Martensite Nucleation under Conditions of Austenite Superplasticity and External Magnetic Field

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Abstract. The thermodynamic conditions corresponding to the instability of the crystal lattice before the martensitic transformation are analyzed. The instability of the crystal lattice before the martensitic transformation can be crucial for the occurrence of such a phenomenon as superplasticity of the martensitic transformation. Phenomena arising in an instability state are considered, a theoretical analysis of possible structural states detected experimentally is carried out. The phenomenon of superplasticity of the martensitic transformation under tension in the \( M_s - M_d \) interval and the effect exerted by the magnetic field in this interval are described. As a result of exposure to an external magnetic field in this temperature range, the resulting magnetostrictive stresses in ferromagnetically ordered austenite nanoclusters under superplastic conditions initiate the formation of martensite.

1. Introduction

The analysis of data on phase transformations in a magnetic field [1–6] leads to the conviction that this problem has not yet been completely solved theoretically. The magnitude of the energy of a constant magnetic field with a strength of up to 2.4 MA/m is 1–2 orders of magnitude less than the driving force of most phase transformations. Only a thermodynamic consideration of the issue can lead to the conclusion that the heat treatment in a magnetic field is futile. However, this conclusion is in contradiction with the actual results [7–11]. It is necessary to take into account the influence of the field on the mechanism of nucleation and the kinetics of phase transformations, which substantially determines the structure and properties of the products of the transformation. Also, it is necessary to take into account the phenomenon of superplasticity of austenite, which can have a significant effect on the development of martensitic transformation when exposed to a magnetic field. When the transformation is thermodynamically possible, even a small energy stimulus can have a significant effect on the kinetics. Thus, a comprehensive study of the effect of the magnetic field on the martensitic transformation seems quite relevant.

The following tasks were posed: to analyze the thermodynamic conditions corresponding to the instabilities of the austenite crystal lattice before the martensitic transformation, to consider the phenomena arising in the instability state, to conduct a theoretical analysis of possible structural states, to consider the phenomenon of superplasticity of the martensitic transformation under tension in the \( M_s - M_d \) interval and the effect exerted by the magnetic field in this interval.
2. Experimental Procedures
Mechanical tests were performed on a tensile testing machine 2054 R-5 with a record of the deformation diagram in the load range 0–50 kN. Deformation of the samples was carried out in the temperature range \( M_d - M_s \). For testing at low temperatures (up to -70 °C), the tensile testing machine was equipped with a cryostat. The sample was placed in an acetone-filled cryostat; the temperature was reduced by adding dry ice to acetone. To measure the temperature, a copper-constantan thermocouple was used with a working temperature range from -270 to 400 °C. During the research, samples were used from a model alloy 26N30 (0.26% C, 30% Ni, the rest is iron).

3. Results and Discussion
In most cases, structural phase transitions are first-order transitions. However, if in principle the transformation can be continuous and the lattice deformation during the transition is small (first-order phase transitions are close to second-order transitions), then they can also be considered in the representations of L. D. Landau [12]. On the one hand, such transformations are characterized by the presence of hysteresis and a region of coexistence of two phases (as in phase transitions of the first kind). On the other hand, when approaching the transition point, the phase structures become similar, for example, by decreasing the degree of tetragonality of the tetragonal phase during the cube — tetragon transition, and certain elastic constants of both phases decrease (\( c' = (c_{11} - c_{12})/2 \)). The elastic constants of both phases remain finite at the phase equilibrium point, but vanish after the point \( T_0 \) (at the points of phase stability loss). The described behavior of the elastic constants is confirmed by the data obtained in [13]. These results suggest that lattice instability occurs prior to the martensitic transformation.

In a number of cases, instabilities of the crystal lattice near the point of martensitic transformation are characterized by short-range order of displacements. They are described using the concept of fluctuation displacement waves [14, 15], which allows one to analyze the diffuse scattering patterns of electrons and X-rays. Electron-diffraction and X-ray diffraction methods in [16] revealed and investigated diffuse scattering in austenite and martensite of Fe-Ni alloys (27–50 %Ni) in the temperature range from -130 to 600 °C. A regular transformation of diffuse scattering is observed, which is associated with a change in the atomic-crystalline structure of austenite and martensite when approaching the temperatures of the onset of direct \( M_s \) and reverse \( A_t \) martensitic transformations. Diffuse scattering is described by the spectrum of fluctuation displacement waves and indicates the presence of significant atomic displacements due to the “softening” of the crystal lattice near the points \( M_s \) and \( A_t \).

From the thermodynamic theory of pre-martensitic states [13–16], a similar theory of solid solution decomposition, it follows that near the point of martensitic transformation there are local regions with short-range order of displacements. These regions, in contrast to Frenkel fluctuations, are characterized by a gradual decrease in order with distance from the fluctuation center and the absence of a clear interphase boundary. In diffraction patterns, they correspond to diffuse scattering regions, the intensity of which is determined by the Fourier transform. The main characteristics of these states can be associated with the elastic modules of the initial phase.

