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Grain size dependence of the γ→α martensite transformation starting temperature

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In the work, a dependence of the $\gamma \rightarrow \alpha$ martensite transformation starting temperature on the grain size D is derived. A formula for the critical grain size D_c is proposed reflecting the effect of physical parameters on D_c; among the parameters are the group velocity v_s and the attenuation Γ_s for s-electrons, the ratio of spatial scales characteristic of martensite crystal nucleation in the elastic field of an individual dislocation, and the energy range critical for the selection of pairs of active electronic states. With $D < D_c$, the martensite transformation is suppressed, $M_s(D_c) = 0$. In the framework of dynamic theory, M_s is identified with the optimum temperature at which nonequilibrium d-electrons generate waves responsible for the growth of martensite crystals. It is shown that the Γ_s dependence of D_c is singular and allows explanation of the existence of concentration boundaries of alloying elements. Comparison is made between the obtained results and available experimental data.

Keywords: martensite transformation, transformation temperature, nonequilibrium, electronic states, generation of waves, electron attenuation, grain size

1. Introduction

In Fe-based alloys, the $\gamma \rightarrow \alpha$ martensite transformation proceeds by rapid cooperative atomic displacements with clearly defined features of a first-kind transition [1]. The spontaneous (on quenching) martensite transformation starting temperature M_s is an important characteristic sensitive to the alloy composition and grain size D of the initial γ-phase. According to classical concepts, M_s in first-kind transitions is lower than the phase equilibrium point T_0 because part of the free energy difference $\Delta F = F_\gamma - F_\alpha$ is bound to go in forming an interface between the co-existing phases. In the $\gamma \rightarrow \alpha$ martensite transformation, the supercooling $\Delta T = T_0 - M_s$ corresponds to ΔF much greater than the work involved in the formation of the interface. In dynamic theories [2, 3], the severe supercooling ΔT is attributed to a peculiarity of martensite crystal nucleation. In the elastic field of a dislocation that lowers the interface energy barrier, the new phase, which is seemingly bound to appear as an equilibrium nucleus, arises as an initial excited state in the form of a prolate rectangular parallelepiped with close lateral dimensions $d_{1,2}$ and oscillation energy sufficient to surmount the interface energy barrier far greater than the barrier in the nucleation region.

The initial excited state triggers a control wave process as a carrier of tensile-compressive plane strain greater than the threshold level. The lateral dimensions $d_{1,2}$ correspond to those of the nonequilibrium interface region at the stage of martensite crystal growth and specifies the martensite crystal thickness. In transition metals, waves can be generated by a nonequilibrium electron subsystem (the phonon maser effect) ensuring the required level of strain transferred by the control wave process. As a result, martensite crystals are formed and their minimum size is specified by the lateral dimension d of the initial excited state and their maximum size (long axes) is limited by the size of the single crystal region of a specimen (for polycrystalline specimens, by the grain diameter D). Analysis made in [2, 3] shows that for the threshold generation conditions to be met over a wide range of temperatures and concentrations of alloy components, a high level of nonequilibrium additives Δf to the Fermi electron distribution function f^0 is required. With the thermodynamic limit $M_s < T_0$, the choice of M_s is dictated by the peculiarities of the microscopic state of a system.

The objective of the work is to determine the dependence $M_s(D)$, in the framework of the dynamic approach,

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to derive a formula for the critical grain size D_c (to meet the condition $M_s(D_c) = 0$) and to interpret the dependence of D_c on the chemical composition of an alloy.

2. Conditions required for the generation of displacement waves by nonequilibrium electrons

At the stage of rapid martensite growth, the interface region in metals is attacked by an intense electron flow mainly due to the chemical potential difference of electrons $\Delta\mu \sim 0.1$ eV proportional to the phase difference in specific volume, for the chemical potential μ depends on the electron density. The quantity $\Delta\mu$ (the gradient of μ) is estimated by the ratio of $\Delta\mu$ to a transition region width of ~0.1–1 μm [2, 3]. Part of the kinetic electron energy is converted to the wave beam energy due to the generation of waves by nonequilibrium electrons. In the space of quasi-momenta, pairs of inversely populated electronic states with opposite-sign nonequilibrium additives to f^0 in the flow mode separate the *s*-surfaces specified by the vanishing condition of the scalar product of the electron group velocity $\mathbf{v}_\mathbf{k}$ and $\nabla\mu$:

$$(\mathbf{v}_\mathbf{k}, \nabla\mu) = 0. \tag{1}$$

The energies of the electronic states are bound to lie in the range Δ close to μ:

$$|\varepsilon_d - \mu| \approx |\varepsilon_t - \mu| \le \Delta, \tag{2}$$

where ε_d is the *d*-electron energy in the range close to the energy ε_t of the peak density of states. The number R_{eff} of pairs of electronic states satisfying (2) is proportional to the area ΔS_{eff} of *s*-surface sheets confined between isoenergetic surfaces with energies $\mu \pm \Delta$. The generation condition has the form:

$$\sigma_0 > \sigma_{\text{th}} = \hbar^2 \Gamma \kappa_f / (W^2 R_{\text{eff}}), \tag{3}$$

where σ_0 is the initial inverse population proportional to $\nabla\mu$; σ_{th} is the threshold inverse population difference; $\hbar$ is Planck's constant; Γ and κ_f are the attenuations of electrons and phonons, respectively (in rad · s^{-1}), W is a matrix element of electron-phonon interactions. Estimates made in [2, 3] show that fulfillment of (3) in Fe alloys is possible at $\Delta \approx 0.2$ eV over a wide range of temperatures and concentrations of alloying elements if ΔS_{eff} is high. The existence of large *s*-surfaces is demonstrated with an example of electron spectra in the strong coupling approximation in [2–6]. The threshold inverse population difference σ_{th} is found to be ~10^{-3}; therefore, the generation is possible at levels $\sigma_0 > 10^{-3}$.

