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Isothermal martensitic transformations

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Abstract. Martensitic transformations have long been considered most characteristically athermal — in the sense that they develop, with changing temperature, at a tremendous temperature-independent rate and cease to occur at isothermal conditions. Over the past decades, however, isothermal martensitic transformations (IMTs), which develop at low temperatures for a long time, have been discovered and studied. This review covers basic experimental data on IMT kinetics, discusses the way IMTs are affected by various influences, examines the current theoretical understanding of their nature, and looks at how they relate to kinetically different phase transformations and other thermally activated low-temperature processes in solids.

1. Introduction

The basic feature of isothermal martensitic transformation (IMT) that sets it apart from all other phase transformations is that the transformation develops at low temperatures for a long time. The laws governing such transformation, its nature, and its relation to other processes in solids constitutes the subject of the present review.

The plan is as follows. Section 2 briefly discusses the general laws governing martensitic transformations and the history of the development of modern ideas about martensitic transformations. Without this material it would be impossible to understand the special features of IMT. Section 3 covers the experimental data on the kinetics of IMT in iron-based alloys. Historically, these were the first alloys in which IMT was discovered and studied in detail. Data on the effect of the chemical composition of alloys and the various factors on IMT are also presented. Section 4 deals with the experimental data on the kinetics of IMT in alloys based on copper and other materials. The results discussed in that section show that IMT is a universal phenomenon. The structure of IMT products is covered in Section 5, and the main aspects of the theory of IMT in Section 6. The relation of IMTs to other thermally activated processes in solids is analyzed in Section 7.

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2. General laws governing martensitic transformations

The study of the general laws governing martensitic transformations, which began at the end of the 19th century, has been covered in a large number of works, whose results are summarized in a number of reviews and monographs (see Refs [1 – 11]). Martensitic transformation causes steel to strengthen during quenching and is the reason for unusual mechanical properties of alloys (properties that have found wide use in various areas of technology and medicine) such as reversible strain caused by this transformation (the shape memory effect), superelasticity, superplasticity, and high damping.

While not so long ago the term 'martensitic transformation' was used only to describe a transformation that takes place in steel undergoing quenching, today it has acquired a very broad meaning. By martensitic transformation, we mean one of the main phase transformations in solids whose principal features are the absence of any change in the concentration of the phases (the diffusionless nature of the transformation) and the rigidly governed, ordered, and

collective nature of the movement of atoms in the process of transformation over distances not exceeding the interatomic distance (the cooperative mechanism of the transformation).

In addition to steel, martensitic transformations have been discovered to occur in many materials: pure metals (Fe, Co, Ti, U, Li, Na, Zr, Ce, Tl, and others), in alloys based on these and other metals (Fe – Ni, Fe – Mn, Ti – Mo, Ti – Ni, Ti – Mn, Ti – Zr, Ti – Cr, Ti – Fe, U – Cr, Li – Mg, Cu – Al, Cu – Zn, Cu – Sn, Au – Cd, Mn – Cu, Co – Ni, In – Tl, and others), and in organic and inorganic compounds. The range of materials in which martensitic transformations are observed continues to broaden. The products of martensitic transformations may be either the thermodynamically stable phases (as in the case of transformations in pure metals) or the metastable phases (the martensite of steel, the martensite phases of the alloys Cu – Al, Cu – Sn, Cu – Zn, Ti – Ni, and others).

The wide occurrence of martensitic transformations, the special nature of this type of transformation, which places it close to other cooperative processes in solids (twinning, kink formation, etc.), and the enormous practical importance explain the substantial interest in martensitic transformations and have resulted in a large number of research papers devoted to this phenomenon, leading to the establishment of the basic laws governing the mechanism, kinetics, and crystallography of the transformation and building a modern theory of the martensitic transformation [1, 4, 7].

The main kinetic features of the athermal martensitic transformations amount to the following:

1. As the sample is cooled, a martensitic transformation begins at a certain temperature T_s (also denoted by M_s), known as the martensite point. Usually, the position of this point is independent of the cooling rate.

2. The rate of the transformation is extremely high even at low temperatures. This has prompted researchers to believe that the martensitic transformation is an athermal process, i.e., a process in which the nucleation and growth of crystals of the new phase is temperature-independent.

3. The transformation extends to the temperature range from the martensite point T_s to a certain temperature T_f (or M_f) below which there is no transformation even in the presence of an untransformed initial phase. In isothermal conditions within the temperature interval from T_s to T_f, the transformation in most cases rapidly decays, but reappears when the temperature is lowered, such that the amount of the forming phase is a function of temperature. The temperature dependence of the amount of forming martensite is described by what is known as the martensite curve, whose general form for all cases is shown in Fig. 1.

4. In most cases, martensite crystals grow with a tremendous rate, close to the speed of sound. The growth rate is practically independent of temperature and is much higher in the direction parallel to the plane of the interphase boundary of the martensite crystal than in the direction perpendicular to that plane. The high and temperature-independent growth rate suggests that the growth of martensite crystals is not a thermally activated process.

5. The transformation develops mainly because new crystals are constantly being formed and not because those formed earlier grow in size. In the case of thermoelastic martensitic transformation, the increase in the amount of the martensite phase may also proceed because of the growth of the earlier created crystals.

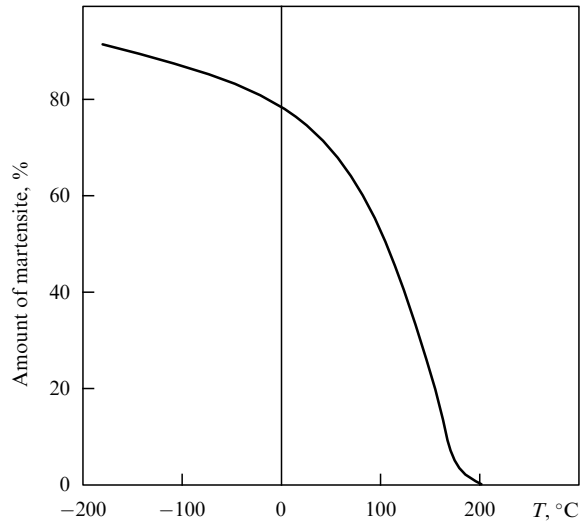

Figure 1. The martensite curve: the temperature dependence of the amount of martensite [9].

3. Kinetics of isothermal martensitic transformation in iron-based alloys

3.1 General laws

Until recently, it was assumed that one of the most characteristic features of the martensitic transformation is the development of the transformation below the martensite point only in cooling and rapid decay at a constant temperature. A slight increase in the amount of martensite in the course of quenching observed occasionally was considered a spurious phenomenon related, for example, to the relaxation of the quenching stresses.

This situation changed dramatically after Kurdyumov, using his theory in which the martensitic transformation was considered a type of phase transformation in the solid state, arrived at the conclusion that at a sufficiently low temperature, the transformation should develop in isothermal conditions [1, 2]. Later, IMT was detected in a series of experiments conducted by Kurdyumov and Maksimova [12 – 14]. Their results triggered a large number of experimental and theoretical works, which led to progress in the understanding of the nature, the mechanism, and the laws governing IMT.

A few words about the history of the problem are in order.

Benedics [15] was probably the first to mention the development of a martensitic transformation at constant temperature (1908) when he discovered the characteristic martensite relief on the microsection of a tempered sample of steel with 1.6%C several hours after the microsection had been prepared. In 1925, Hanemann and Schrader arrived at a similar result [16]. The spontaneous formation of martensite at room temperature was established by Honda and Idai [17], who measured hardness, and by Bain [18], who used the X-ray method. Tamman and Scheil [19] used the results of specific-volume measurements and detected a prolonged (more than 4 hours) isothermal formation of martensite at a relatively low temperature (−17 °C). A significant increase in hardness (from 74.3 to 79.4) as the time of exposure to liquid oxygen was increased from 12 to 24 hours was detected in steel with

0.86%C, 13.66%Co, and 9.31%Cr [20]. These data, together with Tamman and Scheil's data [19], were the first indications of the prolonged process of martensitic transformations at low temperatures.

Data on the development of the martensitic transformation in isothermal conditions can also be found in Refs [21–23]. The researchers found that below the martensite point, austenite transforms isothermally into martensite. In steel with 1.2% C, when the temperature falls below the martensite point T_s, the intensity of the isothermal transformation increased, reached its maximum value when the temperature was 70 °C below T_s, and then decreased [24].

In studying the reasons for the changes in the size of tempered products during operation or in weathering at room temperature, it was found that the change in the length of samples of tool steel observed at room temperature is related to the isothermal transformation of the residual high-temperature phase (austenite) into a structure with a larger specific volume (martensite) [25–27]. The transformation of austenite into martensite does not stop immediately after the cooling of the sample, and up to 5% of residual austenite transforms into martensite isothermally at room temperature. The isothermal transformation of austenite proceeds rapidly during the first hour and a half after quenching and continues at a much lower rate for several months.

