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Influence of structure and composition on atomic mobility in Ni(Al)-based solid solutions and Ni₃Al-based intermetallics

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Abstract

Atomic mobility was characterized by investigating the isothermal relaxation of short-range order (SRO) in a Ni(Al,Ti) solid solution and of long-range order (LRO) in three intermetallic compounds Ni₃Al, Ni₃(Al,Ti) and Ni₃(Al,Ta) by means of residual resistivity measurements. The relaxation in the intermetallics was much slower than in the solid solutions and in both cases the kinetics were strongly affected by a partial substitution of Al by Ti or Ta. The application of power law kinetics led to the determination of relaxation time-constants, and in the solid solutions to the corresponding activation enthalpies for self-diffusion.

I- INTRODUCTION

Nickel-based γ/γ' superalloys are suitable materials for aerospace applications, and it is important to improve further their high-temperature properties. They consist of a short-range ordered matrix i.e. a solid solution of alloying elements in nickel (γ phase), hardened by Ni₃Al-based intermetallic precipitates (γ' phase) with an L1₂ long-range ordered structure. Their properties and their long-time stability are controlled by the atomic mobility in the constituent phases. Most studies of ordering kinetics by means of electrical resistivity measurements have been devoted to SRO in binary solid solutions [1-3] but a few dealt with SRO in ternary alloys [4,5]. In the present work, this method was used for determining the kinetics of the two types of atomic ordering in single phase model alloys. Such information should lead to a better understanding of the technological-superalloy behaviour. The experimental determinations are focussed on the influence of additional elements Ti or Ta, by comparing ternary to binary intermetallics, and the Ni(Al,Ti) solid solution to available data [6,7]

II- EXPERIMENTAL

The investigated alloys (a solid solution: Ni -4at%Al -2at%Ti and three intermetallic compounds: Ni -25at%Al, Ni -21at%Al -4at%Ti and Ni -21at%Al -4at%Ta) were prepared by melting together weighed quantities of high-purity Ni, Al, Ni₃Ti and Ni₃Ta in an inductive plasma furnace. The resulting ingots were homogenized at 1273K for 24h under a vacuum of 10⁻⁶ Pa, then furnace cooled. Two kinds of samples were used: hair-pin shaped specimens, 0.33mm in diameter and 140mm in length, obtained by cold rolling and wire drawing for the ternary solid solution, and rods (1x1x10mm³) cut with a diamond saw for the intermetallic compounds. Samples were finally normalized by annealing at 1273K for 30min under a vacuum of 10⁻⁶ Pa for the solid solution and for 10h at 1173K under a vacuum of 10⁻⁶ Pa for the intermetallics, followed by slow furnace cooling. The method used for investigating self-diffusion consisted in determining the kinetics of ordering. For this

purpose, a deviation from an equilibrium structure state was produced by a small temperature change and the relaxation process was followed by measuring the electrical resistivity at 4.2 K. The experimental apparatus and procedure have been described elsewhere [3,7].

III- RESULTS AND DISCUSSION

Isothermal relaxation curves

Isothermal anneals were performed in the temperature ranges 675-780K for the ternary solid solution and 710-870K for the intermetallic compounds. These ranges were deduced from isochronal experiments [7,8]. The changes of residual resistivity were measured as a function of annealing time at temperatures T_a (annealing temperature) after equilibrating the samples at temperature T_q (quenching temperature).

Resistivity variations (normalized to the total variation amplitude) at different T_a are plotted in figure 1 for the solid solution. The position of the curves on the time scale is generally shifted to longer times with decreasing T_a , as expected for thermally activated processes. However, some exceptions can be seen (e. g. curves (a) and (c)) which show that the relaxation rate does not depend only on the annealing temperature. Similar observations were made in a Ni- 10at% Al solid solution and were attributed to the influence of the magnitude of $\Delta T = T_a - T_q$ [3]. In the present case, since ΔT was the same for curves (a) and (c), the effect is probably related to the sign of ΔT . Similar S-shaped curves were obtained for the intermetallics. The main difference consisted in a much slower relaxation in the intermetallics than in the solid solution.

Ordering kinetics

The kinetic laws used for the quantitative analysis of the experimental results have been previously discussed [1,3]. They are based on a proportionality between the rate of resistivity variation dp/dt and a function of the instantaneous deviation from equilibrium $(\rho - \rho_{eq})$. Figure 2 clearly shows that normalized resistivity changes of the solid solutions do not follow pure exponential kinetics. Furthermore, one can observe in this figure the composition dependence of the relaxation rate: the presence of Ta or Ti results in a shift of the isothermal curves to longer times i.e. in a slower evolution of atomic order. Such a behaviour was also observed in the intermetallics.

