“ORDER-ORDER” KINETICS IN Ni-49.5at.%Al SINGLE CRYSTAL

R.Kozubski, D.Kmieć, E.Partyka, and M.Danielewski

1M.Smoluchowski Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Krakow, Poland

2Department of Solid State Chemistry, Stanislaw Staszic University of Mining and Metallurgy, al. Mickiewicza 30, 30-059 Kraków, Poland

Abstract

“Order-order” kinetics in a single crystal of B2-type ordered β'-Ni-49.5at.%Al was studied by means of resistometry at temperatures between 961 and 1105 K. Reversible isothermal relaxations of the electrical resistivity yielded the activation energy $E_A = 2.3 \pm 0.1$ eV, the same for ordering and disordering processes and markedly lower than the activation energy for Ni diffusion in NiAl. In view of the recently proposed mechanism for Ni-tracer diffusion in NiAl the result is discussed in terms of the formation and elimination of triple defects. The mechanism means a strict correlation between chemical ordering and vacancy formation and provides a possible explanation for the relationship between the activation energies for Ni-diffusion and ordering in β'-NiAl, as well as for the dramatic difference between the rates of ordering/disordering in β-NiAl and the previously investigated γ'-Ni3Al.

Key words: NiAl, long-range order, kinetics, triple defect, resistometry,

*Corresponding author:
fax: +48-12-6337086

e-mail: ufkozubs@cyf-kr.edu.pl
1. Introduction

The B2-ordered intermetallic compound NiAl has for a long time been of technological interest as a potential high-temperature material and a successor of the “classical” L12 superalloys based on Ni$_3$Al. Similarly as Ni$_3$Al, the NiAl shows almost perfect long-range order (LRO) up to its melting point T$_m$ of 1911 K [1], which is substantially higher than that of Ni$_3$Al (T$_m$ = 1660 K). This indicates higher stability of superstructure. Besides, the compositional range of the homogeneous B2 ordered β’-phase of Ni-Al is much wider than that for the L12-ordered γ’-Ni$_3$Al [2]. The corresponding phase diagram is shown in Fig.1.

It has been often remarked, that the design of most of technological processes, e.g. specific thermal treatments, requires that the character of atomic migration in the produced materials is recognised. This means the necessity for carrying out detailed studies of diffusion and structural relaxation (ordering/disordering), which, in turn, involve the consideration of the features of structural defects in the material.

As has been previously mentioned, elementary atomic jumps to vacancies occurring in a superlattice of an intermetallic phase and being the elementary mechanism of any processes involving atomic migration are specifically correlated [3]. In the case of a steady-state diffusion (operating after long time at fixed temperature) this correlation aims at a minimisation of the energetic cost connected with local perturbation of chemical long-range order, whose average degree is constant. The effect gives rise to the well-known mechanisms of diffusion in superlattices as e.g. the “six-jump” mechanism, antistructure-bridge mechanism, triple-defect mechanism etc. (see e.g. [4, 5]). It is clear, that ordering / disordering relaxations need different atomic jump correlation, which should now lead to a change of the degree of atomic long-range order.
After an almost three-decade gap, systematic investigation of diffusion in binary $\beta'$-NiAl has been recently taken up by Frank et al. (Ni tracer diffusion) [6] and by Nakamura et al. [7] (interdiffusion). Frank et al. [6] studied $^{64}$Ni tracer diffusion in single crystals of NiAl with hypo- and hyperstoichiometric compositions and found out that while the activation enthalpy $Q_A = 3$ eV measured for Ni-50at.%Al gradually decreased when increasing Ni concentration $c_{\text{Ni}}$, it practically did not change when increasing Al concentration $c_{\text{Al}}$. In view of the NiAl being a standard triple-defect system, where Ni-vacancy concentration increases with an increase of $c_{\text{Al}}$ [8], the result excluded the concept of nnn Ni-atom jumps as the mechanism of Ni diffusion in NiAl, proposed by Mishin and Farkas [9]. In conclusion, Frank et al. [6] proposed the “triple-defect” mechanism [10] for Ni self-diffusion in Al-rich and stoichiometric NiAl.