Studies of the process of thermal stabilization of austenite in steels with $T_s > 120$ °C have shown that martensite forms in isothermal exposure below T_s [28]. As the temperature drops, the amount of isothermal martensite increases to a certain maximum (3.7%) and then drops almost to zero.

Thus, by 1947–1948, a substantial body of data on the possibility of isothermal transformation of austenite into martensite had been gathered. These data can be generalized as follows. When the temperature of a sample reaches a value that lies within the martensite interval (from T_s to T_f), one can observe an isothermal transformation of austenite into martensite that lasts a certain time. The amount of isothermally forming martensite depends on the degree of supercooling. The transformation proceeds most intensively at temperatures of 50–100 K; under strong supercooling and near the martensite point, the intensity of transformation is lower. The amount of isothermally formed martensite is usually not large, approximately 3–5%.

In light of the then-prevalent idea that a martensitic transformation is a purely mechanical process existing, like twinning, because of purely mechanical reasons [19, 21], the formation of martensite in isothermal conditions was thought to be a phenomenon related to stress relaxation that causes additional formation of martensite at constant temperature.

The modern period in IMT studies began with the already mentioned works of Kurdyumov [1, 2] and Kurdyumov and Maksimova [12–14]. The researchers found that the rate at which austenite is transformed into martensite is temperature-dependent and for all practical purposes vanishes at very low temperatures. In carbon steel (1.65% C), manganese steel (0.7% C, 6.5% Mn, and 2% Cu), and high-speed steel (1.0% C, 7.0% Cr, 3.6% W, and 1.0% V), the martensitic transformation below −50° becomes measurable, while at the liquid-nitrogen boiling point (−196 °C), the rate is very small (Fig. 2). For a relatively low T_s, austenite may be partially (in carbon and high-speed steels) or fully (in manganese steels) supercooled to temperatures that are much lower than T_s. The transformation of supercooled austenite occurs under subsequent heating; the amount of martensite in some cases increases under heating by 30% or even more.

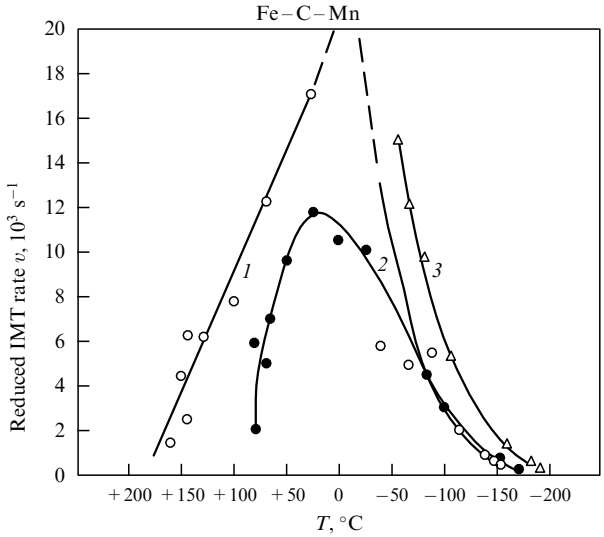

Figure 2. Temperature dependence of the initial reduced IMT rate (v) in manganese steels with different martensite points: (*1*) Fe–0.85% C–2.2% Mn, $T_s = +155$ °C; (*2*) Fe–0.95% C–3.5% Mn, $T_s = +85$ °C; and (*3*) Fe–0.70% C–6.5% Mn–2% Cu, $T_s = -50$° [2].

The character of isothermal martensitic transformations changes as the temperature drops. At high temperatures, at which IMT is still possible, the process decays very rapidly. At lower temperatures, the duration of IMT grows from several minutes to several hours in the temperature ranges from −40 to −50 °C and from −100 to −120 °C, respectively, and exceeds 10 h (in alloy steels) at liquid nitrogen temperatures. For all three types of steel studied, the rate of transformation was found to decrease with temperature. If after cooling to −196 °C the sample was swiftly moved to a medium at room temperature, the austenite state was retained and no martensite was formed. Thus, it proved possible to completely suppress the martensitic transformation both in cooling and in heating.

Estimates of the transformation activation energy yielded 650, 780, and 900 cal mol^{-1} for the U16, EI184, and 38C brands of steel, respectively.

Thus, new important results were obtained in these works. The results helped in understanding the nature of the martensitic transformation and showed that many conventional ideas about the nature and kinetics of the martensitic transformation (that it is impossible to suppress such a transformation by rapid cooling, that the amount of the martensite phase is determined almost completely by the temperature, and others) require re-evaluation and substantial modifications. Further investigations focused on the detailed study of the law governing IMT and the special features of IMT. We now consider the main results of these investigations.

It has been established that IMTs, just as martensitic transformations in general, develop mainly because of the formation of new martensite crystals rather than because of the growth of the already existing crystals. The growth rate of martensite crystals in an IMT is extremely high even at temperatures as low as −196°, and the IMT rate is determined on the whole by the rate of nucleation of martensite crystals.

Using the Fe – 0.85% C – 2.2% Mn steel, Maksimova [29] and Kurdyumov and Maksimova [30] found that as the temperature decreases and moves away from the martensite point, the IMT rate rapidly grows and then rapidly decreases (see Fig. 2). This increase in the IMT rate with decreasing temperature is related to the fact that as we move away from the temperature of equilibrium, the work done in nucleation rapidly decreases, while the energy of thermal vibrations near the maximum rate (about 0 °C) is still relatively high, which ensures a high probability of thermal fluctuations and the appearance of a large number of critical nuclei, which become real under exposure. If this is so, we can follow the entire temperature dependence of IMT by slowing down the process of nucleus formation. The work done in nucleus formation at room temperature can be increased by lowering the temperature of the martensitic transformation. Such an approach has been corroborated by experiments with steel with 0.95% C and 3.5% Mn, which has a lower martensite point ($T_s = 85$ °C). In this steel, an IMT was observed in the entire temperature range of the transformation (see Fig. 2). The reduction of the initial transformation rate was also detected in the steel Fe – 0.7% C – 6.5% Mn – 2% Cu with $T_s = -50$ °C; in this case, only the descending branch of the temperature dependence of the IMT rate was observed.

The temperature dependence of the IMT rate has also been established for a number of Fe – Ni – Mn alloys, in which the nickel content amounted to 22.7 – 23.8% and the manganese content to 3.1 – 3.4% (T_s varied from +12 to −55 °C). In all these alloys, the martensitic transformation was isothermal. As the temperature of the beginning of the transformation decreased, the position of the rate maximum shifted toward a lower temperature, and the lower the martensite point, the greater the shift. Near −196 °C, the transformation rate became close to zero. With these alloys, the entire temperature dependence of the transformation rate was studied for the first time, and it was found to have the same shape (a curve with a maximum) as in other phase transformations.

The presence of an IMT in high-chromium steel with the martensite point near −65 °C was detected by directly cooling the samples to temperatures in the interval from −70 to −150 °C and by pre-supercooling the samples to −196 °C [31]. The initial transformation rate exhibited a distinct temperature dependence with a peak at −140 °C. However, the authors of [31] were unable to fully suppress transformation in the cooling stage in this steel, and they therefore concluded that an isothermal martensitic transformation is always preceded by athermal transformation.

A similar result, the distinct temperature dependence of the amount of isothermally emerging martensite and the initial transformation rate, was obtained in [32] for stainless steel with 14.38% Cr, 9.06% Ni, 0.008% C, and 0.034% N. The researchers showed, in contrast to the results in [31], that IMT may also develop in the absence of athermal martensite. Attempts to represent the data on the temperature dependence of the initial transformation rate in the 'logarithm of transformation rate — $1/T$' coordinates did not lead to a linear temperature dependence at low temperatures. In view of this, it was suggested that the kinetics of a martensitic transformation could not be described by one parameter, the activation energy.

Analyzing their data, the authors of [32] concluded that thermal fluctuation plays an important role in the kinetics of a martensitic transformation. They noted, however, that the nature of this transformation is such that it cannot be considered an ordinary one, because other factors, such as the nucleus size distribution, stress fields, stress relaxation, and the effect of separation of austenite by martensite crystals, play an important role in its development. The researchers believe that a general theory of martensitic transformation must not only include the main ideas of the 'reaction path' theory [33] but also take the important role of thermal fluctuations into account.