The fluctuations of the displacement waves “prepare” the austenite crystal lattice for martensitic transformation, thus, regions with a short-range order of displacements are the most prepared places for the formation of martensite nuclei. The minimum possible size of such fluctuations (about 1 nm) is comparable with the sizes of the minimum critical size of a ferromagnetically ordered cluster (about 0.66 nm [6]) and with the sizes of the critical martensite nucleus calculated from the dislocation model of the martensitic nucleus [17] (the critical radius of the embryo is 3 nm, its critical half-thickness is 0.125 nm). In such regions, the elastic constants decrease almost to zero and therefore even small stresses are enough to initiate a martensitic transformation. As was shown [4–6], before the martensitic transformation begins, ferromagnetic nanoclusters arise in the paramagnetic matrix of austenite. With a high degree of probability, in the places where ferromagnetic nanoclusters are formed, fluctuations of displacement waves can be expected. Under the influence of an external magnetic field, ferromagnetic nanoclusters, having absorbed the magnetic field energy through magnetostrictive stresses, will change
the fields of elastic forces in the crystal lattice, including in regions with short-range order of displacements (where this is much easier to do). A change in the fields of elastic forces in the microvolumes of the matrix lattice contributes to a decrease in the energy barrier for the formation of a critical size nucleus center.

The instability of the crystal lattice before the martensitic transformation can be crucial for the occurrence of such a phenomenon as superplasticity of the martensitic transformation. The martensitic transformation proceeds by a displacement or “shear” process, which at the macroscopic level can be described as a deformation with an invariant plane. In the case where along with the martensitic transformation there is an applied external stress, phenomena such as the martensitic transformation (caused by stress and strain), the formation of new nucleation sites, and also superplasticity can occur. Superplasticity is understood as the ability of a material to plastic deformation many times higher than expected. In some cases, this can be hundreds of percent, but for low-plastic materials, the ability to deform by tens of percent should also be attributed to superplasticity. In another way, superplasticity can be defined as a special state of a material capable of large deformation. Superplasticity due to the state of the metal can be of two types: structural (superplasticity of materials with ultrafine grains) and transformations (superplasticity due to phase transformation).

In the work of Z. Nishiyama [18] it was established that the maximum plasticity is observed in the temperature range from the point \( M_d \) to the point \( M_s \). Here and in the text, \( M_d \) is the temperature lying above \( M_s \), but below the equilibrium temperature of the martensitic transformation of \( T_0 \). Below \( M_d \), martensite may form as a result of deformation of the initial austenite. The phenomenon of superplasticity of austenite before martensitic transformation is used in practice to correct the product. During hardening, an experienced therapist a little earlier than the martensitic transformation begins, removes the tool from the hardening medium and produces deformation. A characteristic of the superplasticity of the martensitic transformation is the presence of a plasticity peak. Below \( M_s \) (after the onset of martensite formation caused by cooling), the ductility sharply decreases. Therefore, the mechanical processing of products in the temperature range \( M_d - M_s \) (where superplasticity is manifested) initiates the formation of martensite as a result of deformation. This is carried out easily even at low stresses, since the superplastic metal material resembles resins, hot glass, thermoplastics, and other viscous bodies in their behavior during deformation [19].

![Figure 1. The influence of the test temperature on the mechanical properties of 26N30 alloy.](image)
To observe the phenomenon of superplasticity, an experiment was carried out with a 26N30 metastable austenitic alloy \((M_s = -60 \, ^\circ C, M_d = 25 \, ^\circ C)\), which was tested by stretching in the temperature range \(M_d - M_s\). The dependence of the mechanical properties on the tensile test temperature is shown in figure 1. As can be seen, in the \(M_d - M_s\) interval, a peak of superplasticity is observed, where the relative elongation is almost 100%. This elongation is explained by the pre-martensitic instability of the crystal lattice, and also by the fact that when martensitic crystals arise (as a result of deformation), high local stresses are removed and thereby the formation and concentration of the neck are prevented. Immediately before the temperature \(M_s\), an abnormal inverse dependence of the yield strength is observed. The decrease in the yield strength of metastable austenitic steel before \(M_s\) is due to the fact that, when tensile near \(M_s\), elastic stresses cause the instantaneous formation of a large number of martensite crystals, which leads to a noticeable macrodeformation (jump in the tensile diagram due to the development of martensitic transformation). An increase in the yield strength occurs after the appearing martensitic crystals begin to play the role of a skeleton when the sample is stretched.

![Figure 2](image1.png)  
**Figure 2.** Schematic diagram of the change in the chemical free energy of the martensitic transformation \(\Delta G\).

![Figure 3](image2.png)  
**Figure 3.** Schmitt factor diagram describing the effect of applied stress.

