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Increasing the achievable state of order in Ni-based Heusler alloys via quenched-in vacancies

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The ability to tune the degree of $L2_1$ order is of utmost importance for the magneto-mechanical properties of Ni-Mn-based Heusler alloys, e.g., the appearance of a martensitic phase in the Ni_2MnAl system. Here, differential scanning calorimetry is established as a convenient tool for determining the state of order by way of its effect on the magnetic transition temperature, and it is used for studying the low-temperature ordering kinetics in Ni_2MnAl. A significant acceleration of ordering kinetics due to excess vacancies retained after high-temperature quenching is demonstrated. Using this effect, equilibrium of order could be attained at temperatures as low as 623 K, where ordering under equilibrium vacancy concentration would take unpractically long. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4905223]

Ni-Mn-based Heusler alloys are a prominent class of functional materials with wide applications both as ferromagnetic shape memory alloys[1,2] and as magnetocaloric materials.[3,4] As full Heusler alloys, these materials are intermetallic compounds of the stoichiometric composition Ni_2MnX, with X chosen from a number of main group elements, where the most prominent representatives are Ga, Al, Sn, Sb, and In.[5] While Ni_2MnGa is the most commonly used ferromagnetic shape memory alloy system, recently also Ni_2MnAl has drawn increased attention, mainly because of its superior mechanical properties.[6] Structurally, the Ni_2MnX alloys crystallize in the high temperature B2 phase and transform at lower temperatures into the higher-ordered $L2_1$ phase.[7] The actual transition temperature thereby varies over a broad temperature range and depends on the X component and the specific alloy composition.[8–11] At still lower temperatures, some of the alloys additionally undergo a transition to a variety of different martensite structures.[10]

The magneto-mechanical properties as well as the functional performance of the Ni-Mn based Heusler alloys are intimately coupled to structural aspects, i.e., to their local atomic order,[12] specifically, the stability of the mentioned martensite phase is favored by a strong $L2_1$ order.[13–16] While the degree of $L2_1$ order is high in the Ni_2MnGa system, it is usually absent in the Ni_2MnAl system.[12,13] As a consequence, the appearance of a martensitic transition in the Ni_2MnAl system is not only limited by the inherent stability of the martensite, but also by the possibility to adjust large degrees of $L2_1$ order. This so far impedes their wider adoption, even though their excellent processability would make them an attractive replacement for the inherently brittle Ni_2MnGa alloys.

Canonically, the degree of $L2_1$ order is accessible directly by structural characterization methods such as x-ray or neutron powder diffraction.[17] However, order adjustments can also be observed indirectly by way of their effect on the magnetic transition temperature,[12] which is conveniently accessible by calorimetry. Such an approach not only decreases the complications in data acquisition but at the same time increases the measurement sensitivity. The coupling between the structural and magnetic properties follows from the distance-dependent interactions of the Mn atoms, which are mainly responsible for the magnetism in these materials, where antisite Mn atoms disturb the ferromagnetic ground-state of the ideal $L2_1$ phase.[18]

Recently, Merida *et al*.[19] demonstrated via positron annihilation lifetime spectroscopy the presence of quenched-in excess vacancies in the ferromagnetic shape memory alloy $Ni_{53}Mn_{26}Ga_{21}$. Yet, a vacancy super-saturation alone does not influence the materials properties. However, the potential of an ensuing acceleration of kinetics during a post-quench annealing has been recognized for a long time,[20] and its importance for adjusting desired properties in specific classes of materials, such as in Aluminum alloys, is accepted.[21] Here, we investigate this question and demonstrate the effect of excess vacancies on the ordering kinetics in the Ni_2MnAl system, yielding a large increase in the magnetic transition temperature and in turn $L2_1$-type order. This suggests also the relevance of excess vacancy mediated order adjustment in other Heusler systems, where achievable order is often the limiting factor in achieving functionality,[22] but where these issues have apparently never been explored.

A polycrystalline ingot with nominal composition $Ni_{50}Mn_{28}Al_{22}$ was prepared from high purity elements ($\geq$99.99%) by induction melting with subsequent suction casting into a rod shape under a high purity Argon atmosphere. The samples were solution annealed for 48 h at 1273 K followed by rapid quenching into ice brine, which we estimate to correspond to cooling rates on the order of several hundred K/s at the $B2$-$L2_1$ transition temperature. Subsequently, isothermal heat treatments at various temperatures were performed, first on samples directly after quenching, and second on samples equilibrium annealed at 853 K for one hour, a temperature well in the B2 regime.[23]