Machlin and Cohen [34] did their research as a response to the works of Kurdyumov and Maksimova [12 – 14]. Their goal was to extend the 'reaction path' theory [33], initially developed in order to explain the athermal features of the martensitic transformation, to IMT. The researchers used the Fe – 29.5% Ni alloy with the martensite point near −18 °C to study the IMT in the temperature range from the martensite point down to −196 °C by the electrical-resistance method. They also studied the response of IMT to heating to temperatures above the martensite point, to plastic prestrain, to stress, and to the presence of martensite that was in the sample at the beginning of isothermal exposure. The researchers concluded that IMTs occur mainly because of the formation of new plates rather than because of the growth of the already existing plates, and the IMT rate depends on the temperature and time of isothermal exposure, the amount of athermal martensite that had formed by the beginning of the transformation, and internal and external stresses. They believed that the formation of martensite nuclei in IMT occurs because of thermal activation of regions of austenite with extremely high local stresses. In addition to isothermal transformation, there is also athermal transformation; in the latter case, no thermal fluctuations are needed for martensite nucleation. Machlin and Cohen [34] concluded that the ideas of Kurdyumov and Maksimova [12 – 14] disagree with the main characteristic features of the martensite reaction, because these ideas do not explain athermal transformation.

Maksimova et al. [35] studied the dependence of the transformation rate on the position of the martensite point and the martensitic transformation interval and the effect of the composition on the IMT kinetics in steels with 2.2 – 6.5% Mn and 0.7 – 0.95% C (T_s in the interval from +155 to −40 °C) and found that the shape of the kinetic curves strongly depends on the position of the martensite point. In steels with $T_s > 20$ °C (155 and 85 °C), two branches of the initial IMT rate were observed: as the temperature decreased, the transformation rate first increased and then decreased. In steel with a low martensite point ($T_s = -50$ °C), only reduction of the initial transformation rate with temperature was recorded. The authors of [35] explain such behavior by the decreasing importance of the thermodynamic factor as the transformation interval shifts toward lower temperatures, which may be related to the change in the work done in the formation of nuclei of the new phase caused by a rise in the yield point as the manganese and carbon content varies. The researchers also expressed the opinion that small portions of martensite may have an activating effect on further development of martensitic transformations in steels with a low martensite point, which are highly elastic at low temperatures.

The effect of the position of the martensite point on the kinetic features of the transformation has been corroborated by Maksimova et al. [35], who experimented with Fe – Ni – Mn alloys (22.5 – 23.8% Ni and 3.1 – 3.4% Mn, with T_s varying between 0 and −80 °C). The researchers found that, qualitatively, all the alloys exhibit the same temperature

dependence of the IMT rate: the transformation rate increases as the temperature decreases, reaches its maximum, and then decreases. Near −196 °C, the transformation does not develop. The lower the martensite point is, the smaller the IMT rate, the lower the temperature of the peak in the transformation rate, and the longer the time of the isothermal process. Also important was the discovery of the possibility (at least theoretical) of complete supercooling of the initial phase.

Dilatometric measurements and measurements of thermal emf for chromium steel containing 1.43% C and 2.55% Cr ($T_s = 25$ °C) [36] showed that the IMT rate rapidly increases as the temperature falls below the martensite point, attains its maximum at −20 °C, and then decreases, vanishing at −150 °C. After a stabilizing treatment (heating to room temperature and a somewhat higher temperature after partial martensitic transformation) was applied to the steel, the researchers discovered (for the first time) that there exists a certain incubation period for IMT: the rate of transformation in the initial moments of exposure was very small, then rapidly increased, reached its maximum value for the given temperature, remained almost constant for some time, and then gradually decreased. The researchers concluded that the nucleation of the crystals is never athermal; rather, it occurs because of thermal fluctuations, and hence it must be assumed that all the martensite emerges isothermally. They believed that this conclusion was a general one for martensitic transformations, including such transformations in carbon steel.

The first to study IMT in a more refined way were Shih et al. [37]. They took an iron–nickel–manganese alloy with 23.2% Ni and 3.62% Mn, which is very close in composition to the one used by Kurdyumov and Maksimova [12], and studied the IMT by the electrical-resistance method in the temperature range from −90 to −196 °C in conditions where no nonisothermal martensite was present. They found that in these conditions, the initial transformation rate is so small that the development of the transformation can be detected only after a prolonged incubation period (up to 20 min at −196 °C). At the onset, the transformation developed with a rate that steadily increased with time (it reached its maximum value after 1.5–2.0% of the martensite had formed), and then gradually decayed. The temperature dependence of the transformation rate had the same shape (a curve with a maximum) as in the previous work done with a similar alloy [12, 13]. The authors of [37] conducted special experiments and found that in this case, when the samples contained at least a small (1.5–2.0%) amount of martensite by the time exposure began, an IMT begins immediately at the maximum rate, and after that the transformation rate only decreases with the passage of time. The researchers believed that this explains the fact that the transformation proceeds with the highest rate at the beginning of isothermal exposure in Kurdyumov and Maksimova's experiments [12, 13], where there was always a small amount of nonisothermal martensite at the beginning of the isothermal transformation. Estimates of the nucleation activation energy yielded values ranging from 13,900 cal mol^{-1} at −90 °C to 6,150 cal mol^{-1} at −196 °C. Just as Kurdyumov and Maksimova did earlier [12, 13], the researchers were able to completely supercool austenite down to −196 °C in an iron–nickel–manganese alloy and in a manganese steel with 1.10% C and 5.24% Mn. In the latter case, the researchers followed the IMT at −196 °C and found that it had the same features as the transformation in the iron–nickel–manganese alloy: a very small initial rate, acceleration of the rate in time, and subsequent slow decay of the process.

Maksimova et al. [35] compared the kinetics of the martensitic transformations in two series of alloys (manganese steels and iron–nickel–manganese alloys) with different martensite points. The goal of their research was to establish the overall picture of how the transformation kinetics changes with the temperature interval of the transformation, on the one hand, and with the alloy composition, on the other. The researchers found that as steels and alloys with higher martensite points are replaced by steels and alloys with lower martensite points, the curves representing the temperature dependence of the IMT rate are shifted and changed in an orderly manner. As the martensite point decreases, the initial transformation rate decreases within the entire temperature range (this is very evident in Fe–Ni–Mn alloys, while not so evident in manganese steels). In Fe–Ni–Mn alloys, irrespective of the position of the martensite point, the temperature dependence of the IMT rate exhibits a distinct peak, which shifts toward lower temperatures as the martensite point decreases (from +25 °C in the N23G alloy with the martensite point at +12 °C to −115 °C in the N24G3 alloy with the martensite point at −55 °C). In manganese steels, the lowering of the temperature interval of transformations leads to a gradual narrowing of the ascending branch of the rate's temperature dependence and to its complete disappearance when the martensite point is low ($T_s = -50$ °C). In Fe–Ni–Mn alloys, as alloys with higher martensite points are replaced by alloys with lower martensite points, the duration of IMT rapidly grows together with a decrease in the initial transformation rate. Hence, the final IMT effects are quantities of the same order for all alloys, although the initial transformation rates for these alloys differ substantially.

3.2 Effect of composition

The effect of nickel content (12.4–35%) and carbon content (0.015–0.95%) on the kinetic features of martensitic transformations and the martensite microstructure was systematically studied in [38, 39] using a large group of Fe–Ni and Fe–Ni–C alloys with T_s in the interval from +20 to −196 °C. In all the alloys, the martensitic transformations were found to intensively develop already in the cooling process (with the rate 10 K min^{-1}) and be of an explosive nature with a very small isothermal component. As the temperature decreases, the explosive effect diminishes due to the decrease in the energy of thermal vibrations in the temperature range from −150 to −196 °C. It is within this temperature interval that the tendency toward an IMT increases. The researchers therefore concluded that the explosive kinetics of martensitic transformations is closely linked to the high values of the yield point of austenite, which ensures the accumulation and storage of elastic energy.