Also other recently performed experiments on ternary admixture diffusion in NiAl confirm the domination of nn atomic jumps in the process and exclude the contribution of the nnn ones [11].

The idea of the present study stemmed from the “order-order” relaxation investigations having for a long time been carried out by one of the authors (R.K.). After a pioneering direct observation of the relaxation in an L1$_2$-ordered superalloy Ni$_3$Al [12], its mechanism has been elucidated by detailed experimental [3] and computer simulation [13] studies. It was revealed that the kinetics of chemical ordering shows specific features closely attributed to the geometry of L1$_2$-type superstructure (e.g. the two different time scales) and yielding a specific insight into the dynamics of atomic migration in non-steady-state conditions.

It was, therefore, naturally intended to continue a comparative research of this kind by examining other types of superstructures. The authors were, however, aware of a number of additional problems and difficulties brought about by other superlattice geometries (different
than the L1₂ one) e.g. tetragonal distortion in L₁₀ and the complex vacancy thermodynamics in B₂ [14].

The first attempt concerned B₂-ordered Fe-44.8 at.% Al, where on the basis of an extensive resistometric investigation, an interpretation of several different mechanisms controlling the process of chemical ordering and operating in specific temperature domains was proposed [15]. The complexity of the observed phenomena was partially due to the non-stoichiometry of the stable FeAl sample.

The β’-NiAl, another B₂-ordered intermetallic, seemed to be especially interesting candidate for a study offering a stable B₂-ordered β’-phase at stoichiometric composition. Due to its being a standard triple-defect system showing a very high vacancy concentration correlated (via triple defects) with the concentration of antisite defects specific features of ordering kinetics might be expected.

2. Samples and Experimental methods

2.1. Samples

A single crystal of NiAl was prepared by means of Bridgeman technique using 4N Ni and 5N Al. Chemical analysis of the final product performed by Bureau des Analyses, CNRS, Vernaison, France indicated the content of 66,9 wt.% of Ni and 31,1 wt.% of Al, which corresponds to 50,5 at. % of Ni.

[100] – oriented slices 10 mm × 10 mm × 1 mm were spark-eroded from the available parallelepiped crystal and tested for homogeneity and superstructure by means of scanning electron microscopy (SEM), X-ray microprobe analysis and X-ray diffraction. The SEM tests
revealed a high homogeneity of the crystal composition; no microstructural defects (grains, twinnings etc.) were detected within the viewing area. Superlattice reflections present on the X-ray diffraction pattern indicated B2-type chemical long-range order. Rough estimation of the lattice parameter (no powdered specimen was available) yielded the value of $a = 0.288$ nm.

Needles of $1 \text{ mm} \times 1 \text{ mm} \times 10 \text{ mm}$ size used in the main resistometric experiments were obtained by means of further spark-erosion from the plates along [100] direction.

2.2. Experimental

The experiments consisted principally of the observation of the variation of the degree of LRO in the specimen after an abrupt change of its temperature – the so-called “order-order” relaxation. Similarly as in the previous study of Ni$_3$Al [3,12], high superstructure stability in NiAl caused that the degree of LRO showed an extremely fine temperature dependence in the range of measurable “order-order” relaxations. As a result, the relaxation amplitudes corresponding to the temperature increments/decrements of 50 K were of the range of 0.1 %, therefore, not detectable by diffraction techniques and the authors resorted to resistometry as a principle experimental method. From the point of view of this method, the fine amplitudes of “order-order” relaxations were advantageous justifying an approximation of a proportionality between the observed changes of electrical resistivity and the corresponding changes of the degree of LRO. Both “in situ” and “residual resistometry (REST)” techniques were used; in each case the electrical resistivity was measured by means of the classical 4-point method with platinum electrodes point-welded to the sample positioned in a quartz tube filled with 5N Ar under slight overpressure. “In situ” measurements were carried out using a fully automated set-up with a mobile resistance furnace whose temperature was stabilised better than 1 K.
The necessity of the application of high annealing temperatures was the reason that REST measurements could not be carried out by means of the usually applied compact annealing-quenching vertical line and also in this case the set-up for “in situ” measurements was used. Because of a low rate of the observed processes (see the next section) and, hence, fast quenches being not indispensable, after each isochronal (22 h) annealing the furnace was removed and the quartz tube containing the sample was fast cooled to RT in a high-pressure stream of cool air. Subsequently, without re-installing the sample, the head of the “in situ” holder was immersed in liquid nitrogen and electrical resistivity of the specimen was measured.

