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Atomic disorder and phase transformation in $L_1_2$-$N_i_3A_l$ by mechanical milling

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Mechanical milling of the ordered $L_1_2$-$N_i_3A_l$ was performed in a high-energy ball mill. The milling process was monitored by x-ray diffraction, high-field magnetization, ac magnetic susceptibility, and differential scanning calorimetry (DSC). It was found that antisite disorder is generated in the early stages of milling and a phase transformation from the disordered $L_1_2$ compound to the disordered fcc solid solution of Al in Ni was observed after milling for long periods. Partial amorphization occurs after prolonged periods of milling. The long-range-order parameter decreases monotonously with time in the early stages of milling and attains a zero value after relatively short periods of milling. The lattice parameter and the relative strain increase with milling time. Magnetic properties of ball-milled $N_i_3A_l$ at 4.2 K differ markedly from those of the ordered state. Based on the magnetic data, it is concluded that short-range disordering could be the third source of energy storage during milling of $N_i_3A_l$. Exothermic heat effects resulting from atomic reordering and phase restoration and/or crystallization are evident in the DSC scans of ball-milled $N_i_3A_l$. © 1995 American Institute of Physics.

I. INTRODUCTION

In a previous investigation it was demonstrated that mechanical milling of ordered $L_1_2$-$N_i_3S_i$ in a high-energy ball mill induces antisite disorder in the early stage of milling and that after prolonged periods of milling a phase transformation from the disordered $L_1_2$ to the disordered fcc solid solution of Si in Ni takes place. This ball-milling-induced phase transformation in $N_i_3S_i$ has the characteristics of a first-order transition. In the present article we deal with the compound $N_i_3A_l$. Ball milling of this compound was extensively studied because of potential high-temperature applications; however, the results obtained so far are still contradictory. The behavior of $N_i_3A_l$ during ball milling is not well understood and even information from different experimental sources does not seem to agree. In those earlier studies, various techniques such as x-ray diffraction and transmission electron microscopy (TEM), and differential scanning calorimetry (DSC) were used. It turned out that a small fraction of amorphous phase was detected well after the disappearance of the long-range-order parameter. Thus, it was argued that the energy stored in the nanograined boundaries is the driving force for amorphization of $N_i_3A_l$; however, it was experimentally observed that the crystallite size decreases mainly in the early stage of milling and that it tends to become constant for longer milling periods. This is in fact a general tendency in various types of compounds during milling as shown, for example, in our preceding studies. When the crystallite size is essentially constant it seems not possible to store further mechanical energy in the form of grain boundaries. Alternatively, short-range disordering could be an additional source of energy storage as proposed in Ref. 1. This is not easy to measure by conventional techniques such as x-ray diffraction and TEM, because ball-milled materials are composed of fine powder particles containing many defects, which make the sample preparation for TEM difficult and x-ray-diffraction intensity too low. However, it was proved in previous investigations that the measurement of magnetic properties can be a very sensitive structural probe. This method does not offer difficulties for sample preparation and can give detailed and precise information on structural changes, in particular in the intermediate stage of milling. Therefore, the milling behavior of $N_i_3A_l$ was restudied using magnetic measurements as a structural probe.