All the alloys studied in Refs. [38, 39] were nominally divided into three groups, with each group characterized by its own specific kinetic features (Fig. 3). The alloys of all three groups behave in approximately the same way in conditions of continuous cooling, but the isothermal nature of the transformation clearly manifests itself only in alloys of group I with relatively high martensite points ($T_s > 10$ °C). At the beginning of isothermal exposure, the alloys of this group had no martensite, and the overall amount of martensite that appeared by the isothermal-kinetics path was found to be 20 to 30%. In alloys of group II (T_s ranging

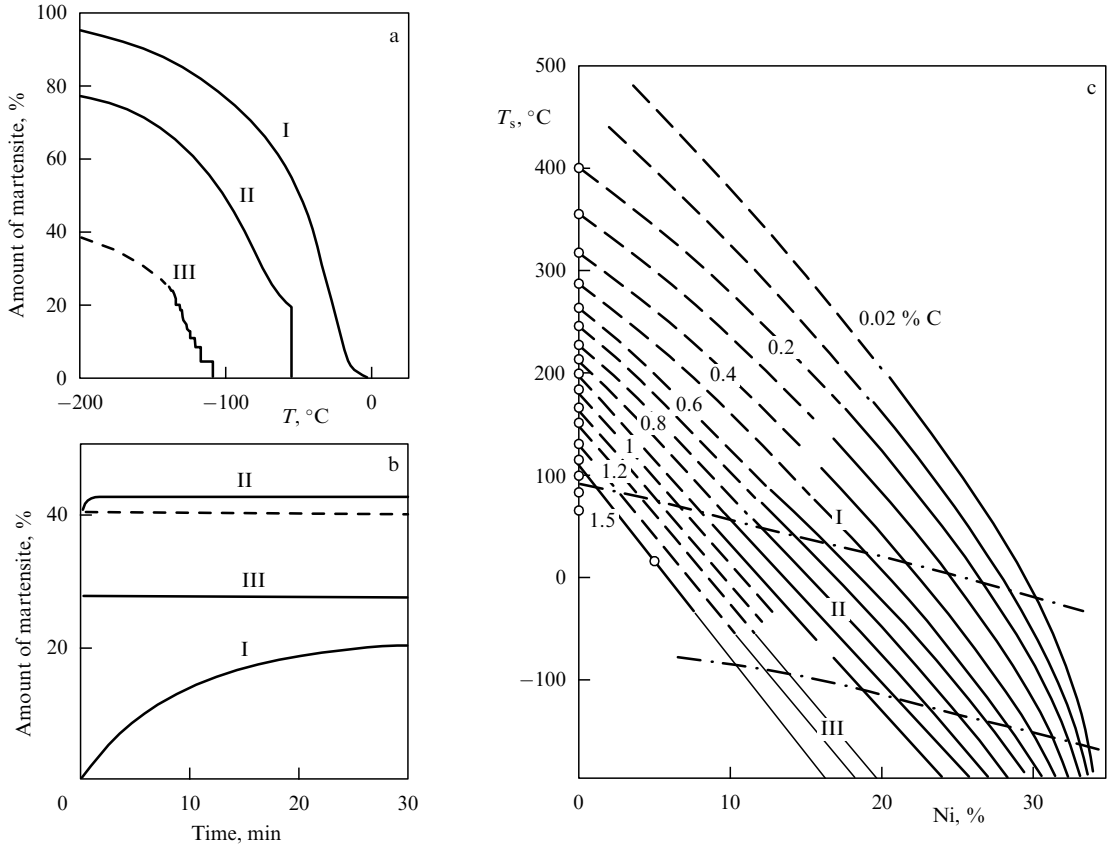

Figure 3. Temperature vs. content regions for martensitic transformations in Fe – Ni – C alloys [39].

from −20 to −100 °C), up to 40 to 50% of the martensite is formed at the start by the athermal-kinetics path in an explosive manner, while an additional amount formed by the isothermal-kinetics path appears with further exposure to temperatures below the martensite point, and the lower the temperature of the explosion, the smaller this additional amount of martensite. In group II alloys, martensite is formed only in an explosive manner, by jumps. The researchers concluded that the appearance of IMT in the alloy they studied depends only weakly on the content of elements and is determined solely by the position of the martensite point. The boundaries between these groups are only nominal.

The dependence of the kinetics on the element content was reported in [40], where martensitic transformations in steels of different compositions were studied. For the martensitic transformation to have the isothermal type, the temperature at which the martensitic transformation begins must be low. IMT may be suppressed through very slow cooling or through exposure at room temperature.

The Fe – 22.7% Ni ($T_s = 165°$) and Fe – 28.8% Ni ($T_s = 13°$) alloys transformed by the isothermal-kinetics path even after exposure to temperatures above the martensite point. As the per-exposure temperature increases, the incubation period and the amount of isothermal martensite decreases. Exposure to temperatures much higher than the martensite point completely suppresses subsequent isothermal transformations.

Isothermal kinetics was also observed in a number of alloys, Fe – (0.35 – 20.8)% Mn – (0.005 – 1.45)% C, at temperatures as low as −180 °C [41, 42]. As the temperature drops, the amount of martensite formed by isothermal exposure increases, reaches its maximum, and then decreases to zero. An increase in carbon content with the manganese content remaining constant leads to an increase in the amount of isothermal martensite and a shift in the maximum of isothermal transformations to lower temperatures. A similar dependence was discovered when the manganese content increased with the carbon content remaining constant.

The results in [43] point to a strong effect of interstitial atoms — carbon and nitrogen — on the features of IMT and the martensite points. The researchers found that as the total content (carbon plus nitrogen) varied from 10^{-3} to 10^{-7} %, the temperature at which IMT begins increases, while the temperature at which athermal martensitic transformations begin does not change.

Isothermal formation of the hexagonal ε-phase in manganese alloys and steels with T_s in the range from +100 to −10 °C, in which no α-phase appears after quenching, was studied in [44], where it was found that for an IMT to develop, there must be a certain supercooling below T_s. In the G20 alloy, an IMT was found to develop in the temperature range from +40 to +70 °C. Below and above this temperature interval and in the course of time, the transformation rate rapidly decreases. In the G25S steel, an IMT develops with the highest rate in the temperature range from −10 to −20 °C, while under continuous cooling, a martensitic transformation develops in the +30 to −70 °C temperature range. As the temperature decreases, the transformation rate also decreases, and there is no transformation at −196 °C. For the G20 and G25S alloys, the initial phase could not be supercooled, and an ε-phase forms in the process of cooling.

In the 40G23 steel, IMTs develop with the highest intensity in the temperature range from −20 to −40 °C, while no IMTs occur below and above this interval. In all studied alloys, after the transformation has decayed (and under cooling), there still remains a large amount of untransformed initial γ-phase. Injection of the carbon content in the Fe – Mn alloys reduces the intensity of the transformation.

Studying a series of Fe – Cr – Ni alloys has shown [45] that varying nickel concentration from 3 to 10% with chromium content remaining constant at 17 – 18% substantially (by approximately 450 °C) lowers the temperature at which athermal transformation begins, while the temperature at which IMT begins changes only slightly. This has led to the conclusion that when the alloy contains less than 7% nickel, martensite first forms by the athermal-kinetic path, while in alloys with more than 7% nickel, isothermal martensite is the first to appear.

The dependence of the type of a martensitic transformation on the element content was also established for a series of Fe – Ni – Cr alloys in [46]. With the total content of nickel and chromium kept practically constant (25 – 26%), the kinetic features of the martensitic transformations in these alloys were found to depend on the nickel-to-chromium content ratio. As the nickel content decreased from 30.5 to 7.6% and, at the same time, the chromium content increased from 4.8 to 17.5%, a transformation from athermal transformation to isothermal transformation was observed. The lowering of the temperature to −196 °C leads to the formation of 5 to 35% martensite, and a subsequent increase in the temperature to the room value leads to formation of more martensite, which suggests that the transformation is isothermal. The most characteristic features of the IMT in the alloys in question are the presence of an incubation period, the presence of a maximum in the transformation rate, substantial amounts of martensite formed by the isothermal-kinetics path, and the lag in transformation under rapid cooling. These features manifest themselves most vividly in Fe – 20% Ni – 5% Cr and Fe – 15% Ni – 10% Cr alloys.

The result of all this research (Refs [35, 38 – 46]) shows that changing the concentration of the alloy components can strongly influence kinetic features of martensitic transformations, e.g., lead to a shift from athermal (explosive) transformation to isothermal transformation. No work gives an explanation of the concentration dependence of the transformation kinetics, with the exception of Ref. [35], where an attempt is made to link the possibility of an IMT to the strength characteristics of the alloys (the elastic limit and the ultimate strength), which affect the relaxation processes in the transformation. But the role of the strength characteristics is not very clear. For instance, it was shown in [47] that the yield point for Fe – Ni alloys containing from 20 to 30% nickel remains practically the same. At the same time, when there is less than 29% nickel in the alloy, the transformation is isothermal, while with more than 30%, the transformation is athermal.

Additional research is needed if we want to know the nature of changes in the kinetics of martensitic transformations induced by changes in the composition of alloys.

3.3 Effect of external factors

A very large number of works devoted to IMT deal with studies of the effect on the IMT kinetics of various external factors, such as stress, plastic strain, magnetic field, and neutron irradiation.

3.3.1 Effect of plastic strain and stress. Experiments with manganese steels have shown that a 30% strain at temperatures above the martensite point suppresses martensitic transformations under subsequent cooling or substantially increases the stability of austenite, with the effect more pronounced in the carbon-free alloys Fe – Ni – Mn [48]. The overall amount of martensite formed under strain and subsequent cooling is always smaller than in the strain-free alloy. When the samples, strained and cooled to −196 °C, were heated, the amount of martensite increased.

