HIGH-TEMPERATURE X-RAY DIFFRACTION STUDIES OF LATTICE DYNAMICS IN $\text{Ni}_3(\text{Fe}, \text{Nb})$ ORDERED ALLOYS

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A study is performed on characteristics of lattice dynamics in the initially ordered ternary $\text{Ni}_3(\text{Fe}_{1-x}\text{Nb}_x)$ ($x = 0$ to 10 at.%) alloys using high temperature X-ray diffractometry for the temperature range from 300 K to 1300 K. Aspects investigated included temperature and concentration dependencies of the full mean square atomic displacements $\bar{U}_i^2$, the Debye characteristic temperature Θ_D , and linear thermal expansion coefficient α . It is found that the $\bar{U}_i^2$, Θ_D , and α parameters show anomalous change at temperatures where the alloys are subjected to order-disorder phase transitions. It is further found that Nb addition results in the considerable increase in the parameters $\bar{U}_i^2$ and α and decrease in Θ_D . Moreover, the addition of Nb stabilizes Ni_3Fe ordered structure and shifts the order-disorder transition to higher temperature.

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1. Introduction

Recently there is much interest in nickel and iron-based ordered alloys especially for high temperature applications [1]. In this context the stability of crystal structure and the effect of structural state on crystal lattice dynamics at wide temperature range is an important consideration. Moreover, the data on crystal lattice dynamics parameters may be also used for studying the character and nature of interatomic interactions in the alloys. Studies of this nature were reported for Ni_3Fe single crystals at low [2] as well as at high temperatures [3], which has shown the sensitivity of the lattice dynamics parameters to the order-disorder phase transition in these crystals. The intermetallics V_3Pt , V_3Rh and Ti_3Ir having A15 structure were also investigated in which room temperature lattice dynamics parameters were measured [4] with X-ray powder diffractometry.

The aim of this work is to investigate the effect of the atomic ordering state on lattice dynamics parameters in polycrystalline ternary $\text{Ni}_3(\text{Fe}_{1-x}\text{Nb}_x)$ alloys with the use of high-temperature X-ray diffractometry. The temperature range was from 300 K to 1300 K.

2. Determination of characteristic lattice dynamics parameters using X-ray diffraction analysis

It is well known [5] that the atomic scattering factor, f , for an atom undergoing thermal vibration is defined as

$$f = f_0 e^{-M}, \quad (1)$$

where f_0 is the atomic scattering factor for an atom at "rest" (i.e., with no thermal vibration); e^{-M} is the temperature factor. Because the intensity of any diffraction line depends on f^2 , the calculated intensities must be multiplied by e^{-2M} to allow for thermal vibration. The quantity M depends on both the amplitude u of thermal vibration and the scattering angle 2θ . In Debye approximation the quantity M will be given as

$$M = \frac{6h^2}{mk_B\Theta_D} [1/4 + \phi(x)/x] \left(\frac{\sin \theta}{\lambda} \right)^2, \quad (2)$$

where h is the Planck constant, m is the mass of the vibrating atom, k_B is the Boltzmann constant, Θ_D is the Debye characteristic temperature of the substance in K, $x = \Theta_D/T$, T is the absolute temperature, and $\phi(x)$ is a Debye function.

At the same time in the solid solutions there exist the dynamic and static displacements of atoms from exact lattice site positions. The static displacements of atoms arise mainly due to atomic size differences and chemical interatomic interaction potential differences in solid solutions. There may also be other factors such as a state of strain or residual stresses which may lead to the static displacements of atoms.

If we assume that dynamic and static displacements of atoms are independent of each other, the full mean square displacements of atoms according to [6] will be given as

$$\bar{U}_f^2 = \bar{U}_{st}^2 + \bar{U}_d^2 = \bar{U}_{st}^2 + A \frac{k_B T}{m} + \frac{h^2}{4mk_B T}, \quad (3)$$

where $\bar{U}_f^2$, $\bar{U}_{st}^2$, $\bar{U}_d^2$ are the full, static, and dynamic mean square displacements of atoms, respectively;

$$A = \int_0^\infty g(\omega)/\omega \, d\omega,$$

$g(\omega)$ is the number of vibration in frequency range from ω to $\omega + d\omega$.

In the Debye model of lattice vibrations the number of vibrations A can be taken as independent on temperature T . Note that Eq. (3) is satisfied for the temperatures $T > \Theta_D/2\pi$. Therefore, X-ray diffraction experiments for determination of the full mean square displacements of atoms can be performed at $T > \Theta_D/2\pi$.