II. EXPERIMENTAL PROCEDURES

The starting compound $N_i_3A_l$ was obtained by arc melting of weighed amounts of pure nickel and aluminum in a purified argon atmosphere. Arc melting was repeated several times in order to obtain a homogeneous sample. The arc-melted button was crushed to powder and annealed at 1323 K for 35 days and at 1073 K for 15 h. The x-ray-diffraction pattern of the annealed sample shows single-phase material. Ball milling was carried out in vacuum in a hardened steel vial (inner diameter 6.5 cm) with a tungsten carbide bottom. Inside the vial, a hardened steel ball with a diameter of 6 cm was kept in motion by a vibrating frame (Fritsch: Pulverisette 0), upon which the vial was mounted. In order to prevent reactions with oxygen or nitrogen, the milling was performed under continuous pumping. During the milling the vacuum was kept at a level of about 10^-6 Torr. The starting amount of material was a few grams. X-ray-diffraction patterns were taken from the samples milled for different periods and after x-ray diffraction the powder was used for high-field magnetization and ac magnetic susceptibility measurements, and subsequently for DSC analyses. X-ray-diffraction patterns were taken at room temperature by means of a Philips...
diffractometer with vertical goniometer using Cu Kα radiation. For an accurate measurement of the lattice parameters the powder sample was mounted on the sample holder with silicon as a standard. The high-field magnetization measurements at 4.2 K were performed in the Amsterdam High Field Installation, in which magnetic fields up to 40 T can be generated in a semicontinuous way. A stepwise field profile up to 21 T was used. The sensitivity of this magnetometer is about $10^{-5}$ Am$^{-1}$. The ac magnetic susceptibility measurements were carried out from room temperature to liquid-helium temperature in self-constructed equipment (see Refs. 15 and 18 for details). DSC was carried out in a Perkin-Elmer DSC-7 in a flux of argon gas at a speed of 30 cm$^3$/min to protect the sample against oxidation. A heating rate of 20 K/min was used in the DSC scans. The scan was repeated twice for each sample. The temperature and the reaction heat were calibrated by pure indium and zinc standards.

III. RESULTS AND INTERPRETATION

Figures 1 and 2 give the x-ray-diffraction patterns of Ni$_3$Al after milling for various periods. The pattern of the as-prepared Ni$_3$Al (0 h) is characteristic of the ordered $L_1_2$-(Cu$_3$Au) structure. The diffraction peaks are indexed in Fig. 1. The mixed $hkl$ indices (100), (110), (210), and (211) correspond to the superlattice reflections. Upon milling, the intensities of the superlattice reflections decrease with increasing milling time. After 10 h of milling no superlattice reflections are observed any more. The long-range-order (LRO) parameter $S/S_0$ was calculated from the superlattice-reflection intensities relative to the fundamental-reflection intensity by

$$\frac{S}{S_0} = \left( \frac{I_S}{I_f} \right) S_{S_0}^{1/2},$$

where $(I_S/I_f)S$ is the intensity of the superlattice reflection relative to that of the fundamental reflection at a value $S$ of the LRO parameter and $S_0$ is equal to unity for the case of complete order. The obtained results are plotted in Fig. 3 as a function of milling time. It is clear that the LRO parameter decreases linearly with increasing milling time and reaches a zero value at about 6 h of milling (by extrapolation). This tendency is similar to that reported before for Ni$_3$Al (Ref. 6) and Ni$_3$Si.$^1$ Among the various $S$ values also an $S$ value of about 0.1 is observed in the present study, which is not ex-
FIG. 4. Variation of the lattice parameter of Ni₃Al as a function of milling time.

FIG. 5. Average crystallite size (open squares and left-hand-side scale) and relative strain (solid circles and right-hand-side scale) of Ni₃Al as a function of milling time.

FIG. 6. High-field magnetization curves of Ni₃Al at 4.2 K after milling for various periods.

The broadening of the x-ray-diffraction peaks is ascribed to the reduction of the crystallite size and the development of internal strain. The size broadening and the strain broadening can be separated. The average crystallite size and relative strain were thus calculated from the x-ray-diffraction patterns. The unmilled sample was used as a standard specimen and the three-fundamental reflections were employed in the evaluation. The obtained average crystallite size and relative strain are plotted in Fig. 5 as a function of milling time. The crystallite size decreases monotonously with milling time in the early stage and tends to become constant after long periods of milling. The final value of crystallite size of Ni₃Al is approximately 25 nm. This value is of the same magnitude as reported earlier. The relative strain increases sharply with milling time and reaches a constant value of about 0.55% after 5 h of milling. This also indicates atomic disordering in Ni₃Al.