In studying the effect of a 14% pre-strain (a degree of compression at which the martensitic transformation slowed down but did not stop completely) on the kinetic features of the austenite-to-martensite transformation in the Fe – 23% Ni – 3.4% Mn alloy, a substantial decrease in the IMT rate was detected (Fig. 4) [48]. In strained samples, the transformation was found to take more time than in strain-free samples, and the overall amount of martensite may not differ too much from the amount in the strain-free samples. The transformation activation energies for a 14% strained material and for a strain-free material are approximately the same and equal to 600 cal mol^{-1} (2.52 kJ mol^{-1}).

For nickel and manganese steels with martensite points below 0 °C, the dependence of the kinetics of martensitic transformations on the degree of strain was found to be more complicated [49]. Small strain (from 2 or 3% to 15%, depending on the steel's composition) leads to a substantial increase in the amount of martensite under subsequent cooling, while large strain leads to a decrease in the amount of martensite. The dependence of the amount of martensite on the degree of strain has a maximum, and the lower the martensite point of the steel, the higher (on the degree-of-strain scale) is the location of this maximum. The values of T_s for steels with low martensite points first increase somewhat with the degree of pre-strain, but then decrease. For steels with relatively high martensite points (−15 and +70 °C), the values of T_s continuously decrease as the degree of pre-strain grows, and this starts at the lowest degrees of strain.

The effect of plastic strain at 20, 100, and 150 °C on the features of IMT kinetics in stainless steel was studied in [50]. In the steel Kh18N8 (18% Cr and 8% Ni), the researchers detected an activating effect of small (up to 10%) and an

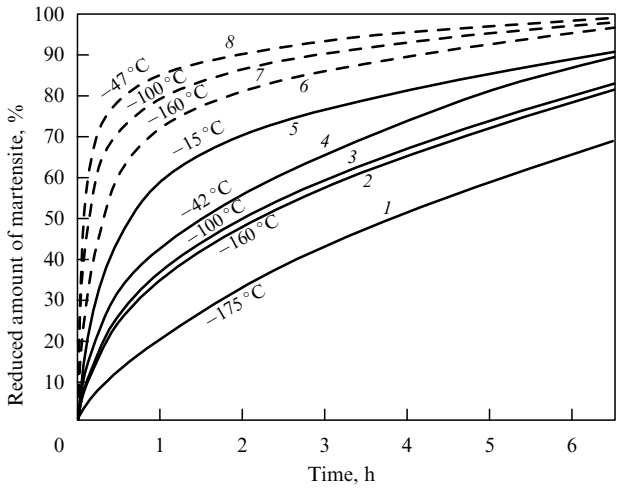

Figure 4. Reduced amount of martensite vs. exposure time at different temperatures for 14% strained (curves *1* – *5*) and strain-free (curves *6* – *8*) Fe – 23% Ni – 3.4% Mn alloys [48].

inhibitory effect of large (14 – 41%) degrees of strain at 100 °C on the course of martensitic transformations under cooling and subsequent heating. Low-temperature annealing (at 100 – 400 °C) leads to a rise in the stability of austenite and a decrease in the amount of martensite that forms under subsequent cooling. In the steel Kh17N9 with distinct isothermal kinetics of martensitic transformations, an 8% strain at 100 °C activates the transformation (the initial transformation rate increases, the overall volume of the martensite phase grows, the temperature interval of the transformation broadens, and the martensite points moves up). A 17% strain suppresses the transformations (the martensite point and the temperature interval of the transformation shift toward lower temperatures). The researchers link the observed effects to the facilitation or inhibition of the formation of martensite nuclei.

The IMTs in the Fe – 22.7% Ni – 3.1% Mn alloy with $T_s = -10$ °C are extremely sensitive to strain at room temperature [51]. Starting with small degrees of strain (1.5%), an inhibition of martensitic transformations under subsequent cooling was observed, i.e., the martensite point was lowered, the transformation rate decreased, and the maximum of this rate shifted toward lower temperatures as the degree of strain increased (e.g., an increase in the degree of strain from 9.5 to 18% shifts the martensite point by 30 °C). The strain temperature also has a strong effect on the transformation kinetics: the closer the strain occurs to the martensite point, the greater the effect.

A similarly strong suppression of martensitic transformation in the Fe – 22.4% Ni – 3.4% Mn alloy with $T_s = -30$ °C under plastic strain was observed in [52]; a 10 – 12% strain at room temperature leads to a decrease in the amount of martensite formed under subsequent cooling to −196 °C and heating to room temperature, from 33 to 0.1 – 0.2%. Such strain causes a rise in Vickers hardness by 30 – 40 H_V units and a physical broadening of the X-ray line $\{311\}_\gamma$. No other effects differ from those established in [51]. The initial ability of austenite to transform under a 10% strain is restored only when the sample is heated to 1000 °C.

Phase hardening has a similar effect on the martensitic transformation kinetics. Such hardening occurs when a certain amount of martensite is first formed and then transformed into austenite under heating. Studies of the N23G3 alloy [53] have shown that after direct and reverse transformations of approximately 30% of austenite, the subsequent martensitic transformation is suppressed and there is an incubation period (whose duration depends on the temperature of isothermal exposure) before the isothermal transformation begins. For small and large supercooling, the length of the incubation period reaches 10 min or even 40 min at −10 °C and −165 °C, respectively. An incubation period of up to 20 min at −196 °C was discovered in the transformation in steel with 1.1% C and 5.24% Mn and in steel with 1.4% C and 2.5% Mn after exposure to room (or somewhat higher) temperature. After the initial portions of martensite are formed, the IMT process accelerates considerably (this is a manifestation of the autocatalytic nature of the martensitic transformation, of which more is to be said below).

The time it takes to approach the martensitic transformation temperature also has a strong effect on the transformation rate, i.e., the transformation rate increases as the temperature slowly drops [53].

Stress generated by cooling has a strong effect on the development of a martensitic transformation [54]. For the N23G4 alloy ($T_s = -30$ °C), as the rate of cooling to −196 °C increases, the amount of martensite formed under subsequent heating with the rate 10 °C per minute changes from 9% for cooling with the rate 2.5 °C per minute to 35% for cooling with the rate 200 °C per minute. At all temperatures, the transformation intensity is higher for higher cooling rates. On the basis of their results, the researchers concluded that stresses of the first kind (microstresses) have no effect on the IMT rate, while the role of shear stresses (stresses of the second kind), which are generated near martensite crystals that have formed at low temperatures, is essential.

A number of papers [37, 55 – 57, 59 – 62, 58] were devoted to the study of the effect of structural imperfections and pre-accumulated martensite on the kinetic features of IMT. We consider these results in Section 3.4.

3.3.2 Effect of magnetic field on IMT. In steels and alloys with paramagnetic austenite and ferromagnetic martensite, a magnetic field increases the difference in Gibbs energies between the austenite and the martensite and elevates the phase equilibrium temperature T_0. In such materials, a martensitic transformation may be induced by a magnetic field. For instance, it was demonstrated in [65] that pulsed magnetic fields with the strength of several hundred kiloersteds elevate (by several dozen kelvins) the temperature at which athermal IMT begins; the martensite formed by applying the field was found to be preserved after the field was switched off. The effect of a dc magnetic field on isothermal IMT was first established in Ref. [66]. For the H23G3 alloy with isothermal transformation kinetics ($T_s = -10$ °C), the 18.6 Oe field results in an increase of the temperature at which the transformation begins and an increase in the transformation rate.

For the Fe – 26 mass% Ni – 2 mass% Mn alloy with an isothermal kinetics of martensitic transformations, it was found that when the sample was cooled to −60 °C and was placed in a dc 20 kOe magnetic field, the transformation rate increased threefold [67]. The authors estimated that in a dc magnetic field, the activation energy of a martensitic transformation changes.

The amount of martensite that forms because of a dc magnetic field and the formation rate depend on the temperature at which the field is applied. For the Fe – 24.9 mass% Ni – 3.9 mass% Mn alloy placed in a pulsed magnetic field, an IMT develops most rapidly at 153 K, while at higher or lower temperatures, the transformation rate is much lower [68]. At 4.2 K, an IMT does not develop, but when a pulsed magnetic field is applied to the sample, athermal martensitic transformation begins.