For determination of the full mean square displacements of atoms by X-ray diffraction method it is necessary to measure at least the intensities of two diffraction lines. In this case according to [7] $\bar{U}_f^2$ will be defined as

$$\bar{U}_f^2 = \frac{3\lambda^2}{16\pi^2} \ln \left[\frac{I(\theta_2) L(\theta_1) P_1 |F_1|^2 A(\theta_1)}{I(\theta_1) L(\theta_2) P_2 |F_2|^2 A(\theta_2)} \right] (\sin^2 \theta_1 - \sin^2 \theta_2)^{-1}. \quad (4)$$

In Eq. (4) λ is the wavelength of the incident X-ray beam, $I(\theta)$ is the integrated intensity of diffraction line, $L(\theta)$ is the Lorentz polarization factor, P is the multiplicity factor, F is the structure factor, $A(\theta)$ is the absorption factor, θ_1 and θ_2 are the Bragg angles for the first and second diffraction lines, respectively.

The lattice vibrations affect not only the integrated intensities of diffraction peaks, but also in the diffractogrammes it leads to nonmonotonic diffuse scattering intensities. Diffuse scattering which contributes to the intensities of the diffraction peaks is known as the first-order thermal diffuse scattering. According to Chipman and Paskin [8, 9] the contribution of this first-order scattering can be taken into account by including a factor, $(1 + \sigma)$, in the following form:

$$I_r = I_m(1 + \sigma)^{-1}, \quad (5)$$

where I_r , I_m are the real and measured intensities of the diffraction lines. Thus the measured intensity can be written as

$$I_m \sim f_0^2 \exp(-2M)(1 + \sigma) \quad (6)$$

where

$$\sigma = 4\pi X_m^2 M a \cos \theta \Delta \theta / 3n\lambda = 2M\beta \quad (7)$$

and

$$\beta = 2\pi X_m^2 a \cos \theta \Delta \theta / 3n\lambda, \quad (8)$$

$X_m = ag_{\max}$, a is the lattice parameter, $g_{\max}$ is the radius of the sphere, which is equal to the first Brillouin zone, n is the number of atoms per unit cell, $\Delta \theta$ is the width of peak at background level (in radians).

In Eq. (6) the $(1 + \sigma)$ factor can be replaced by

$$1 + \sigma = \exp(\sigma) = \exp(2M\beta). \quad (9)$$

Then

$$I \sim f_0^2 \exp[-2M(1 - \beta)]. \quad (10)$$

For the fcc crystal structure $X_m = (3/\pi)^{1/3}$ and $n = 4$, therefore

$$\beta = (1/2)(\pi/3)^{1/3} \frac{a \cos \theta}{\lambda} \Delta \theta. \quad (11)$$

The simple calculation shows that usually $\beta \ll 1$.

Combining Eq. (10) with Eq. (4), one can get the following equation for the full mean square displacements of atoms:

$$\begin{aligned} \bar{U}_f^2 = \frac{3\lambda^2}{16\pi^2} \ln \left[\frac{I(\theta_2) L(\theta_1) P_1 |F_1|^2 A(\theta_1)}{I(\theta_1) L(\theta_2) P_2 |F_2|^2 A(\theta_2)} \right] \\ \times [(1 - \beta_1) \sin^2 \theta_1 - (1 - \beta_2) \sin^2 \theta_2]^{-1}. \end{aligned} \quad (12)$$

According to [4] the Debye characteristic temperature Θ_D can be calculated as

$$\Theta_D = (9h^2T/\bar{U}_d^2 4\pi^2 m k_B)^{1/2}. \quad (13)$$

Equation (13) is satisfied at temperatures $T > \Theta_D$, i.e. when

$$\frac{1}{4} \frac{\Theta_D}{T} + \phi(\Theta_D/T) \sim 1. \quad (14)$$

In Eq. (13) m is the average mass of atoms which may be determined as

$$\langle m \rangle = \langle A \rangle 1.66 \times 10^{-24} \text{ grams},$$

where $\langle A \rangle = \sum C_s A_s$, C_s is the concentration of s component in the alloy and A_s is the atomic weight of s component.

For solid solutions according to Eq. (3) $\bar{U}_d^2 = \bar{U}_f^2 - \bar{U}_{st}^2$ and for the determination of the $\bar{U}_d^2$ it is necessary to plot the function $\bar{U}_f^2 - h^2/4mk_B T$ against temperature. The extrapolation of this plot to 0 K allows us to find the value of the static mean square displacements of atom $\bar{U}_{st}^2$.

