains 100 μm in size.

The electrical resistance of the sample was measured by a four-probe method using a computer-controlled device. Mechanically strained tungsten electrodes were in mechanical contact with the specimen held under He. The programmed temperature controller allowed the sample temperature to be linearly changed or stabilised within 0.5 K. In the case of isothermal measurements the specimen resistance was additionally corrected for temperature fluctuations.

3. Results

First the temperature of the $\gamma'-(\gamma + \gamma')$ boundary was determined. The sample was stabilised at 773 K until a constant level of electrical resistance was attained and then heated to 1250 K at a rate of 0.5 $K\ min^{-1}$. The resulting curve (figure 2) showed a dramatic anomaly at about 830 K and, after differentiation, also a maximum dR/dT at 800 K. The effects were associated with the $\gamma'-(\gamma + \gamma')$ boundary and the Curie point, respectively.

The curves shown in figure 2 have the same character as those obtained by Efthimiadis *et al* [11], whose sample, however, was annealed at 1100 K, i.e. just within the $\gamma + \gamma'$ region, and hence the measurement did not start from a state of the alloy homogeneity. This was probably the reason why the maximum dR/dT at 800 K was not so pronounced.

In order to make the LRO kinetics measurements interpretable it was essential to work within the γ' -phase region without crossing the $\gamma'-(\gamma + \gamma')$ boundary. This was ensured by starting from a well defined equilibrium LRO state at 813 K reached after the electrical resistance of the sample had been stabilised at that temperature.

Two series of experiments were performed.

(i) The long-range ordering kinetics were found. After a constant and stable sample resistance had been attained at a given temperature, the subsequent measurement was carried out after the temperature had been rapidly decreased by 10 K. For technical reasons, the lowest temperature reached was 743 K where the sample resistance relaxed for 5 days towards the equilibrium value.

(ii) The long-range disordering kinetics were then determined. The same procedure as in (i) was repeated when heating the sample also by steps of 10 K starting from 743 K. This procedure was continued up to 840 K where the character of the resistance relaxation changed abruptly—apparently because the $\gamma'-(\gamma + \gamma')$ boundary was crossed.

In a similar way to that used in the previous work, the experimental $R(t)$ curves were analysed by fitting single exponentials:

$$[R(t) - R(\infty)]/[R(0) - R(\infty)] = \exp(-t/\tau) \quad (1)$$

where τ is the fitted relaxation time of the process.

Two examples of the fits representing both series of the experiments are shown in figure 3 and the resulting values of the relaxation times τ corresponding to temperatures T are displayed in table 1.

4. Discussion

First it should be noted that in contrast with the alloy Ni_3Al the electrical resistance of $\text{Ni}_3\text{Al}_{0.4}\text{Fe}_{0.6}$ relaxed 'normally' with LRO, i.e. in the whole temperature range the resistance decreased when LRO increased and vice versa. In view of [11], which has already been quoted, it becomes evident how important it is that care should be taken to perform the LRO kinetics experiments at well determined conditions, e.g. without passing from a homogeneous to a heterogeneous ordering region. The negative temperature coefficient of the alloy resistance reported in [11] and also visible in figure 2 appeared within the $\gamma + \gamma'$ region, i.e. it originated from the heterogeneous disordering (γ -phase precipitation). Hence, in the studied alloy the homogeneous and heterogeneous long-range disordering processes gave rise to opposite electrical resistance responses.

The data were analysed conventionally by means of the Arrhenius plots which led to the following conclusions.

(a) Between 740 and 795 K, i.e. below the Curie point [11], both the fitted ordering and the fitted disordering relaxation times fulfilled reasonably the Arrhenius formula

$$\tau = \tau_0 \exp(E_A/kT) \quad (2)$$

where T is an absolute temperature, E_A is the activation energy and τ_0 is a constant (figure 4). The activation energy E_A of ordering was, however, about 0.2 eV higher than that of disordering. This result is especially interesting when noting that, within the temperature range common to both series of measurements, the relaxation times of disordering were systematically longer than those of ordering (table 1).