A detailed study of the effect of a dc magnetic field with the strength up to 4.0 MA m^{-1} (50 kOe) on the kinetics of the martensitic transformation and the microstructural features of isothermal martensite at temperatures up to 4 K was conducted in [69] with the Fe – 23.6 mass% Ni – 3.6 mass% Mn alloy N24G4 with an isothermal transformation kinetics. Martensite already appears in a 0.4 MA m^{-1} (5-kOe) field. The field initiates prolonged formation of martensite at a constant temperature: in a 50 kOe field, the transformation continues for 120 min. The temperatures at which the martensitic transformation starts and finishes (T_s and T_f), as well as the amount of martensite that forms in the process, depend on the magnetic field strength and increases with it. On the other hand, the width of the transformation interval remains practically the same.

3.4 The autocatalytic effect in a martensitic transformation

In contrast to what is commonly known as normal phase transformations, in which the effect of the newly formed phase on the development of the transformation can be ignored because of the high rate of the relaxation processes, this effect must play an important role in a martensitic transformation, and we can assume that it determines many features of the martensitic transformation. The autocatalytic effect, i.e., the effect of small initial amounts of martensite on the rate of the subsequent transformation, was first reported in Ref. [37]. In the absence of martensite, the IMT developed with the incubation period 1 min at −120 °C and 2 min at −100 °C, but in the presence of even a small amount of martensite, no incubation period was detected and the isothermal transformation began at a finite rate. A distinct relation was detected [56, 57] between the amount of martensite that formed under cooling to −196 °C (M_c) and under subsequent heating to room temperature (M_h). In all cases, $M_h/M_c > 1$, i.e., the transformation is clearly autocatalytic. As the amount of martensite formed during cooling increases, M_h/M_c rapidly increases and reaches a maximum at $M_c = 0.8-1$ %; for larger amounts of martensite, M_c rapidly (hyperbolically) decreases. Such an effect is observed after all kinds of treatment, i.e., plastic strain, phase hardening, and subsequent annealing. Similar results have been obtained for the Fe–23.7% Ni–2.8% Mn and Fe–22.9% Ni–3.1% Mn alloys.

The authors of Refs [58–62] studied the effect of small amounts of martensite that had formed in the process of cooling to −196 °C and under subsequent exposure to this temperature, on subsequent IMT in a series of Fe–Ni–Mn alloys. The autocatalytic effect was found to manifest itself already in the IMT process at −196 °C: the transformation began at a very low rate, which gradually increased and then gradually decreased in the course of several hundred or thousand hours. As a result, despite the very low initial transformation rate, in the course of 6000 hours at −196 °C, a considerable amount (16–18%) of martensite is formed.

The martensite accumulated at −196 °C changes the kinetics of the subsequent transformation at higher temperatures: the initial transformation rate dramatically increases (by several orders of magnitude), the maximum of the IMT rate shifts (by 30–50 °C) toward higher temperatures, and the martensitic transformation interval broadens considerably [59]. Accumulation of 1% martensite at −196 °C elevates the martensite point by 100 °C. The greatest activation effect is observed at the initial stages of the transformation [56, 58].

The first portions of martensite have the greatest effect on the IMT kinetics. As the amount of martensite pre-accumulated at low temperatures increases, activation ceases to increase, saturation sets in, and the effect of subsequent portions is weaker.

A study of the influence of the pre-transformation temperature on the activation effect has shown (see Ref. [60]) that partial transformation at −130 °C and −160 °C, just like the transformation at −196 °C, activates subsequent transformation, but as the pre-transformation temperature increases, the activation effect gradually decreases (Fig. 5).

The described experiments were used to study the effect of pre-transformation at low temperatures on the subsequent development of the transformation at a higher temperature. It was found that the accumulation of martensite at a higher martensitic transformation temperature (−78 °C) does not activate subsequent transformation at a lower temperature (−110 °C and −155 °C) and actually inhibits the process: as the amount of martensite pre-accumulated at −78 °C increases, the initial rate and the effect of isothermal transformation in the course of 30 min at −110 °C and −155 °C dramatically decreases. Thus, the data suggest that the presence of martensite (even in minute quantities) not only activates the transformation process but may also inhibit the further development of IMT.

To establish whether this or another effect (activation or inhibition) of pre-accumulated martensite on the further

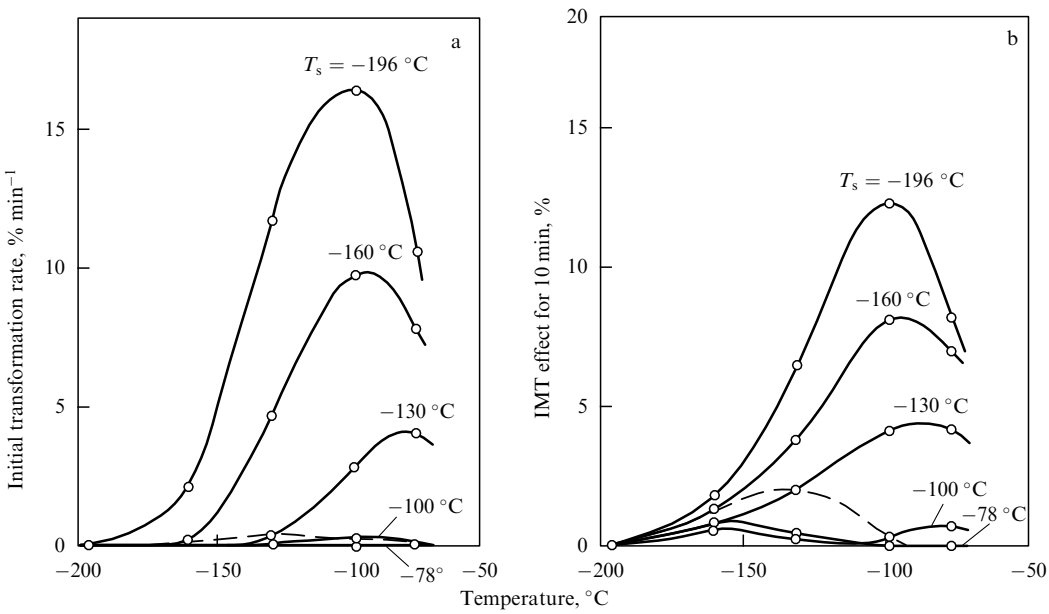

Figure 5. Temperature dependence of the initial rate of IMT (a) and IMT effects for 10 min (b) after accumulation of 3.5% of martensite at the temperatures indicated. The dashed curves represent the dependence of the rate and transformation effects in an annealed alloy. The alloy is Fe–22.8% Ni–4.0% Mn–0.02% C [62].

Table 1. Comparison of points T_M, T'_M, T_0, and T_D (°C) for Fe – Ni – Mn alloys

No	Ni, %	Mn, %	T_M, °C	T'_M, °C	T_A, °C	$T_0 = \frac{T_M + T_A}{°C^2}$,	T_D, °C	$T_0 - T_M$, °C	$T_0 - T'_M$, °C	$T_0 - T_D$, °C
1	23.6	3.6	−80	55	470	195	35	275	140	160
2	23.6	3.5	−80	60	475	195	35	275	135	160
3	22.8	4.0	−90	50	490	200	25	290	150	175
4	22.7	4.3	−70	15	470	200	15	270	185	185

development of the transformation is determined by the absolute level of the temperature at which martensite forms or by the relative position of the temperatures of pre-transformation and subsequent transformation, a study of IMT was carried out for a number of temperatures (−78 °C, −100 °C, −130 °C, and −160 °C) after equal amounts of martensite had been respectively accumulated at higher and lower temperatures. It was found that the effect (activation or inhibition) of pre-accumulated martensite on the subsequent process is determined not by the absolute level of the temperature of the pre-transformation but by the relative position of the temperatures of pre-transformation and subsequent transformation [60]. Irrespective of the absolute level of the temperature of pre-accumulation of martensite, the presence of martensite activates the subsequent transformation at a higher temperature and inhibits the transformation at a lower temperature. The larger the difference of the temperature of pre-transformation and subsequent transformation, the stronger the effect of activation or inhibition, with the activation effect usually being much stronger than the inhibition effect.

When pre-transformation occurs not at a single temperature but at a sequence of temperatures, the result (activation or inhibition of the subsequent transformation) is determined mainly by the transformation that occurred at the last temperature.

Prolonged exposures to a series of temperatures before and after activation have shown that despite the dramatic increase (by many orders of magnitude) of the initial IMT rate caused by activation, the final IMT effects in activated and nonactivated samples are practically the same.

Because a characteristic feature of martensitic transformations is the presence of a large hysteresis (more than 200 °C for iron-based alloys) between the thermodynamic phase equilibrium temperature T_0 and the temperature at which the transformation starts (the transformation may be either a direct one, i.e., under cooling, or a reverse one, i.e., under heating) [1], in connection with the discovery of the marked rising of the martensite point after partial low-temperature transformation, it proved interesting to estimate the position of the temperature T_0 for studied alloys and to resolve the question as to what extent activation reduces hysteresis in a martensitic transformation. Because no direct experimental methods for determining T_0 exist, this temperature was assumed to be the median temperature of the interval between the beginning of the $\gamma \to \alpha$ and $\alpha \to \gamma$ transformations [63].