Since the martensitic transformation is carried out by the cooperative shear motion of atoms, it is easy to imagine that the applied elastic stress promotes the transformation. However, the role of plastic deformation in the martensitic transformation is very complex. To understand the martensitic transformation caused by deformation, it will be more productive to consider not the influence of deformation, but the effect of the applied stress. The figure schematically shows the change in the chemical free energy of martensite and austenite depending on temperature. In this figure, \(T_0\) is the temperature at which austenite and martensite are in thermodynamic equilibrium. The difference between the free energies of austenite (\(\gamma\)) and martensite (\(\alpha\)) \(\Delta G^{\gamma\rightarrow\alpha}_{M_t}\) at a temperature of \(M_t\) is a critical driving force for the onset of martensitic transformation. When stresses are applied to austenite at a temperature \(T_1\) between \((M_t, T_0)\), the driving force of the transformation \(F\), due to the stresses, is added to the chemical driving force \(\Delta G^{\gamma\rightarrow\alpha}_{M_t}\). The martensitic transformation begins at a critical stress, when the total driving force is equivalent to \(\Delta G^{\gamma\rightarrow\alpha}_{M_t}\). In figure 2, \(F_{cr} = \Delta G^{\gamma\rightarrow\alpha}_{M_t} - \Delta G^{\gamma\rightarrow\alpha}_{M_t}\) it represents the critical driving force necessary for the martensitic transformation caused by stress.
at $T_1$. The value of this driving force of the transformation depends on the stress and orientation of the transformed martensitic plate relative to the applied stress (see Figure 3):

$$F_{tr} = \tau \gamma_0 + \sigma \varepsilon_n,$$

where: $\tau$ – shear stress acting along the shear direction during the transformation in the habit plane of martensite; $\gamma_0$ – shear strain during transformation along the shear direction of the shape strain in the habit plane; $\sigma$ – normal component of stress acting perpendicular to the habit plane; $\varepsilon$ – dilatational component of the shape deformation during transformation.

The figure 3 shows the Schmitt factor diagram describing the effect of the applied stress $\sigma$ along the axis $A$ when the martensitic transformation is induced in the H-plane $P$ with the normal $N$, where $S$ is the direction of shape deformation for martensite and $S_m$ is the maximum elongation in the H-plane during shape deformation. When a stress $\sigma$ is applied to the sample, for any given orientation of the martensitic plate, $\tau$ and $\sigma$ can be expressed as follows:

$$\tau = \frac{1}{2} \sigma (\sin 2 \Theta) \cos \alpha;$$

$$\sigma = \frac{1}{2} \sigma (1 + \cos 2 \Theta),$$

where: $\sigma$ – absolute value of the applied stress; $\Theta$ – angle between the axis of the applied stress and the normal to the habit plane; $\alpha$ – angle between the direction of shear during the transformation and the direction of maximum shear in the habit plane induced by the applied stress. Based on equations (1), (2) and (3), the driving force of the transformation due to the applied stress $\sigma$ can be expressed as:

$$F = \frac{1}{2} \sigma (\gamma_0 (\sin 2 \Theta) \cos \alpha \pm \varepsilon_n (1 + \cos 2 \Theta)).$$

When the martensitic transformation is induced by the stress applied to the polycrystalline austenite, and the grain orientations in the austenite are randomly distributed, the martensitic plate is formed first, the orientation of which provides the maximum value $F$.

An external magnetic field acts on ferromagnetically ordered clusters in austenite, which leads to local anisotropic deformation of the atomic lattice, which is caused by the forces of exchange and magnetic interactions. Calculations show that a single-domain particle always tends to be elongated, since this form reduces the energy of the demagnetizing field [20]. In crystals with a direction of easy magnetization $<100>$, these strains can easily interact with the Bane strain or initiate the mechanism of reconstructive martensitic transformation proposed by V. S. Kraposhin [21]. Due to the anisotropy of local spontaneous and forced magnetostrictive deformations in microvolumes with a spin order, the structural equivalence of the octahedral interstitials (in the BTC sublattice of the Bane) is violated and a favorable situation arises for the preferred ordered arrangement of carbon atoms in the interstices of the type $[[0, 0, 1/2]]$ and $[[1/2, 1/2, 0]]$, which is controlled by an energy difference of $10^{-22}$ J [22] created by a uniform magnetostrictive stress of the order of 10 MPa along the [001] axis. In this case, the probability of formation as a result of the transformation of the ordered phase in those microvolumes of the matrix where short-range order has already taken place can significantly increase. It should be noted that the preferred orientation of carbon under the action of magnetostrictive deformations will lead to greater deformation than magnetostriction itself. This increased deformation creates stresses in the surrounding austenitic matrix, which, under the conditions of austenite superplasticity, become sufficient to initiate shear martensitic transformation (for example, by the mechanism described in [21]) already outside the ferromagnetically ordered nanocluster.

4. Conclusions

Thus, it was shown that before the start of the martensitic transformation, crystal lattice instability is observed, which is accompanied by a decrease in the elastic constants at the transformation point to zero.
and causes the presence of superplasticity in the $M_S - M_D$ range. As a result of exposure to an external magnetic field in this temperature range, the resulting magnetostrictive stresses in ferromagnetically ordered austenite nanoclusters under superplastic conditions initiate the formation of martensite.

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