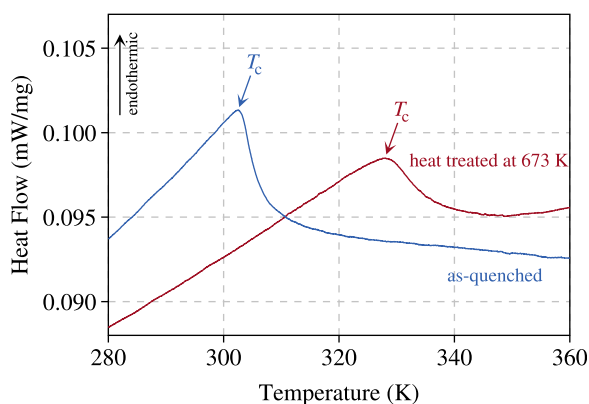a)Electronic mail: pascal.neibecker@frm2.tum.de

FIG. 1. DSC curve of the *as-quenched* (blue) and 48 h at 673 K heat-treated (red) sample measured upon heating with 10 K/min illustrating the shift in the magnetic transition temperature T_c.
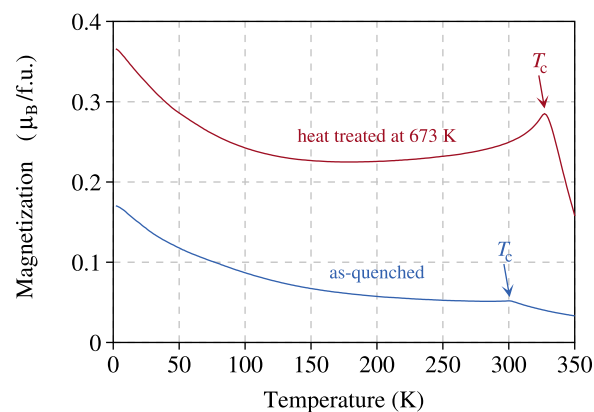

FIG. 2. Magnetic measurements at 1 T of the *as-quenched* (blue) and 48 h at 673 K heat-treated (red) sample showing a shift in the magnetic transition temperature as well as changing magnetic interactions from predominant antiferromagnetic in the *as-quenched* sample to increased ferromagnetic interaction in the heat-treated sample.

Equilibrium annealing at 853 K was performed *in situ* in a Differential Scanning Calorimeter (DSC) followed by rapid cooling to cryogenic temperatures with a cooling rate of 80 K/min. The samples quenched from 1273 K are in the following referred to as *as-quenched* while the samples annealed at 853 K are referred to as *equilibrium annealed*. The magnetic transition temperatures were determined via Differential Scanning Calorimetry on a Perkin Elmer DSC 8500 device. The isothermal heat treatments were performed *in situ* in the DSC. The heating and cooling rates employed in the isothermal heat treatment experiments were 10 K/min. To ensure consistency of data interpretation, the magnetic transition temperatures were cross-checked employing magnetic measurements on a Quantum Design Physical Property Measurement System (PPMS).

Figure 1 shows DSC measurements of the alloy in the *as-quenched* and the 48 h at 673 K heat-treated condition. To describe the magnetic transition, we model the calorimetric signal by two continuously joint second-degree polynomials convolved with a centered Gaussian kernel. In this phenomenological description, we identify the cross-over temperature obtained after fitting with the critical temperature of the magnetic transition T_c. The reproducibility of the results is convincing with independent measurements of the same state of order yielding a deviation of the associated critical temperatures below 0.1 K. Figure 1 displays a shift in the transition temperature from approximately 304.0 K to 327.9 K induced by the heat treatment. A martensitic transition was not observed in the studied composition and temperature range. The corresponding magnetization measurements of the *as-quenched* and the 48 h at 673 K heat-treated sample in Figure 2 confirm the discussed increase in magnetic transition temperature as well as a change from dominant antiferromagnetic order in the *as-quenched* condition to increased ferromagnetic order in the *equilibrium annealed* condition.

The results presented in Figs. 1 and 2 demonstrate that heat treatments at lower temperatures lead to an increase in the critical temperature T_c characteristic for the magnetic transition. This allows us to conclude that the respective heat treatment has an effect on the order of the alloy, obviously increasing the L2$_1$-type order and thus stabilizing the ferromagnetic phase. A similar observation, namely, the evolution

of the martensite start temperature of a Ni$_{53}$Mn$_{25}$Al$_{22}$ sample during heat treatment, has been reported by Kainuma *et al.*[23]

Figure 3 shows the magnetic transition temperature as a function of isothermal heat treatment at 573 K (only *as-quenched*), 623 K and 673 K for *as-quenched* and *equilibrium annealed* samples. Its initial values in both states, namely, *as-quenched* and *equilibrium annealed*, differ only by approximately 2.7 K. As evidenced by detailed pertinent experiments (not shown here), in this temperature region the resulting state of order is not given by the equilibrization temperatures but by the quenching/cooling rates due to the different points of kinetical freezing.