The values of the temperatures of the beginning of the $\gamma \to \alpha$ (T_M) and $\alpha \to \gamma$ (T_A) transformations and the values of T_0 calculated on the basis of these data for a group of Fe – Ni – Mn alloys are listed in Table 1 [62]. Comparison of the values of T_0 and T'_M (the martensite point after activation) has shown that activation substantially reduces hysteresis (approximately from 280 to 140 °C) but does not nullify it. The martensite point after activation (T'_M) is close to the upper boundary of the transformation caused by strain (at the point T_D). We note that for the investigated Fe – Ni – Mn alloys, as well as for the binary alloys of the Fe – Ni group [63], T_D does not coincide with T_0 but is much lower (in the Co – Ni system, T_D is almost equal to T_0 [64]). Moreover, for Fe – Ni – Mn alloys, the temperature range between T_0 and T_D (about 170 °C) is much larger than the respective range for Fe – Ni alloys (about 50 °C) [50].

The above results were obtained for Fe – Ni – Mn alloys. The study of Fe – Ni – Cr alloys (N23Kh4) showed (see Fig. 6) that the effect of activation of isothermal martensitic transformation is also present in these alloys after partial transformation at a lower temperature. The activation patterns proved to be similar to those for Fe – Ni – Mn alloys. In the manganese steel 50G10, a rise in the martensite point (by more than 50 °C) after rapid cooling to −196 °C has also been recorded. These results suggest that the effects discovered in Fe – Ni – Mn alloys are not specific to these alloys but are of a general nature.

The transformation activation effect caused by the stresses generated near the martensite crystals influences the subsequent nucleation of new crystals [61, 62]. The effect of the pre-transformation temperature is related to the elastic-strain accumulation during transformation, whose size depends on the ultimate strength and yield point of the material. A strong temperature dependence of these quantities at low temperatures has been detected in Kh19N9 and N36G6 alloys in specially designed experiments [62]. For the

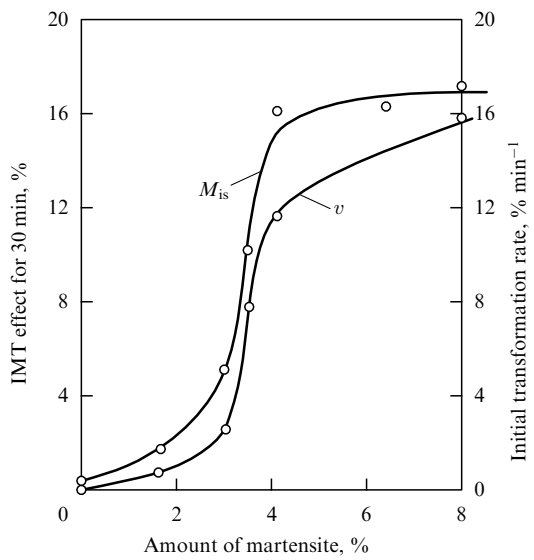

Figure 6. Variation of the initial IMT rate (v) and the IMT effect at −78 °C during 30 min in the Fe – 22.8% Ni – 4.4% Cr alloy vs. the amount of the martensite (M) accumulated prior to transformation at −196 °C [62].

same reason, low-temperature pre-strain intensifies IMT, in contrast to high-temperature pre-strain (which does not).

4. Isothermal martensitic transformation in alloys based on copper and other materials

The main laws governing IMP and the effect of various parameters (such as element concentration, grain size, cooling rate, the amount of martensite that forms prior to the transformation, phase hardening, pre-strain, and annealing) were studied using iron-base alloys. Up to the 1980s, there were simply no data on IMP in other alloys (not iron-based). Only Holden [70] discussed the possibility of isothermal development of martensitic transformations in U – (1 – 3) at. % Cr: at room temperature, slow growth (with the rate 0.5 mm h^{-1}) of martensite crystals was detected.

The question of whether IMTs are related to other special properties of iron-based alloys and of the possibility of IMTs in other materials remained open.

In the 1980s, an attempt was made to find alloys that are not iron-based and yet exhibit IMT. Paper [71] was the first to describe an experiment in which an isothermal martensitic transformation involving a gallium-alloyed Cu – Sn alloy was reliably detected. The papers that followed [72 – 74] dealt with the main laws governing the IMT in such alloys and with the influence of the alloy composition and various factors (ageing, strain), and the crystal structure of the initial phase and the martensitic phase formed athermally or isothermally.

The research involved Cu – Sn – Ga alloys of the following composition: 23.50 – 24.0 mass% Sn and 1.5 – 2.0 mass% Ga [71]. Such alloys exhibit special properties due to the restricted solubility of gallium in copper and tin. As shown by electron microscope studies, the high-temperature bcc β-phase begins to decay already during quenching. The kinetics of martensitic transformations was investigated by the electrical-resistance method, by measuring the strain induced by the martensitic transformation, and by measuring the intensity of diffraction reflections of the martensite phase. It was found that at $-196\,^{\circ}$C, which was below the martensite point M_s (T_s), slow isothermal transformation continues for 20 to 60 min after partial martensitic transformation by the athermal-kinetics path. The rate of the isothermal transformation was found to decrease with the passage of time. Figure 7 shows the temperature curves representing the dependence of the reversible strain that accumulates during the transformation in Cu – Sn and Cu – Sn – Ga alloys with almost the same martensite points. In the first alloy, the martensitic transformation stops at $-196\,^{\circ}$C and no further martensite is formed if the sample is exposed to this temperature. In the Ga-alloyed Cu – Sn alloy, the martensitic transformation starts at $-170\,^{\circ}$C, up to 50% of the martensite is formed as the temperature drops to $-196\,^{\circ}$C, and the martensitic transformation continues for 20 to 30 min if the sample is exposed to this temperature (the vertical section in Fig. 7b).

The curves representing the dependence of the amount of the accumulated reversible strain δ and the electric resistance R on time t are shown in Fig. 8. The principal variations of these quantities occur in the first 4 to 8 min; after that, the transformation rate drops substantially. We note that the IMT proceeds in jumps: a certain portion of martensite forms in a fraction of a second, then for 5 to 10 s nothing happens, and then again a new portion of martensite forms.

The isothermal nature of martensitic transformations in Cu – Sn – Ga alloys is corroborated by the results of neutron diffraction studies of variations in the intensity of the (002) line of the martensite phase [74]. The measurements showed that the increase of martensite at a constant temperature continues for 60 min, although the main portion of martensite forms in the first 15 to 20 min. When the sample is heated to above A_f, the temperature at which the reverse transformation under heating ends, a reverse martensitic transformation occurs and the initial phase is completely restored.

In the above-mentioned alloys, it is impossible to supercool the initial phase: in alloys with $T_s = -70\,^{\circ}$C and $-170\,^{\circ}$C, partial martensitic transformation by the athermal-kinetic path occurs under a dramatic drop in temperature to $-196\,^{\circ}$C, and then it continues by the isothermal-kinetic path when the sample is exposed to the last temperature, and the higher the martensite point, the greater the amount of athermal martensite; accordingly, the fraction of isothermal martensite decreases.

The Cu – Sn – Ga alloys are decaying alloys, and their exposure to a certain temperature (100 – 200 °C) at which tin-enriched particles of the δ-phase (with an fcc lattice) precipitate may substantially alter the state of the initial

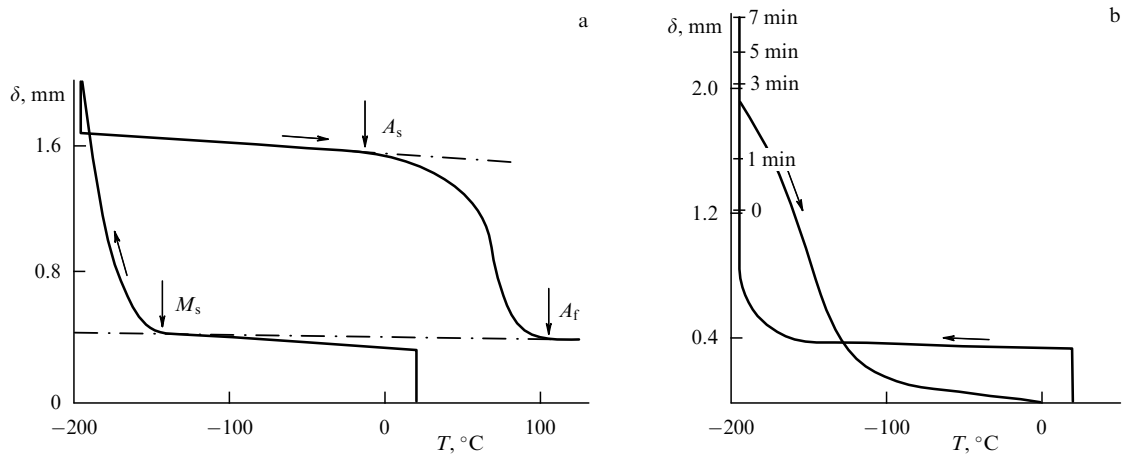

Figure 7. Temperature dependence of the reversible strain accumulated during a martensitic transformation in a Cu – Sn alloy (a) and a Cu – Sn – Ga alloy (b) [71].