3. Results

First “in situ” resistometric tests showed purely linear temperature dependence of the sample resistivity between room temperature (RT) and 1223 K (the highest temperature attainable by means of the equipment). The sample was then annealed for 24 h at that temperature. No detectable variation of its electrical resistivity indicated structural stability and lack of any running processes. After abruptly decreasing sample temperature to 1073 K a slow relaxation of its resistivity was observed. The curve saturated after about 10000 s (the relaxation time was ranging up to 5000 s), which means that a possible increase of the degree of LRO proceeded very slowly: in the case of e.g. Ni$_3$Al this range of ordering rate was observed at about 800 K [3]. The final preparation of the sample (before a systematic examination for “order-order” relaxations was started) consisted of a 1 week annealing at 956 K. At the end of the annealing the electrical resistivity of the sample showed a perfectly constant level.
The main cycle of the “in situ” experiments consisted of a measurement of the electrical resistivity of the sample during the following sequence of isothermal annealings starting after the sample was stabilised at 956 K (see above):

\[ T^{(1)} = 1011 \text{ K} \rightarrow T^{(2)} = 1060 \text{ K} \rightarrow T^{(3)} = 1105 \text{ K} \rightarrow T^{(6)} = 961 \text{ K} \leftarrow T^{(5)} = 1012 \text{ K} \leftarrow T^{(4)} = 1061 \text{ K} \]

Each annealing was initiated by an abrupt change of temperature executed at the end of the preceding relaxation period. The coincidence of the annealing temperatures \( T^{(1)}, T^{(5)}, \) and \( T^{(2)}, T^{(4)} \) made it possible to verify possible reversibility of the relaxations. The raw experimental data were subject to a correction for possible temperature fluctuations. Fig.2 shows the normalised isotherms \( R_{\text{nor}}(t) \) of the corrected electrical resistivity of NiAl registered after both abruptly heating and cooling the sample to the annealing temperatures \( T=1011 \text{ K} \) (Fig.2a) and 1060 K (Fig.2b). The curves yielded rather poor fits to single exponentials, however, no evident manifestation of two (or more) times scales was found. The analysis was, therefore, made by fitting \( R_{\text{nor}}(t) \) with classical superpositions of exponentials with a log-normal distribution of relaxation times (accounting for a normal distribution of activation energies, see e.g. [3b]):

\[
\frac{R_{\text{nor}}(t)}{R_{\text{nor}}(t = 0)} = \int_0^\infty d\tau P(\tau) \exp\left(-\frac{t}{\tau}\right),
\]

where

\[ (1) \]
\[ P(\tau) = \text{const.} \times \exp\left\{ -\frac{[\ln(\tau) - \ln(\tau_{av}(T))]^2}{\beta^2} \right\} \]

In all cases the fits yielded \( \beta \approx 1 \) indicating that the applied procedure was reasonable (standard deviation of the activation energy from its average value was small). The average relaxation times \( \tau_{av} \) resulting from the fits are displayed in Table 1.