High-field magnetization curves (at 4.2 K and up to 21 T) of Ni₃Al milled up to 60 h are displayed in Fig. 6. The magnetization at 21 T is plotted in Fig. 7 as a function of milling time. Both the magnetic susceptibility and the value of the magnetization at 21 T of the unmilled material are nearly the same as reported by de Boer. Thus, our starting compound is of good quality. Upon ball milling both the magnetic susceptibility and the value of the magnetization at 21 T change drastically. The magnetization decreases almost linearly with increasing milling time (see Fig. 7) up to about 5 h of milling. Upon longer milling it decreases further until 40 h of milling, where a constant value is reached. No clear change is observed upon continued milling. In Fig. 8, M² vs B/M plots at 4.2 K, so-called Arrott plots, are given after milling up to 60 h. If the value of the intersection on the B/M axis is negative in M² vs B/M plots, the material is in the ferromagnetic state at this temperature; otherwise, it is paramagnetic. Thus, samples milled up to 2 h are ferromagnetic at 4.2 K, but, after milling for 20 h or longer, the samples become nonmagnetic or paramagnetic. For the samples milled for 5 and 10 h, from only the Arrott plots the...
magnetic features are not clear. Apparently additional information is needed. For this, the temperature dependence of the ac susceptibility of Ni$_3$Al after various periods of milling was measured as shown in Fig. 9. A clear magnetic transition is observed in the starting compound upon cooling. The transition temperature is about 44 K, which is not far from 42 K, the value of Curie temperature reported in Ref. 25. Upon ball milling, this transition becomes weaker and the transition temperature shifts somewhat to lower temperature. After milling for 20 h or longer, this transition disappears completely. The fact that the magnetic transition still exists in the samples milled for 5 h (not shown in the figure) and 10 h suggests that both samples are still ferromagnetically ordered at 4.2 K and thus are ferromagnets. Therefore, ferromagnetic Ni$_3$Al becomes nonmagnetic (or paramagnetic) after milling for 20 h or longer. This could mean that the structure of materials milled for 20 h or longer is essentially different from that of those milled for shorter periods. Together with the fact that the lattice parameter of Ni$_3$Al largely increases after 20 h of milling, it can be concluded that the material completely transforms to the disordered fcc solid solution after milling for 20 h. This is further supported by DSC analysis.

The ball-milled materials are in metastable states. Therefore, DSC analysis may provide further information on the structural development during milling. DSC traces for the samples milled for typical periods are presented in Figs. 10 and 11. After 1 h of milling, a weak exothermic peak is detected at about 610 K (peak II). Peak II becomes more

![FIG. 7. Magnetization of Ni$_3$Al at 4.2 K and 21 T as a function of milling time.](image)

![FIG. 8. $M^2$ vs $B/M$ plots (Arrott plots) of Ni$_3$Al at 4.2 K after milling for various periods.](image)

![FIG. 9. Temperature dependence of the ac susceptibility of Ni$_3$Al in an ac field of 0.12 mT and a frequency of 109 Hz after various periods of milling.](image)

![FIG. 10. DSC scans of Ni$_3$Al after milling up to 60 h.](image)
pronounced upon further milling. After 10 h of milling, another exothermic peak is observed at about 420 K (peak I). In samples milled between 20 and 280 h, the shape of peak II is different from that in samples milled for periods shorter than 20 h and longer than 280 h. In fact, another exothermic peak at about 800 K is also detectable in some of the ball-milled samples (peak III). Since peak I and peak III change unsystematically, we focus our attention on peak II. The transition temperature of peak II changes substantially with milling time, i.e., it decreases with increasing milling time up to 40 h of milling and increases upon further milling up to 440 h. This is more clearly seen in Fig. 12, where the transition temperature of peak II $T_m$ is plotted as a function of milling time; however, the transition temperature shifts to lower temperature again after 680 h of milling. The physical meaning of these heat effects is as follows: peak I is due to the release of lattice strain and short-range ordering (SRO), peak II is due to LRO, and peak III is due to the crystallite growth. In the samples milled between 20 and 280 h, peak II is then due to the phase restoration from the disordered fcc solid solution to ordered $L1_2$. These statements are based on the further experiments as performed on Ni$_3$Si (Ref. 1) and other compounds reported in previous studies (see, for example, Refs. 10 and 17). That is, the samples milled for typical periods were heated in the DSC to different temperatures where the heat effect occurs and then rapidly cooled to ambient temperature. Subsequently, x-ray-diffraction patterns were taken of various samples and a comparison was made. From the fact that the shape and temperature of peak II in the sample milled for 680 h are different from those in the samples milled for shorter periods, it is inferred that partial amorphization occurs in this sample. The broad character of this transition reflects that this transition includes two overlapping heat effects, i.e., crystallization and phase restoration. It is remarkable that the shape observed in the present investigation is similar to that reported in Ref. 6 in which a small fraction of amorphous phase was detected by TEM. Moreover, in Ref. 6 the transition temperature of the sample with an amorphous fraction is also lower than that of the sample without amorphous phase. The total heat content is calculated from the respective DSC scans and plotted in Fig. 12. A rapid increase is observed up to 40 h of milling. Upon further milling, the heat content tends to become constant with a value of 8.3 kJ/mol of atoms. The heat content saturates at the point where the transition temperature of peak II is at a minimum value.