The effect on the critical temperature T_c when heat-treating the *equilibrium annealed* samples is low, amounting to a modest increase in the magnetic transition temperature ΔT_c of 11.8 K for a 28 h heat treatment at 673 K and of 7.8 K for 623 K.

A point worth noting is that the increase in the transition temperature (and equivalently the state of order) is higher for the heat treatment at the higher temperature, although the transition temperature corresponding to the equilibrium state of order should be lower. This demonstrates the impossibility to attain equilibrium of order on practicable timescales even
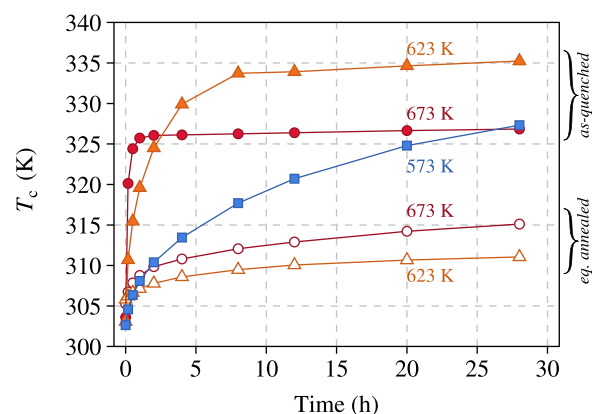

FIG. 3. Magnetic transition temperature T_c as obtained by DSC measurements for consecutive timesteps between 573 K and 673 K for *as-quenched* (solid symbols) and at 853 K *equilibrium annealed* (empty symbols) samples.

better than the small increments in T_c still taking place towards the end of the experiment.

Although the initial state of order in the *equilibrium annealed* and *as-quenched* conditions is essentially similar, the kinetic behavior is strikingly different. Not only is the overall change in magnetic transition temperature significantly larger with a ΔT_c of 22.5 K and 31.3 K for 673 K and 623 K heat treatments when starting from *as-quenched* conditions, but also the kinetics are clearly accelerated with respect to the *equilibrium annealed* samples, corresponding to a factor of more than 100. This acceleration enables the adjustment of order at significantly lower temperatures in the *as-quenched* samples, specifically after 28 h at 673 K a steady state is clearly reached with a T_c of 326.5 K, and for 623 K the resulting value of 334.8 K is even higher, although perhaps still short of its final value.

The only plausible explanation for the observed behaviour, where T_c in the *as-quenched* samples starts out from a lower value than in the *equilibrium annealed* ones but quickly overtakes it during an identical heat treatment protocol, lies in postulating the existence of quenched-in vacancies, which is backed by the recent demonstration of quenched-in vacancies in the related system Ni$_2$MnGa.[19] We can deduce the excess vacancy concentration after quenching from the above-mentioned acceleration of kinetics of more than a factor of 100, implying a corresponding relation between excess and equilibrium vacancy concentration. Control experiments with different cooling rates and/or different equilibrization temperatures (not shown here) prove that the vacancy concentration during heat treatment in what we term the *equilibrium annealed* samples is indeed the equilibrium concentration.

At this point, an important issue is left to resolve, namely, whether the steady state that is reached during heat treatment of the *as-quenched* samples actually corresponds to the equilibrium state, or whether the sample runs out of excess vacancies before it arrives at equilibrium. This question can be settled by continuing the heat treatment at a different temperature after the sample has reached its steady state for the initial treatment temperature. Figure 4 shows the pertinent results: At 673 K, the steady state is reached after one hour. An independent second experiment perfectly reproduces these values during the first hour and has therefore entered the steady state with respect to T_c. When switching to 623 K at this point, T_c experiences a notable additional increase, with a rate that is much larger than in the *equilibrium annealed* samples (Figure 3). Therefore, we can conclude that there is still a vacancy excess after the sample has reached its steady state, although the reduced rate compared to the evolution during heat treatment entirely at 623 K indicates a corresponding reduction in vacancy concentration. Continuing with an alternating sequence of, respectively, 673 K for 30 min and 623 K for 150 min displays a slightly contracting envelope of the measured values of T_c (inset of Figure 4) and therefore a further decreasing vacancy concentration. However, considering the reduced driving force with the initial condition close to the presumed equilibrium order, the difference in kinetics with respect to the *equilibrium annealed* samples is low and already in the same order of magnitude.