The values of \( \tau_{av} \) fitted a common Arrhenius plot (Fig.3), which resulted in the activation energy for “order-order” kinetics \( E_A = 2.3 \pm 0.1 \text{ eV} \) and the pre-exponential factor \( \tau_0 = (2 \pm 2) \times 10^{-7} \text{ s} \). It is essential that the activation energy appeared lower than the one measured by Frank et al. for Ni-tracer diffusion in NiAl. The result is crucial from the point of view of the discussion presented in the next paragraph and, therefore, its reliability has been additionally stressed in Fig.3 by tracing lines representing Arrhenius plots with the activation energy of 3 eV.

Fig.4 shows the Arrhenius plot of Fig.3 together with the previously obtained one corresponding to the relaxation times of “order-order” kinetics in \( \gamma' \)-Ni\(_3\)Al-B [3]. The graphs are accompanied by the Arrhenius plots of Ni-tracer diffusion coefficients \( D \) in NiAl and Ni\(_3\)Al [6,22] re-scaled to the temperature range of the measured “order-order” relaxations. It is remarkable that while the disproportion between “order-order” relaxation rates in NiAl and Ni\(_3\)Al-B is very large, the corresponding effect on Ni-tracer diffusivities in this two compounds is much weaker. It should be stressed that both cited values of \( D \) [6,22] were measured by the same group and, in the case of Ni\(_3\)Al, similar results were obtained for polycrystalline and single crystals. The latter fact justifies the comparison of \( \tau \) measured for polycrystalline Ni\(_3\)Al-B [3] and a single crystal of NiAl.
Because of the extremely low rate of the “order-order” relaxations in NiAl and, hence, the necessity for high annealing temperatures and very long annealing times to be applied, it was impossible to continue the study by measuring the isotherms of 77 K – resistivity. The only available variant of REST was a registration of a “recovery” isochrone, which might confirm and support the results obtained “in situ”.

The low rate of “order-order” relaxations forced, however, a dramatic increase of the annealing time (with respect to the usual conditions): the initial annealing at $T_{in} = 1173$ K was followed by a sequence of 22 h annealings at temperatures $T_{a}^{(n)}$ increased by steps of 30 K from 680 K up to $T_{in}$ and then decreased back with the same steps. The resulting isochrone measured in the way described in section 2.2. and shown in Fig.5 indicates that the observed process was reversible.

4. Discussion

4.1. Origin of the observed variation of electrical resistivity

Perfect reversibility of the observed variation of the electrical resistivity of NiAl indicates that no parasitic effect as oxidation, crack propagation, precipitation etc. influenced the results. However, it has to be kept in mind that the system response to temperature changes applied in the experiments consists of the equilibration of both vacancy and antisite concentration, both processes affecting the electrical resistivity qualitatively in the same way. While extremely
low vacancy concentration in $\gamma'$-Ni$_3$Al justified the negligence of the vacancy equilibration effect on the measured resistivity relaxations, which might thus be related to chemical ordering, this might not be the case of $\beta'$-NiAl, where vacancy concentration is by almost 6 orders of magnitude higher than in $\gamma'$-Ni$_3$Al [16].

Direct experimental evidence of the dynamics of the pure vacancy equilibration in Ni$_{47}$Al$_{53}$ by means of an accurate dilatometric measurement has recently been reported by Schaefer et al. [17]. The observed rate of the length relaxation in the sample is compared in Fig.6 with the rate of the resistivity relaxations in Ni$_{50.5}$Al$_{49.5}$ reported in this paper. A difference by about two orders of magnitude is visible. Although the compositions of the samples investigated in both experiments considerably differed, the excess of Al in the Schaefer’s specimen generated structural vacancies rather than antisite defects and, therefore, local atomic configurations, in which thermal vacancies migrated from their sources showed in both cases very high degree of LRO. Consequently, it is justified to claim that the resistivity relaxations in NiAl observed in the present paper might hardly be attributed to pure vacancy equilibration and hence, must have reflected chemical ordering.

4.2. Dynamics of point defects in a triple defect $\beta$-NiAl.

As will be shown below, it is the triple-defect character of $\beta$-NiAl, which determines the detailed interpretation of the results.