(b) The pre-exponential factors τ_0 fitted for ordering and disordering within the ferromagnetic phase of the alloy were relatively close to each other. It is, however, too early to comment on their values. It is only concluded that both values approximate the usually reported quantities ranging from 10^{-17} to 10^{-11} s (see, e.g., [3, 12]).

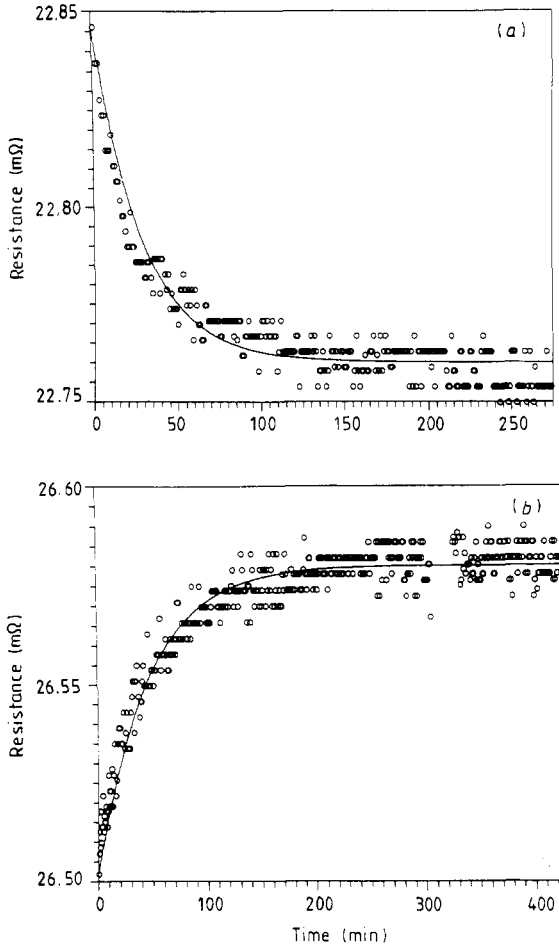


Figure 3. Resistance relaxations of $Ni_3Al_{0.4}Fe_{0.6}$ at 793 K for (a) ordering and (b) disordering: —, fitted exponentials.

Table 1. The relaxation times τ for various T .

Ordering		Disordering	
T (K)	τ (10 s)	T (K)	τ (10 s)
743	3800 ± 1400	752	2400 ± 600
761	910 ± 330	762	1400 ± 360
772	500 ± 140	773	700 ± 220
783	340 ± 170	784	370 ± 110
793	168 ± 72	793	270 ± 110
803	132 ± 66	803	180 ± 66
		812	144 ± 66
		817	84 ± 54
		823	78 ± 72
		828	66 ± 46
		833	84 ± 54