The linear thermal expansion coefficient α by X-ray diffraction method can be defined as

$$\alpha = \frac{\Delta d}{d_1 \Delta T} = \frac{d_1 - d_2}{d_1(T_1 - T_2)}, \quad (15)$$

where d_1 and d_2 are the interplanar distances at temperatures T_1 and T_2 , respectively.

3. Materials and procedure

Alloys $\text{Ni}_3(\text{Fe}_{1-x}\text{Nb}_x)$ were prepared from high purity metals (99.99%). Three specimens were prepared: Ni-25Fe; Ni-18Fe-7Nb; Ni-15Fe-10Nb. The alloys were produced in an arc furnace with a nonconsumable tungsten electrode on a water-cooled copper base in the high-purity helium. Specimens were machined in the shape of discs, and polished to mirror finish. Disordered state was induced by annealing the alloy at 1000°C for 2 hours followed by quenching the encapsulated specimens into water. To obtain the ordered state, the samples after quenching were annealed at 450°C for 1000 h in the vacuum. Examination showed that all samples were in the austenitic phase.

The integrated intensities of (200) and (400) fundamental diffraction lines were measured *in vacuo* on $\text{Cu } k_\alpha$ radiation monochromatized by flat single crystal of silicon (plane (111)). The incidental errors in the integrated intensities of (200) and (400) diffraction peaks are about 5%. A scintillation counter was used to register the scattering intensities.

The integrated intensities of (200) and (400) diffraction lines were measured at temperatures of 293–1273 K. The measurements were performed in diffractometer maintained under vacuum with pressure 3×10^{-4} Pa. Variation in pressure was negligible and maintained between 3×10^{-4} and 5×10^{-4} Pa. A molybdenum furnace was used where the temperature could be controlled with a sensitivity of $\pm 4^\circ\text{C}$.

The integrated intensity measurements were performed at constant number of pulses. At the background region 10^4 pulses were taken, and at the diffraction

peaks region the number of pulses was 10^5 . The measurements were repeated 10 times for each diffraction peak. Then the number of pulses per 1 second was calculated.

The X-ray diffraction data were used to calculate $\bar{U}_f^2$, Θ_D and α parameters from Eqs. (12), (13), and (15). For this purpose the Lorentz polarization $L(\theta)$ and atomic scattering factors $f(\theta)$ were calculated by interpolation method. The structure factor of $\text{Ni}_3(\text{Fe}_{1-x}\text{Nb}_x)$ ternary alloys was calculated from

$$F(\theta) = f_{(\text{Fe,Nb})}(\theta) + 3f_{\text{Ni}}(\theta) \quad (16)$$

where $f_{(\text{Fe,Nb})} = c_{\text{Fe}}f_{\text{Fe}} + c_{\text{Nb}}f_{\text{Nb}}$, c is the concentration and $f(\theta)$ is the atomic scattering factor. The atomic scattering factor, f , was calculated as

$$f = f_0 + \Delta f'_K + 1/2 \frac{(\Delta f''_K)^2}{f_0 + \Delta f'_K} \quad (17)$$

where $\Delta f'_K$ and $\Delta f''_K$ are dispersion corrections whose values were taken from [10].

4. Results and discussion

Full mean square displacement of atoms, $\bar{U}_f^2$, calculated for Ni-25Fe, Ni-18Fe-7Nb, and Ni-15Fe-10Nb alloys as a function of temperature T is given in Fig. 1. The quantity $\bar{U}_f^2 - h^2/4mk_B T$ is shown in Fig. 2 which when extrapolated to 0 K gives static square mean displacement values of 0.013, 0.011 and 0.050 for Ni-25Fe, Ni-18Fe-7Nb, and Ni-15Fe-10Nb alloys, respectively. The temperature dependencies of the Debye characteristic temperature, and the linear thermal expansion coefficient α in the alloys are shown in Figs. 3 and 4, respectively.

Fig. 1. Temperature dependencies of the full mean square displacements of atoms $\bar{U}_f^2$ for $\text{Ni}_3(\text{Fe,Nb})$ alloys: $\square\square$ Ni_3Fe ; $\bullet\bullet$ Ni-18Fe-7Nb; $\circ\circ$ Ni-15Fe-10Nb.