The idea of a triple defect has been proposed by Wasilewski [18] as one of possible ways for chemically disordering a system (creating antisite defects) without disturbing the proportions between the numbers of sublattice sites. The thermodynamics of a triple defect has been extensively studied for many years both in general and in application to NiAl (see e.g. [19-21] and references therein); the main interest being, however, focused on the effects brought about by non-stoichiometry (formation of structural vacancies).
The elementary atomistic events connected with a thermally activated ordering/disordering in an A-B binary with a superstructure consisting of two sublattices (α and β) have recently been clearly listed and analysed by Kogachi et al. [14]:

In order to enable atomic migration, as well as to maintain the proportions between the numbers of sublattice sites a pair of $V_\alpha$ and $V_\beta$ thermal vacancies has to be generated first. Further evolution of the system depends on the relationships between the formation energies of vacancies and antisites. In the case of vacancy formation requiring much more energy than antisite formation (the common case of L1$_2$-ordered systems) the migrating pair of vacancies may continuously generate/eliminate $A_\beta$ and $B_\alpha$ antisite defects, whose average numbers are equal. Such a process has been recently simulated for Ni$_3$Al [13]. In the opposite case, much more probable in B2- than in L1$_2$- or L1$_0$-type superstructures, a formation of a particular antisite defect (e.g. $B_\alpha$) requires much more energy than does the formation of an $\alpha$-vacancy ($V_\alpha$). In such a case, the system disorders by preferentially creating $A_\beta$ antisites; each act resulting in a triple defect: one $A_\beta$ antisite and two $V_\alpha$ vacancies. As the $V_\alpha$ vacancies can no longer be active in producing new $A_\beta$ antisites a progress of thermally activated disordering requires a formation of new pairs of $V_\alpha$ and $V_\beta$ thermal vacancies. As a result, the concentrations of thermal vacancies and antisites are of the same order of magnitude, as results also from theoretical calculations (see e.g. [21]).

The energetics, which favours triple-defects in a A-B binary causes well-known phenomena in non-stoichiometric systems: formation of structural $V_\alpha$ vacancies in B-rich and formation $A_\beta$ antisites in A-rich compositions. It should, however, be stressed that the departure from stoichiometry has no direct effect on the thermodynamics of thermally activated ordering/disordering: thermal activation (generation/elimination) of antisite defects means predominant creation/elimination of triple defects. Therefore, the activation energy for “order-
order” kinetics should be understood as the activation energy for the generation (disordering) and annihilation (ordering) of triple defects. Both cases will be discussed separately.

4.3. Model of an atomistic mechanism for “order-order” relaxations in stoichiometric NiAl

The following model refers to the $\beta$-NiAl considered as an ideal “pure” triple defect system. In this sense, the model should be treated as an approximate description of a real process occurring in NiAl, where the proposed ordering/disordering mechanism dominates among other less active ones.

4.3.1. Disordering

Frank et al. [6] carefully analysed the energetics of triple-defect-mediated Ni-diffusion in NiAl and deduced that the measured value of the activation energy $E_A = 3 \text{ eV}$ may be understood as a sum of the formation energy for a triple defect $E_F^{(TD)}$ and the effective migration energy $E_M$ assigned to a displacement of a Ni-antisite (actually, a displacement of the entire triple defect). It becomes quite clear that “order-order” kinetics, as consisting of the creation of triple defects only (without the Ni-antisite displacement) should show lower activation energy.