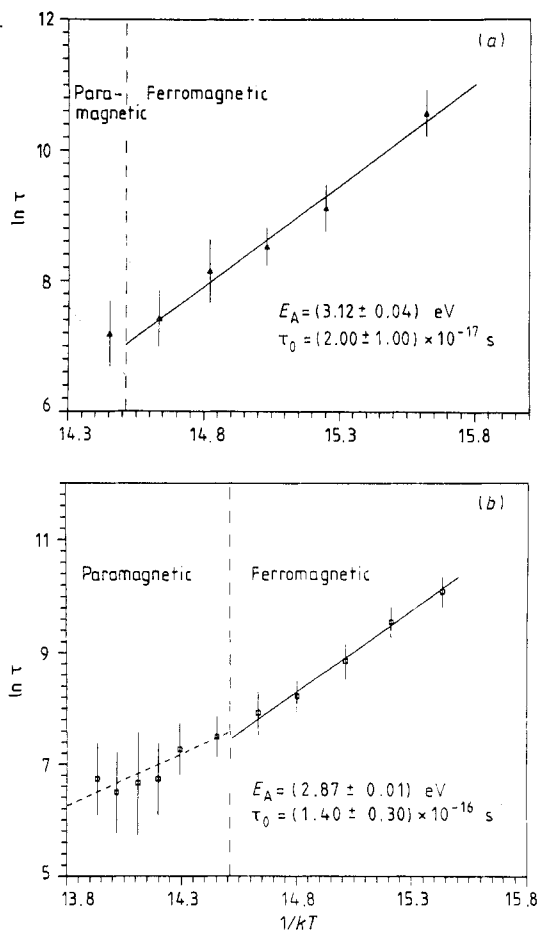


Figure 4. Arrhenius plots of the relaxation times of (a) ordering and (b) disordering in $\text{Ni}_3\text{Al}_{0.4}\text{Fe}_{0.6}$; —, fits to points corresponding to temperatures between 743 and 795 K (ferromagnetic region).

(c) Only one experimental point represents long-range ordering within the paramagnetic phase (figure 4(a)). However, the results obtained for disordering show that the magnetic transformation considerably modified the slope of the Arrhenius plot (figure 4(b)). Because of large errors of the relaxation times of disordering above 800 K the activation energy in this region was only roughly estimated as 1.9 eV.

It has been reported that magnetic ordering affects atomic migration in a crystalline lattice, e.g. the activation energy of diffusion in Fe–Al measured in the ferromagnetic state was about 0.2 eV higher than the value obtained above the Curie point [13]. In our case, however, the difference between the activation energies of LRO estimated below and above 800 K seems too high to result exclusively from the latter effect. Two other factors may additionally contribute to the decrease in E_A in the vicinity of the γ' –($\gamma + \gamma'$) boundary:

- (i) the effect of slowing down the relaxation process when approaching the critical temperature (phase boundary)—the critical slowing down;
- (ii) a relatively strong temperature dependence of degree of LRO.

The effect of critically slowing down the LRO kinetics was observed in alloys with $L1_2$ structure (see, e.g., [14, 15]). Although the precision of the measurements reported in this paper was insufficient to detect critical phenomena, an effective increase in the relaxation times near T_C might be observed.

The dependence of the activation energy of ordering on the degree of LRO was predicted within the model of vacancy diffusion in $L1_2$ structures proposed by Schoijet and Girifalco [2]. The work was published 20 years ago; however, it is still quoted in the most recent articles. According to the model, two effects should be detected at temperatures not too far from T_C :

- (i) a gradual decrease in the activation energy of LRO, resulting in a deviation of $\tau(T)$ from the Arrhenius law;
- (ii) a difference between the activation energies of long-range ordering and disordering ($E_A^{\text{ord}} > E_A^{\text{disord}}$).

Taking into account that the LRO kinetics study reported in this paper was carried out within the region $1 < T_C/T < 1.12$ it may be concluded that the experimental results are in a full qualitative agreement with the model.

On the other hand, it is interesting to note that LRO relaxations in $Ni_3Al_{0.4}Fe_{0.6}$, both ferromagnetic and paramagnetic, were more than ten times faster than in Ni_3Al even though in the case of the latter alloy the measurements were performed at higher temperatures.

It would be very interesting to answer the question of what is the origin of such a large difference between the relaxation rates—and of whether the problem lies in the activation energies or correlation factors of diffusion, or perhaps there are other reasons.

Although the activation energy of LRO in a paramagnetic state of $Ni_3Al_{0.4}Fe_{0.6}$ is considerably lower than the value of 3 eV reported for Ni_3Al (also a paramagnet) [3], it must be admitted that both quantities were only roughly estimated. Continuation of the systematic study of the alloys $Ni_3Al_{1-x}Fe_x$ is thus well motivated.

Acknowledgments

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