In the samples milled for long periods the total heat content is identical to the heat content of peak II, and therefore should be associated with the heat evolved during the phase restoration from the solid solution to the $L1_2$ structure. A question to be answered is then whether the value of 8.3 kJ/mol of atoms can be understood quantitatively. From Miedema’s semiempirical model26 a formation enthalpy of $-33$ kJ/mol of atoms for the $L1_2$ compound Ni$_3$Al is found. On the other hand, applying Miedema’s model to the formation enthalpy of the solid solution yields $-23$ kJ/mol of atoms.27 The difference is 10 kJ/mol of atoms and so this should be the heat evolved during phase restoration. Taking into account that both formation enthalpies are only estimates, the agreement with our measured value is excellent.

The disappearance of the (small) heat effect of peak I in samples milled for longer periods, i.e., after the transformation to the solid solution by milling, is remarkable. This could mean that the recovery of SRO in the somewhat disordered $L1_2$ structure is easier than in the solid solution, either because less atomic jumps are necessary in the $L1_2$ structure or because the activation energy for atomic jumps is lower in the $L1_2$ structure. It could also be that in the solid solution, as soon as the increase of SRO starts (at a different temperature than in the $L1_2$ structure), the phase restoration starts, so that both processes coincide.
IV. DISCUSSION

From the above it is clear that antisite disorder is created in $L_12\text{Ni}_3\text{Al}$ during the early stage of milling and that after long periods of milling a phase transformation from disordered $L_12$ to the disordered fcc solid solution is completed. After 680 h of milling, a small amount of amorphous phase may be present.

Let us first discuss the milling periods shorter than 20 h. In this period, both lattice parameter and lattice strain increase, indicating the occurrence of atomic disorder. The LRO parameter derived from the x-ray superlattice reflections decreases linearly and reaches a zero value after about 6 h of milling. This may mean that the material reaches a completely disordered state after 6 h of milling and that a phase transformation to the fcc solid solution is realized. Then the material is not able to store further energy in the form of atomic disorder. The high-field magnetization also decreases monotonously with increasing milling time as seen in Fig. 7. It is interesting to note that, when the $S$ value becomes zero after about 6 h of milling, the magnetization still continuously decreases upon further milling. The magnetization starts to become constant after 20 h of milling, well after the disappearance of the superlattice reflections ($S=0$). A similar tendency is observed in the change of lattice parameter, i.e., after 20 h of milling it starts to become constant. These observations strongly suggest that structural changes still take place even after the disappearance of LRO. It could be that existing SRO is destroyed or that the measured intensities of the superlattice reflections are not completely decisive for the evaluation of atomic order, or that the material decomposes into two phases with different composition (fcc solid solution and some amorphous phase). Of course, there might be another possibility for the decrease of magnetization between 6 and 40 h of milling. That is the reduction of the crystallite size, whereby a substantial fraction of atoms could reside in grain boundaries; however, this does not seem probable because the average crystallite size tends to become constant already after about 5 h of milling with a final size of about 25 nm. This value is much larger than the limit for the reduction of magnetization due to strain-boundary atoms, which is usually 4–6 nm. Therefore, nanocrystallinity does not seem to explain the decreasing magnetization. As discussed for CoZr in Refs. 12 and 21, an accurate measurement of the change of the relative intensity, i.e., the LRO parameter, is difficult because ball-milled materials contain many defects which make the diffraction intensity very low and the diffraction peaks rather broad. The change of the magnetization reflects the change of the nearest-neighbor configuration of the magnetic element (here Ni). Therefore, the magnetization is more sensitive to structural changes than the x-ray intensities. The information obtained from x-ray diffraction is limited, in particular during the intermediate state of milling. The results from DSC analysis also support the generation of atomic disorder in Ni$_3$Al and show the continuation of disordering even after the disappearance of the superlattice reflections ($S=0$). Disordering decreases the stability of the compounds and thus decrease the reordering temperature ($T_{\text{peak II}}$ decreases with milling time).

