Isothermal Martensitic Transformation of $\gamma$-FeN in a Magnetic Field

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Isothermal martensitic transformation of the $\gamma$-FeN was found to occur in magnetic field at temperatures above the $M_s$. Molar fraction of martensite monotonically increases with increasing isothermal aging time, and saturates at a value proportional to applied magnetic field. Temperature and magnetic field dependence of the saturation value indicates that the transformation does not proceed above the temperature where the value become zero in a given magnetic field. Application of magnetic field reveals intrinsic isothermal character of the martensitic transformation in the $\gamma$-FeN hidden behind the complication associated with magnetization process of the $\alpha'$ phase.

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1. Introduction

Martensite transformations are classified into two distinctive categories, isothermal and athermal ones, with regard to temperature and time dependence of the molar fraction of martensite phase, $f$, in materials. The $f$ of alloys in the former category is a function of both temperature and time, but that in the latter depends only on temperature. Due to this clear difference, the kinetics of these two transformations were considered to be different. Kakeshita et al. demonstrated using the Fe-Ni-Mn system, which shows isothermal or athermal process at different compositions, that isothermal alloys undergo athermal transformation in magnetic field and the athermal ones exhibit isothermal transformation under hydrostatic pressure.1,2) They quantitatively explained the observed TTT curves with unified phenomenological theory they constructed, and concluded the kinetics for the athermal and isothermal processes is essentially the same.2–4)

Binary Fe-C and Fe-N steels exhibit fcc $\rightarrow$ bct martensitic transformation and this structure change is widely accepted as a typical example of the athermal process.5) When the $\gamma$ phase in fcc structure is quenched below the martensite start temperature, $M_s$, it partially transforms into the $\alpha'$ phase in the bct structure. Because magnetic character of $\gamma$ and $\alpha'$ phases are paramagnetic and ferromagnetic, respectively, spontaneous magnetization of samples is proportional to the $f$. Therefore, magnetic measurements are best suited to monitor progress of the martensitic transformation occurring in the $\gamma$ phase quantitatively. If magnetization of the $\gamma$ phase increases during isothermal aging, this exclusively means the isothermal transformation takes place as far as temperatures lower than room temperature are concerned, and is another example showing the athermal and isothermal processes are indistinguishable in kinetics.

Present author and collaborators have been associated with research to produce Fe-N alloys with single phase bct structures through the $\gamma \rightarrow \alpha'$ martensitic transformation, and found magnetic field promotes this structural change.6,7) With using static high magnetic field of $2.8 \times 10^7$ A/m at 4.2 K, the amount of $\gamma$ phase is reduced as low as 7%,7) and the $\alpha'$ phase is found to possess magnetization of $2.95 \times 10^{-4}$ Wb-m/kg.6) This means magnetization would grow up exceeding pure Fe if the remaining $\gamma$ phase were eliminated. In order for this particular interest, it must be clarified what limits, and why magnetic field increases the $f$. Therefore, it is essentially important to reveal physics underlying the martensitic transformation of the $\gamma$-FeN. The author measured the $f$ as a function of magnetic field, temperature, and time in order to provide a clear evidence whether the isothermal transformation takes place or not in the $\gamma$-FeN.

2. Experimental Procedure

Commercial iron foils (0.01 mm in thickness, 10 mm $\times$ 10 mm in size, and 99.8% in purity) were annealed for grain growth and decaburization at 1270 K in dry hydrogen gas for 1 hour, and successively nitrified with a mixture of NH$_3$ and H$_2$ gas at 923 K for 1 hour. Foil thickness and annealing time were optimized to assure composition homogeneity in a sample. Nitrified samples were subsequently quenched into distilled water without having contact with the air, and single phase polycrystalline samples of $\gamma$ were obtained. The surface of the samples was shiny silver and no surface treatment was applied through out present research.

X-ray diffraction spectra were measured with a two-circle goniometer equipped with a graphite monochromer. Mo $K\alpha$ radiation was used for precise determination of lattice parameter and longer penetration depth than Cu or Co $K\alpha$ radiation. Lattice parameter was determined using the Nelson-Riley plot with 21 diffraction lines after deconvoluting the K$_{\alpha_1}$ and K$_{\alpha_2}$ lines. Samples with lattice parameter of 0.3646 nm $< a_0 < 0.3647$ nm were selected for measurements. According to composition dependence of lattice parameter, corresponding nitrogen concentration is 9.6 at% N.8)

Isothermal magnetic measurements were carried out using a SQUID magnetometer (Quantum Design MPMS 5.5 System). The $\gamma$ phase sample (5 mm $\times$ 10 mm in size) was sandwiched with a folded aluminum foil without putting any glue, in order to avoid subjecting mechanical stress during transformation. The aluminum foil was taped inside of a gelatin capsule, and mounted in a sample transfer rod of the magnetometer. Actual temperature at sample position was checked using a transfer rod incorporating a Cernox resistance thermometer. DSC spectra were recorded with Perkin-Elmar Pyris
Diamond DSC with a liquid nitrogen cooler. Sample temperature was calibrated with a reference to the melting point of indium and ethyl ether. Difference in temperature readings between cooling and heating runs was checked with specific heat of Tb at magnetic transition, and is smaller than 1 K at scanning rate of 10 K/min.

3. Results

First of all, the $M_s$ temperature should be determined in conventional manner. Figure 1 shows DSC curve measured at 10 K/min of cooling rate. Spiky exothermic peaks starting at 181 K are clearly observed. These peaks originated in variant formation during the martensitic transformation process. The author admits the $M_s$ thus determined tends to scatter for sample by sample ranging $170 \text{ K} < M_s < 200 \text{ K}$, but is in agreement with the data in Ref. 9). No noticeable exothermic or endothermic peaks was observed in heating process, as expected from the fact that the $\gamma/C_{11}$ phase possesses lower Gibbs free energy than the $\gamma/C_{13}$ phase over the temperature range studied.