It is seen from Figs. 1, 3, and 4 that the full mean square displacements $\bar{U}_f^2$, the Debye characteristic temperature Θ_D , and the linear thermal expansion

Fig. 2. Temperature dependencies of the function $\bar{U}_f^2 - h^2/4mk_B T$ for $\text{Ni}_3(\text{Fe,Nb})$ alloys: $\square$ Ni_3Fe ; $\bullet$ Ni-18Fe-7Nb ; $\circ$ Ni-15Fe-10Nb .

Fig. 3. Temperature dependencies of the Debye characteristic temperature Θ_D : $\square$ Ni_3Fe ; $\bullet$ Ni-18Fe-7Nb ; $\circ$ Ni-15Fe-10Nb .

coefficient α show linear variations with abrupt changes and maxima occurring at temperatures around 700–850 K. It is known that this temperature interval corresponds to order–disorder phase transition in these alloys [11]. Further, it is known that with the addition of Nb, the order–disorder transition temperature in Ni_3Fe shifts to a higher temperature [11]. Similar shifts are evident in the figures which correlates with this observation.

It is interesting to note that the temperature dependence of parameters $\bar{U}_f^2$, Θ_D , and α deviates from linearity at temperature below order–disorder transition. This indicates that the pre-transition phenomena are well in progress in $\text{Ni}_3(\text{Fe,Nb})$ alloys below the transition temperature, as reflected by the fact that the long-range order parameter, η , is less than unity in this temperature region

Fig. 4. Temperature dependencies of the linear thermal expansion coefficient α : $\square$ Ni_3Fe ; $\bullet$ Ni-18Fe-7Nb ; $\circ$ Ni-15Fe-10Nb .

[12, 13]. Krivoglaz [14] has shown that the mean square static displacements $\bar{U}_{\text{st}}^2$ increases proportionally with $1 - \eta^2$. Atomic size factor is also relevant in this context as is experimentally well established by Taylashov [13] who showed that the effect of η on $\bar{U}_{\text{st}}^2$ increases with increase in atomic size factor.

It should be noted that in pure Ni_3Fe the jump of $\bar{U}_{\text{f}}^2(T)$ near order-disorder temperature is only moderate, whereas this jump becomes more and more pronounced in other alloys with increasing Nb content (Fig. 1). This variation implies a considerable distortion of the crystal lattice in Ni_3Fe superstructure caused by the addition of Nb.

Beyond the maxima the temporary decrease in $\bar{U}_{\text{f}}^2$, which occurs with increasing temperature cannot be connected with $\bar{U}_{\text{st}}^2$, rather it should be tied up to the decrease in the dynamic mean square displacements of atoms $\bar{U}_{\text{d}}^2(T)$.

Figure 3 shows that the variation of the characteristic Debye temperature with temperature as well as with Nb concentration is rather complex. An aspect which is clearly brought out, however, is the effect of Nb in the post transitional temperatures (Fig. 3). Following order-disorder transition there is a sharp decrease in Θ_{D} with Nb addition. Such a decrease may be attributed to the existence of the submicro regions of the different concentration of Nb atoms and/or some form of the local short-range order in the alloys [15].

The variation of linear thermal expansion coefficient α displays interesting features especially in pre-translational temperature range. As seen in Fig. 4 in pure Ni_3Fe the coefficient increases gradually over a wider temperature range and reaches a maximum when the transition temperature is reached. With the addition of Nb, however, this range over which the coefficient is affected is narrow implying a greater stability for long-range order in $\text{Ni}_3(\text{Fe}, \text{Nb})$ as compared to pure Ni_3Fe . This greater stability in the Nb containing alloys has been verified experimentally [11, 16].

5. Conclusions

A study of lattice dynamics in ordered $\text{Ni}_3(\text{Fe}_{1-x}\text{Nb}_x)$ polycrystalline alloys (Nb up to 10 at.%) was done using high-temperature X-ray diffractometry over a temperature range between 300 K and 1300 K. The study has shown that the full mean square displacement, $\bar{U}_f^2$, the Debye characteristic temperature Θ_D and the linear thermal expansion coefficient α show abrupt changes at temperatures around 700–850 K which corresponds to order–disorder phase transition temperature in these alloys. It is found that Nb addition to Ni_3Fe increases the static mean square displacement of atoms, decreases the Debye characteristic temperature and sharply increases linear thermal expansion coefficient. Details of temperature dependence of these lattice dynamics parameters are such that Nb addition stabilizes the ordered structure of Ni_3Fe and shifts the order–disorder transition to higher temperatures.

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