In the relaxation time approximation, the stationary nonequilibrium additives to $f_\mathbf{k}^0$ (see, e.g., [7]) have the form:

$$f_\mathbf{k} - f_\mathbf{k}^0 \approx \frac{\partial f_\mathbf{k}^0}{\partial y_\mathbf{k}} \frac{\tau}{k_B T} (\mathbf{v}_\mathbf{k}, \nabla\mu), \tag{4}$$

$$f_\mathbf{k}^0 = \frac{1}{e^{y_\mathbf{k}} + 1}, \quad y_\mathbf{k} = \frac{\varepsilon_\mathbf{k} - \mu}{k_B T}, \tag{5}$$

where k_B is Boltzmann's constant; $\varepsilon_\mathbf{k}$ is the electron energy with a quasi-momentum $\mathbf{k}$. Considering for simplicity that $\mathbf{v}_\mathbf{k} \approx -\mathbf{v}_{\mathbf{k}'}$, σ_0 is expressed as:

$$\sigma_0(\nabla\mu) = f_\mathbf{k} - f_{\mathbf{k}'} \approx \frac{\partial f_\mathbf{k}^0}{\partial y_\mathbf{k}} \frac{2\tau}{k_B T} (\mathbf{v}_\mathbf{k}, \nabla\mu). \tag{6}$$

The fulfillment of the condition $\sigma_0 > \sigma_{\text{th}}$ in a wide range of the concentration C_{le} of alloying elements can be substantiated in the framework of a two-zone model on the assumption that the attenuation Γ_s of mobile *s*-electrons is comparable with $(\varepsilon_d - \mu)\hbar^{-1}$ and is many-fold greater than the attenuation Γ_d of 3*d*-electrons active in the generation of phonons (to the lifetime of *s*-electrons $\tau_s \sim 10^{-15}$ s characteristic of 3*d*-metals corresponds $\hbar\Gamma_s \sim 0.6$ eV). The population density of states with $\varepsilon_d > \mu$ can be kept at a rather high level $f_d^0 \sim 0.1$ due to the scattering of *s*-electrons of energy

$$\mu - \frac{\hbar\Gamma_s}{2} < \varepsilon_s < \mu + \frac{\hbar\Gamma_s}{2} \tag{7}$$

into *d*-states.

In the presence of the *s*–*d* electron scattering, the level of thermal excitation $k_B T$ can be much lower than $\varepsilon_d - \mu$ without a decrease in *d*-state population density. In a similar way, for states with $\varepsilon_d < \mu$ at $\mu - \varepsilon_d > k_B T$, the *d*–*s* scattering provides additional smearing of the *d*-electron distribution. As a result, $\hbar\Gamma_s$ plays a role similar to $k_B T$, and the energy range of *d*-electrons is

$$\mu - \frac{\hbar\Gamma_s}{2} - k_B T < \varepsilon_d < \mu + \frac{\hbar\Gamma_s}{2} + k_B T.$$

If $\varepsilon_t > \mu$ and $\varepsilon_t \in (\mu + \Delta)$, the *d*-state population at $k_B T \ll \hbar\Gamma_s$ requires

$$\frac{\hbar\Gamma_s}{2} \approx \bar{\varepsilon}_d - \mu, \tag{8}$$

where $\bar{\varepsilon}_d$ is the average energy of the actual interval. The attenuation Γ_s is naturally expressed as the sum:

$$\Gamma_s(T, C, d_m) = \Gamma_s(T) + \Gamma_s(C) + \Gamma_s(d). \tag{9}$$

The contribution of $\Gamma_s(T)$ in (9) is associated with scattering at thermally activated instabilities (vacancies, phonons, magnons, etc.) and is decreased with decreasing T. In a binary alloy, $\Gamma_s(C) \sim C(1 - C)$ is associated with impurity scattering, where C is the concentration of alloying additives. The contribution of $\Gamma_s(d)$ is governed by the influence of an instability of characteristic transversal spatial scale d due to the energy release in the excitation region on the attenuation of *s*-electrons (i.e., $d \approx d_{1,2}$); this contribution was not considered in [2, 3]. For crystals without an internal twin structure (as is the case with a packet martensite), d is a characteristic mesoscale of the active region in which wave beams are generated. For the formation of twin crystals where the control wave process involves rather short-wave displacements [8–10], we should also take into account the scale d_{tw} coincident with the thickness of the principal twin component ($d_{\text{tw}} \ll d$).