However, the activation energy resulting from the Arrhenius plot of the disordering “order-order” relaxation times should not be related directly to $E_F^{(TD)}$, but rather to an energy yielded by a dynamic scheme for a triple defect formation. The scheme (Fig.7a) might be imagined as a sequence of (i) a generation of a virtual pair of Ni- and Al-vacancies associated with a formation energy $E_F^{(\text{VNi-VAI})} \approx 2.4 \text{ eV}$, as estimated in [6] and recently in [21], and (ii) an immediate jump of a nn Ni-atom to the Al-vacancy associated with a migration energy
\( E_M^{(Ni-TD)} \approx 0.2 \text{ eV} \) [6] constituting only about 20% of the effective migration energy \( E_M \) of Ni diffusion in NiAl. The resulting dynamic activation energy \( E_A^{(TD)} \) for triple effect formation results equal to about 2.6 eV, therefore, lower than the activation energy for Ni diffusion in NiAl. As shown in section 4.3.3., the effective value of \( E_A^{(TD)} \) is still a bit lower.

### 4.3.2. Ordering

The mechanism for ordering i.e. the annihilation of triple defects (Fig.7b) must definitely consist of a jump of the Ni antisite back to its own sublattice, which, however, means a generation of a high-energy Al vacancy. As a final decrease of the system energy takes place only after the elimination of the pair Ni- and Al-vacancies, continuation of ordering is controlled by the kinetics of the vacancy elimination process. This, however, is possible exclusively via diffusion to possible sinks. It is remarkable, that, in view of the model, the escaping vacancies cannot generate any further stable ordering on their way. As a consequence, the effective activation energy of the process is dominated by a sum of two migration energies: \( E_M^{(1)} \) related to the initial Ni-atom jump to Ni-sublattice and \( E_M^{(2)} \) related to the escape of the redundant vacancy pair. As the pair cannot escape by means of the triple defect mechanism (being actually a mechanism for triple-defect migration), some other mechanism must be involved. This, however, means that the value of \( E_M^{(2)} \) is likely to be higher than the migration energy for the triple-defect diffusion [5]. Therefore, after the diagram of Frank et al. (Fig.11 in ref. [6]), a sum of \( E_M^{(1)} \) and \( E_M^{(2)} \) should be higher than 2 eV.

Altogether, the ordering and disordering “order-order” relaxations in a triple defect system seem to have different mechanisms: the activation energy for ordering is predominantly contributed by migration energy for diffusion, while the activation energy for disordering
follows mainly from the formation energy for pairs of vacancies. It is clear, however, that according to the presented model, both activation energies may result equal in the case of NiAl - which would explain the result of the present study.

4.3.3. Overall rate of “order-order” kinetics

The above model also explains the relationship between the rates of “order-order” kinetics in \( \beta' \)-NiAl and in \( \gamma' \)-Ni\(_3\)Al [3]. This is just the strict correlation between ordering/disordering and vacancy elimination/formation in NiAl which makes that, despite the enormous difference between vacancy concentrations (\( c_v(\text{NiAl})/c_v(\text{Ni}_3\text{Al}) \approx 10^6 \) [16]) and a substantial opposite difference between the activation energies [3], the ordering kinetics is much slower in NiAl than in Ni\(_3\)Al. Although the vacancy concentration changes after each temperature change, only those vacancies, which are currently created or eliminated are active in disordering or ordering in \( \beta' \)-NiAl.

If the equilibrium concentration of of the pairs \( V_{\text{Ni}}-V_{\text{Al}} \) is given by:

\[
c_{2v}(T) = c_0 \times \exp\left[-\frac{E_F}{kT}\right]
\]

then the temperature dependence of \( \Delta c_{2v} \), the increment/decrement of \( c_{2v} \) after changing the temperature by \( \Delta T \) is given by:

\[
\Delta c_{2v}(T) = \frac{dc_{2v}}{dT} \Delta T = c_0 \times \frac{E_F}{kT^2} \times \exp\left[-\frac{E_F}{kT}\right] \times \Delta T
\]
The Arrhenius plots of both $c_{2v}$ and $\Delta c_{2v}$ calculated for $E_F = 2.4$ eV (in agreement with [5]) are shown in Fig.8. Within the temperature range of the presented measurements both plots are linear and thus, the temperature dependence of $\Delta c_{2v}$ yields an effective activation energy, which results a little lower than the formation energy $E_F$ corresponding to $c_{2v}$. The latter result, as well as the fact that only ONE antisite may be created or eliminated by a single $V_{\text{Ni}}$-$V_{\text{Al}}$ pair explains the observed low rate of the “order-order” relaxations occurring at relatively low value of the activation energy – i.e. the resulting abnormally high value of the pre-exponential factor $\tau_0$ of the relaxation times.