Fig.1: Normalized resistivity changes versus logarithm of annealing time for the Ni(Al,Ti) solid solution. Open symbols = down-quenching. Full symbols = up-quenching.

Fig.2: Normalized deviation from equilibrium versus annealing time at a temperature $T_a=705K$ ($\Delta T=\pm 30K$) in solid solutions. Dashed line: single exponential fit of $Ni_{54}Al_4Ta_2$ data (from [7]).

Analysis of the present data was based on a power law relationship deduced by Schulze and Lücke [9] from the theory of chemical reaction rates. It has been previously applied to SRO relaxation [3,5,7]; we show here that it can also be used in the case of LRO. In a normalized form, it can be written as:

$$-(dp/dt) / (\rho_0 - \rho_{eq}) = (\tau^*)^{-1} [(\rho - \rho_{eq}) / (\rho_0 - \rho_{eq})]^\gamma \quad \text{with} \quad (\tau^*)^{-1} = \tau^{-1} [(\rho_0 - \rho_{eq})/B]^\gamma$$

where ρ_0 is the initial resistivity, ρ_{eq} the equilibrium resistivity and B a proportionality factor between a pertinent order parameter and the order-induced resistivity. Such a law corresponds to a kinetic process of order γ represented by a unique time constant τ . Figure 3 illustrates, for the Ti-substituted solid solution and intermetallic, the dependence of the normalized relaxation rate on the normalized deviation from equilibrium. In the solid solutions (fig 3a), the dependence is linear except, in some down-quenching experiments, for a positive initial deviation related to a vacancy excess; this linear relationship with slope γ (table1) represents the whole relaxation phenomenon, and the intercepts with the rate axis give the effective relaxation time constants, τ^* . For the intermetallics (fig 3b), initial deviations are observed in both up- and down-quenching experiments. They cannot be assigned to a vacancy excess but rather to a faster process occurring in the first part of the evolution. The linear parts of the curves then correspond to the slower process with an effective time constant τ^* deduced from the intercepts of the linear parts with the rate axis.

Fig.3: Logarithm of normalized rate of resistivity change versus logarithm of normalized deviation from equilibrium for Ti-substituted (a) solid solution and (b) intermetallic

The temperature dependence of the relaxation rate was analyzed, in the Arrhenius plot of figure 4, in terms of τ^* (the effective time constants of the whole relaxation for the solid solutions [7] and of the slower process for the intermetallics) instead of τ , since no values of the factor B are available for the ternary solid solutions and the intermetallics.

Solid solutions			Intermetallic compounds		
Ni94Al6 [6]	Ni94Al4Ti2	Ni94Al4Ta2 [6]	Ni75Al25	Ni75Al21Ti4	Ni75Al21Ta4
1.3 ± 0.1	1.8 ± 0.2	1.5 ± 0.1	1.0 ± 0.1	1.6 ± 0.2	1.4 ± 0.1

Table 1. Values of the exponent γ deduced from the application of the power law kinetics.

The time-constants data clearly lie on two separated groups of curves: those corresponding to intermetallics are about two order of magnitude larger than those of the solid solutions. The presence of Ti or Ta results in a significant increase of τ^* within each group. It is proposed that such an effect is promoted by a decrease of the vacancy mobility due to the large positive size effect of these elements [10]. The linear relationship between τ^* and reciprocal temperature leads to the determination of activation enthalpies for self-diffusion in the case of the solid solutions (table 2). It is not possible to derive meaningful activation enthalpies from the curved plots of the intermetallics .

Fig.4: Arrhenius graph of the relaxation time constants deduced from the application of the power law kinetics.

Materials	Ni	Ni ₉₄ Al ₆	Ni ₉₄ Al ₄ Ti ₂	Ni ₉₄ Al ₄ Ta ₂
Q(eV)	2.88	2.73 ± 0.20	2.79 ± 0.24	2.96 ± 0.20

Table 2. Self-diffusion enthalpies of nickel [11] and of the solid solutions [7].

IV- CONCLUSION

In Ni-Al based alloys the relaxation of atomic order, as characterized by residual electrical resistivity, was found to be much slower in the intermetallics than in the solid solutions. The presence of Ti or Ta decreases the atomic mobility in both types of alloys. The application of a phenomenological kinetic law led to the determination of effective time-constants. In the solid solution, activation enthalpies could be obtained, whereas the Arrhenius plots were curved for the intermetallics, suggesting the occurrence of a more complex relaxation process.

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