External magnetic field drives the transformation as reported in Ref. 6,7). Therefore, isothermal magnetization measurements were carried out at temperatures above the $M_s$. Figure 2 shows magnetization of $\gamma$-FeN as a function of aging time for various magnetic fields at 231 K. Magnetization shows abrupt increase in initial stage, and gradually saturates. This time dependence resembles the $f$ for the isothermal Fe-Ni-Mn alloys.5) As can be seen from the figure, higher magnetic field resulted in higher saturation value of magnetization, and the value seems to be proportional to magnetic field. Magnetization increases in stepwise because of formation of variants. All magnetization data measured exhibited this particular behavior characteristic to martensitic transformation, but steps are less prominent in stronger magnetic field or higher saturating magnetization. This saturating “stepwise” time dependence was also observed at 221 K and 241 K. Higher magnetic field is needed for the same magnetization at higher temperature.

It should be noted that the $\gamma$-FeN must be cooled from room temperature to desired temperature without overcooling because this results in higher $f$. Present magnetometer equips temperature control function but it may cause overcooling of 20 K in this temperature range. In order for avoiding this unfavorable effect, the sample was inserted into the sample space more than 4 hours after the temperature became stable in the area. Magnetic field was raised immediately after the sample was placed. It takes about 4 min to reach $4 \times 10^5 \text{ A/m}$ and start measurement. The author mounted a small piece (2.9 mg in weight) of Tb in the same manner as the $\gamma$-FeN, and measured its magnetization as a function of time to estimate how quickly the sample is cooled. As magnetic susceptibility of Tb in the temperature range under discussion is strongly temperature dependent, it immediately tells actual temperature of the sample. Magnetization of the $\gamma$-FeN in $4 \times 10^5 \text{ A/m}$ and sample temperature thus estimated are plotted together against time in Fig. 3. Obviously, the magnetization increased even after temperature was completely stabilized. Therefore, the isothermal martensitic transformation is not an artifact, but really takes place in magnetic field at temperatures above the $M_s$.

4. Discussion

The molar fraction of martensite, $f$, is determined from gross magnetization of a sample assuming spontaneous magnetization of $2.95 \times 10^{-4} \text{ Wb m/kg}$ for the $\alpha'$ phase6) and $\chi = 4 \times 10^{-13} \text{ H m}^2/\text{kg}$ for the $\gamma$ phase. Though the magnet-
to a sum of the driving force and the energy for the temperature \( T \) that the austenite needs to be supercooled below the needed. Therefore, the transformation between austenite and martensite equals to the driving force supercooling is called “driving force”, and the transformation generates lattice strain and this would suppress progress of the structural change. If the accumulated strain energy were proportional to the \( f \), \( f_s \) would be proportional to \( H \) as shown in Fig. 4.

Assuming the linear relationship between the \( f \) and \( H \), the \( M_{s\text{iso}}(0) \) is estimated to be 230 K and above the \( M_s \). This extrapolation suggests the martensitic transformation would take place at any temperatures below 231 K in zero magnetic field if the sample were isothermally kept for infinite time. But, the \( \gamma \)-FeN had been accepted as the athermal alloy, and this means the isothermal transformation did not take place above the \( M_s \), at least, in zero magnetic field. Therefore, it would be more plausible to deduce that an additive mechanism suppresses the isothermal transformation and causes further supercooling in the range \( H < 4 \times 10^5 \text{ A/m} \).

The most prominent magnetic phenomenon occurring in the range \( H < 4 \times 10^5 \text{ A/m} \) is magnetization process of the ferromagnetic \( \alpha' \) phase. Its coercive field is about 6 \( \times 10^3 \text{ A/m} \) and magnetization almost saturates at 4 \( \times 10^5 \text{ A/m} \). If the magnetization process affects nucleation or growth of the \( \alpha' \) phase, this would be possible to explain why the isothermal process had not been observed in zero magnetic field. In other words, this complicity associated with the magnetization process of the \( \alpha' \) phase covers up intrinsic isothermal character of the martensitic transformation in the \( \gamma \)-FeN, and magnetic field reveals it. 

Magnetostriiction and difference in thermal expansion coefficient between \( \gamma \) and \( \alpha' \) phases need to be considered in detail since the lattice strain plays an important role in the kinetics of the transformation as mentioned above. The directional magnetostriction would be one of the keys to solve the question in low or zero magnetic field. In order to test validity of present explanation, measurements in \( H \ll 4 \times 10^5 \text{ A/m} \) and thermal expansion coefficients are in progress.

5. Conclusion

The \( \gamma \)-FeN is found to isothermally transform into the \( \alpha' \) phase in magnetic field above the \( M_s \). Molar fraction of martensite monotonically increases with increasing isothermal aging time, and saturates at a value proportional to applied magnetic field. Temperature and magnetic field dependence of the \( f_s \) indicates that martensitic transformation does not proceed above \( M_{s\text{iso}}(H) \). Application of magnetic field reveals intrinsic isothermal character of martensitic transformation in the \( \gamma \)-FeN hidden behind complication associated with magnetization process of the \( \alpha' \) phase. Most likely, the nucleation or growth of the \( \alpha' \) phase is suppressed in low or zero magnetic field, and the transformation proceeds as if it is the athermal process once it started.

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REFERENCES