The substantially weaker slowing-down of Ni diffusion in NiAl with respect to Ni$_3$Al, following from the fact that its mechanism in NiAl is evidently different than that of ordering, indicates once again that the practice for drawing conclusions on ordering kinetics on the basis of diffusion characteristics is highly questionable.

4.4. Interpretation of the results of the analysis of REST isochrone

In view of the above model for disordering and ordering process in NiAl as a triple-defect system, the usually applied Schulze-Lücke-type analysis of a REST isochrone [23] is invalid as it neglects the strict correlation between vancancy and antisite concentrations in the material. There is just a definite need for a new fitting scheme to be elaborated. For the time being, the measured isochrone (Fig.5) is presented only as an additional proof for the reversibility of the investigated phenomenon.
4.5. Reference to other experimental results

Most of the relevant literature data on NiAl concern either diffusion (see e.g. [6,7]), or point-defect thermodynamics (see e.g. [16] and references there in). To the authors’ knowledge, the only study on ordering kinetics in NiAl has been due to H. Ko et al. [24], who investigated ordering kinetics in a single crystal of stoichiometric composition by means of “in situ” resistometry. The experiments consisted of high-temperature annealing at temperatures $T_q$ between 1273 and 1673 K, water quench and a measurement of isotherms of the electrical resistivity at temperatures $T_a$ lower than $T_q$ by $\Delta T$ between 450 and 800 K. The isotherms were fitted by weighted sums of two exponentials. The activation energy of about 1.5 eV shown by the faster process was interpreted as the activation energy for vacancy migration. Although the analysis of the isotherms done in terms of linear kinetics might be questioned because of very big temperature decrements applied (some curves seem to fit rather Johnson-Mehl-Avrami-type functions), the result might be complementary to the one obtained in the present paper. It is reasonable to expect that the annealing temperatures $T_q$ were high enough to activate the formation of pairs of Ni- and Al-vacancies without the subsequent generation of Ni-antisites. Such vacancy pairs might be then eliminated at $T_a$ in a fast process accompanied by a slower ordering kinetics.

4.6. Reference to theoretical considerations

Although the concept of a triple defect is quite old [18] its implementation with atomic dynamics concerned only steady-state diffusion [6,10]. It is remarkable that although
correlation between the formation of thermal vacancies and antisites follows directly from equilibrium thermodynamics, the effect was just lost in most of theories of vacancy formation and ordering kinetics because of imposing artificial limitations upon vacancy concentration (see e.g. [19,25]). On the other hand, most of the computer simulation methods, both Monte Carlo and molecular dynamics, as recently applied [13,26] provided no access to vacancy formation. Verification of the proposed model of “order-order” kinetics in a triple-defect system requires, therefore, that the existing theories and simulation algorithms for ordering kinetics are extended upon complete thermodynamics including vacancy formation.

5. Conclusions

1. Reversible “order-order” relaxations in a single crystal of B2-type long-range ordered Ni-49.5at.%Al measured at temperatures between 961 and 1105 K yielded an activation energy equal to 2.3 ± 0.1 eV, which is lower than the value obtained for Ni-tracer diffusion in NiAl. In general, the relaxations were much slower than the ones observed in L12-type long-range ordered Ni3Al.

2. The proposed model explaining the results is based on the triple-defect character of the β’-NiAl compound: thermally activated creation/elimination of antisite defects is understood as the creation/elimination of triple defects. This assumption implies a strict correlation between ordering/disordering and the elimination/formation of thermal vacancies. The model explains both the relationship between the activation energies for ordering and Ni-tracer diffusion in β’-NiAl and the extremely low rate of “order-order” relaxations in this compound.