In the direct measurements of Merida *et al.*[19] on the annihilation of excess vacancies in the related system Ni$_2$MnGa, the vacancy concentration drops by an order of magnitude during 30 min of annealing at 623 K. This close agreement with our results further corroborates our interpretation and lends some justification to assuming that diffusive dynamics in Ni$_2$MnAl, where no direct diffusion measurements have been reported, are qualitatively similar, but somewhat faster than the values identified for Ni$_2$MnGa by tracer diffusion measurements,[24] presumably because of the lower degree of order here. Indeed, comparing the time evolutions of T_c in the *as-quenched* samples gives an activation energy of $E_A = 1.83(5)$ eV for the ordering process. This L2$_1$-ordering involves the swapping of Mn and Al, so its activation energy has to be the migration energy of species that diffuses slower, as the quenched-in vacancy concentration is not thermally activated. In the case of Ni$_2$MnGa, this would be Ga, with a migration energy of 1.89(15) eV as obtained by subtracting the vacancy formation energy[19] from the Ga self diffusion activation energy.[24] Again, the close correspondence between these values is very satisfactory.

In general, it has to be pointed out that while our results leave no doubt that quenched-in vacancy enhanced order adjustment is a relevant process in this system, its quantitative aspects will depend on circumstances beyond easy control by the experimentator. This concerns the achievable quenching rate for retaining vacancies as well as the sample microstructure, where a lower density of vacancy sinks such as grain boundaries and dislocations corresponds to a slower vacancy concentration relaxation rate, which will increase both the quenched-in vacancy concentration and the amount of ordering that can be effected by an excess vacancy before annihilation. Above issues will also inevitably lead to spatial inhomogeneities of resulting states of order: This applies both to the macroscopic scale, as due to heat conduction the achievable quenching rates will be lower inside the sample than on its surface, as well as to the microscopic distribution of vacancy sinks, in whose vicinity vacancy concentration relaxation will happen faster. However, the fitted widths of the magnetic transitions never exceed 3 K, indicating that spatial inhomogeneities of order are not too large.
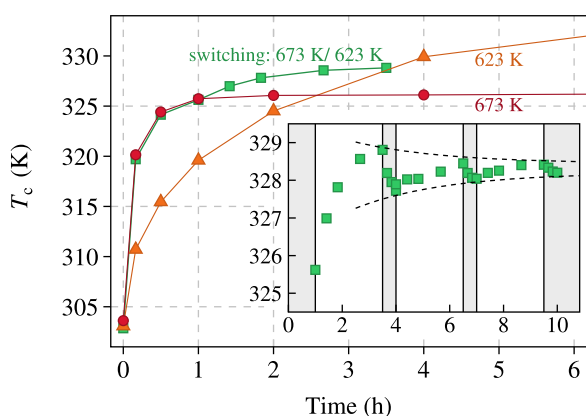

FIG. 4. Isothermal heat treatment curves of *as-quenched* samples at 673 K, 623 K, and at 623 K after one hour at 673 K. Inset: Isothermal treatment sequence alternating between 673 K (gray areas) and 623 K (white areas), corresponding to green squares in main figure.

Finally, our results allow to derive an order-of-magnitude estimate of the spatial processes of vacancy concentration equilibration: In default of diffusion data for Ni_2MnAl, we invoke the similarity to Ni_2MnGa and assume a ratio of Ni and Mn to Al-diffusivities of 5×10^5 at the relevant temperature range,[24] neglecting the effects of a lower degree of $L2_1$-type order compared to Ni_2MnGa. As motivated above, the adjustment of local order takes a few jumps per Al atom, which corresponds to about 10^6 Ni jumps. Using a quenched-in vacancy concentration of 10^{-3} as in Ni_2MnGa,[19] this would correspond to 10^9 vacancy jumps. As the time-scale of order relaxation coincides with the vacancy concentration relaxation as discussed above, we can conclude that a vacancy jumps on the order of 10^9 times before annihilating, or covers a distance of $5\,\mu$m, coinciding with the scale of grain boundaries in our sample.

In summary, DSC measurements revealed the importance of excess vacancies in the process of order adjustment in Ni_2MnAl samples. In this respect, it was shown that a large amount of quenched-in excess vacancies makes it possible to reach equilibrium order at temperatures as low as 623 K. These findings suggest that the order of applied heat treatment steps in combination with the applied solution treatment procedures will eventually play a crucial role in adjusting large degrees of $L2_1$ order and designing materials well suited for shape memory applications. Understanding the dependence of the ordering kinetics from the excess vacancies present in the material could thus pave the way for increased usage of Heusler alloys such as Ni_2MnAl.

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