It must be pointed out that in principle the presence of SRO could be detected by modulations of diffuse x-ray intensity and changes in SRO could then be detected by changes in this modulation; however, in ball-milled samples even the disappearance of superlattice reflections is already difficult to detect. Due to the presence of strain and due to the nanocrystalline character of the material after milling, there is no hope that this technique of diffuse x-ray intensity modulation could be applied successfully in the present case. It can only be applied to very carefully and specially prepared samples, consisting of elements with quite different scattering factors.

Now we discuss the milling period between 20 and 440 h. In this period the material becomes a completely disordered fcc solid solution. A large increase of the lattice parameter is observed after 20 h of milling and the magnetization decreases further. The expected first-order transition is not clear from the x-ray patterns. The expected splitting of the diffraction peaks as observed for Ni$_3$Si (Ref. 1) was not observed in the case of Ni$_3$Al. This may be due to the fact that in Ni$_3$Al the value of the lattice parameter of the fcc solid solution is not far from that of disordered $L_12$. During this period, the peak temperature of the transition corresponding to the phase restoration (peak II) increases with milling time. This is due to a decrease of the number of prenuclei for phase restoration similar to that observed in Ni$_3$Si.1

A weak indication was obtained of partial amorphization in the sample after 680 h of milling. This was inferred from the results of DSC analysis.

It should be emphasized that the ball milling was performed under continuous pumping in a vacuum of better than 10$^{-6}$ Torr. In this way reactions with nitrogen or oxygen were avoided. The essential part of the bottom of the ball mill is made from tungsten carbide, so the iron contamination from the milling media can be very small. In previous experiments elemental analysis showed that iron contamination is negligible. Furthermore, in these investigations usually the samples were annealed after milling to reobtain the original state. In all these cases all original properties, including magnetic properties, were recovered (see Refs. 10 and 28 for more details). Also, in the present study we did not observe any additional peaks in the x-ray-diffraction patterns of various samples milled even for long periods. The x-ray-diffraction pattern and magnetic properties were completely restored upon annealing the various ball-milled samples. Thus, the influence of oxygen or iron contaminations is negligible in ball-milled Ni$_3$Al and the observed phenomena are the intrinsic behavior of Ni$_3$Al upon mechanical milling.

V. CONCLUSIONS

In conclusion, antisite disorder is generated in $L_12\text{Ni}_3\text{Al}$ during the early stage of milling and a phase transformation from the $L_12$ to the fcc solid solution of Al in Ni is induced after long periods of milling. Partial amorphization occurs after prolonged periods of milling. Evidence for disordering in Ni$_3$Al was obtained from all techniques used in the present study. The LRO parameter
calculated from the superlattice reflections turns out to decrease upon milling and to disappear completely already after very short periods of milling. The increase of both the lattice parameter and the relative strain upon milling also suggests antisite disordering in Ni₃Al. Heat effects corresponding to the atomic reordering and phase restoration are observed. More precise information on the structural development in Ni₃Al is obtained from magnetic measurements during the intermediate stage of milling. Therefore, it is demonstrated that magnetic properties are more sensitive than x-ray diffraction to monitor structural changes during non-equilibrium processing such as ball milling and can provide more detailed information on disordering, thus leading to a much better understanding of ball-milling-induced phase transformations. Based on the magnetic data, it is concluded that SRO could be the third source of energy storage during milling of Ni₃Al.

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