3. It is remarked that possible simulation studies of the process definitely require that the simulation algorithms account for a complete thermodynamics of thermal vacancies.
Acknowledgements

The authors are grateful to Professor Alan J. Ardell, University of California, Los Angeles for kindly providing them with a NiAl single crystal.

Thanks are due to Professor Wolfgang Pfeiler and Professor Bogdan Sepiol, Institut fuer Materialphysik, Vienna University for carefully reading the manuscript and stimulating discussions.
References


Figure captions

Fig.1. Phase diagram of Ni-Al binary system [27]. A scheme of the B2-type superstructure is inserted in the $\beta'$-NiAl phase domain.

Fig.2. Reversible relaxations of the electrical resistivity of Ni-49.5at.%Al:

(a) $T_a = 1060$ K; $T_i = 1011$ K (○), $T_i = 1105$ K (●);

(b) $T_a = 1011$ K; $T_i = 956$ K (○), $T_i = 1061$ K (●).

Fig.3. Arrhenius plot of the relaxation times for ordering (▲) and disordering (□) in Ni-49.5at.%Al. Dashed lines mark plots corresponding to the activation energy of 3 eV.

Fig.4. Arrhenius plots of the relaxation times $\tau$ for “order-order” kinetics and of the Ni-tracer diffusion coefficients D in NiAl [6] and Ni$_3$Al [22]:

NiAl: $\tau$-ordering (□), $\tau$-disordering (Δ), D (+);

Ni$_3$Al: $\tau$-ordering (■), $\tau$-disordering (▲), D (×);

Fig.5. REST isochrone of Ni-49.5at.%Al: up-step annealing (●), down-step annealing (□).

Fig.6. Arrhenius plot of the length-relaxation times measured in Ni-53at.%Al after step-heating (Δ) and step-cooling (●) [17] and of the relaxation times for ordering (■) and disordering (□) in Ni-49.5at.%Al measured in the present work.

Fig.7. Proposed schemes of the triple-defect mediated disordering (a) and ordering (b)

in $\beta$-NiAl: ○ – Ni atoms , ● – Al-atoms, □ – vacancies.

Fig.8. Arrhenius plots of V$_{Ni}$-V$_{Al}$ concentration $c_v$ (□) and its increment $\Delta c_v$ (Δ) as defined by Eqs. 2 and 3.
Table 1

Average relaxation times $\tau_{av}$ of “order-order” relaxations in NiAl proceeding at temperatures $T_a$.

<table>
<thead>
<tr>
<th>Sequential number</th>
<th>$T_a$ [K]</th>
<th>Relaxation type</th>
<th>$\tau_{av}$ [1000×s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1011</td>
<td>disordering</td>
<td>47 ± 5</td>
</tr>
<tr>
<td>2</td>
<td>1060</td>
<td>disordering</td>
<td>14 ± 2</td>
</tr>
<tr>
<td>3</td>
<td>1105</td>
<td>disordering</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>4</td>
<td>1061</td>
<td>ordering</td>
<td>15 ± 2</td>
</tr>
<tr>
<td>5</td>
<td>1012</td>
<td>ordering</td>
<td>53 ± 6</td>
</tr>
<tr>
<td>6</td>
<td>961</td>
<td>ordering</td>
<td>210 ± 20</td>
</tr>
</tbody>
</table>
\[
\ln(\tau) = -\ln(D) - \frac{1}{kT}
\]
Fig. 5.
Fig. 7a

(a)

$V_{\text{Ni}} - V_{\text{Al}}$ pair formation

Ni-atom jump to antisite position
Fig. 7b

(b)

Ni-atom jump to regular position

$V_{Ni} - V_{Al}$ pair elimination (escape)
Fig. 8.

$E_A = 2.24 \text{ eV}$

$E_A = 2.4 \text{ eV}$