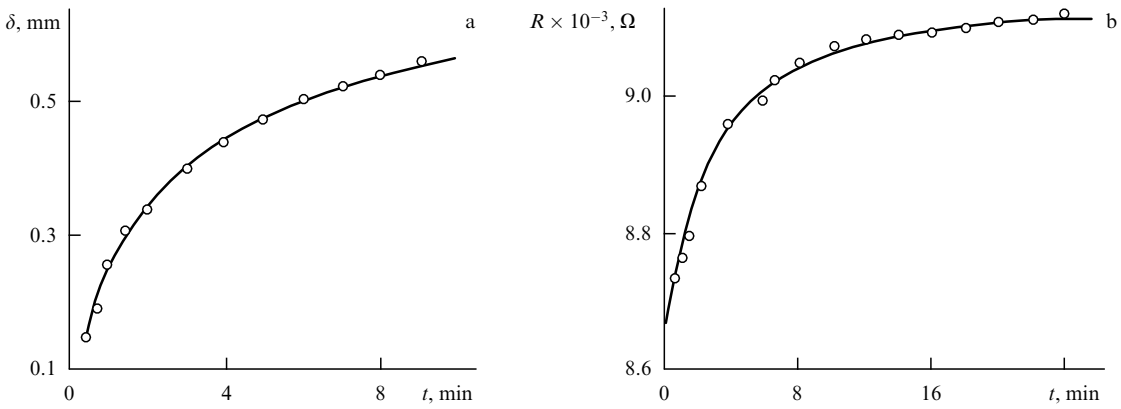

Figure 8. Dependence of the reversible strain δ that accumulates during a martensitic transformation in a Cu – Sn – Ga alloy (a) and the electric resistance R of the sample (b) during the time of exposure to the temperature $-196\,^{\circ}$C [71].

phase, the characteristic transformation temperatures, and the size of hysteresis [72]. As the results in Refs [71 – 74] show, IMTs occur in these alloys only if the homogeneization processes have not been completed under heating for quenching, or in pre-aged samples. In view of this, the researchers suggested that IMTs are possible only at a certain level of strength. A comparison of the values of microhardness and the transformation kinetics has shown that IMT can be observed in the cases where microhardness is in the range 3 – 4 GPa [72]. This microhardness is attainable under aging at 100 – 200 °C during a certain period or by straining (e.g., via rolling) by 5 – 10%. The electron microscope study [72] demonstrated that already in the quenching stage, the initial δ-phase partially decays with the formation of an fcc phase similar to the δ-phase that emerges in Cu – Sn of similar composition. Aging at 100 °C for 5 min or at 150 °C for 1 to 2 min does not lead to substantial structural changes compared to the tempered state but results in a higher microhardness.

As mentioned earlier, it was reported in Refs [71, 72, 74] that an IMT in Cu – Sn – Ga alloys occurs after athermal martensite has been partially formed. It turns out, however, that in certain states of the initial phase, the athermal kinetics in these alloys can be totally suppressed, and hence the martensitic transformation takes the isothermal-kinetics path [73]. Such a state can be achieved via the subsequent treatment that changes the structural state of the initial phase: quenching from 680 °C and rolling by 5 – 10% or aging at 200 °C for 1 to 5 min. After thermal treatment, an IMT is observed in a wide temperature interval from +20 to −196 °C. Figure 9 shows the temperature dependence of the reversible strain accumulated in two stages: on section *ab* at +23 °C over the course of 20 – 25 min, and on section *de* at −196 °C over the course of approximately 15 min. On section *cd*, the martensitic transformation is athermal. The reverse transformation during heating is also done in two stages: from −150 to 0 °C, and from 55 to 200 °C.

A sample may undergo an ITM at different temperatures (Fig. 10). After each isothermal exposure, the sample is heated to temperatures above 100 °C and is then cooled to the appropriate temperature. It takes 10 – 15 min to complete the IMT, the transformations proceed in steps, and a certain portion of the martensite phase is formed at each step. Thus, by thermally treating the Cu – Sn – Ga alloys, which changes the initial state, the athermal component in the martensitic transformation can be completely suppressed, with the result that the transformation to martensite takes the isothermal-kinetics path. No reverse isothermal transformation can be recorded. The IMT rate for Cu – Sn – Ga alloys depends on the sample's temperature and substantially decreases as the temperature lowers. However, in contrast to iron-based alloys, this rate remains high even at −196 °C (Fig. 11). Various combinations of athermal and isothermal martensitic transformations can be achieved with Cu – Sn – Ga alloys. As the quenched alloys are cooled to −196 °C, the transformation proceeds as either an athermal or a combined athermal and isothermal one [71, 72]. After aging, the sequence of the different kinetics paths may be as follows: athermal plus isothermal (at low temperatures), isothermal plus athermal (at temperatures in the range −196 to 0 °C), or only isothermal (after rapid cooling to a temperature below T_s). The implementation of this or that kinetics or a sequence depends on the state of the initial phase determined by its aging and precipitation of δ-phase particles. Tin-depleted and tin-enriched regions of the initial phase with different

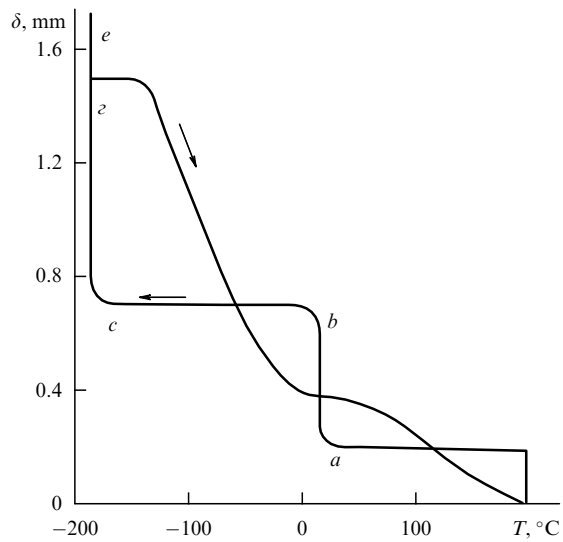

Figure 9. Temperature dependence of the reversible strain δ that accumulates during a martensitic transformation in a Cu – Sn – Ga alloy when the transformation follows the isothermal-kinetics path (*ab* and *de*) or the athermal-kinetics path (*cd*) [73]. L

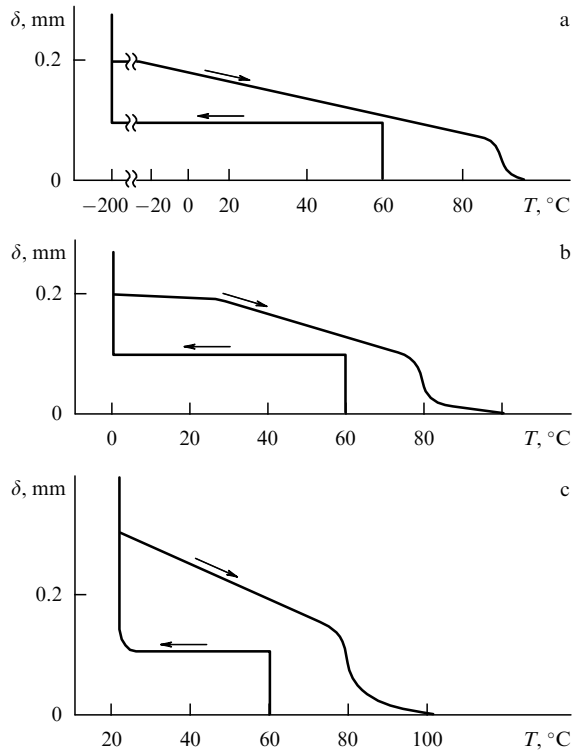

Figure 10. Isothermal accumulation of martensite (vertical sections) in the Cu – Sn – Ga alloy at −196 °C (a), 0 °C (b), and 23 °C (c) [73].

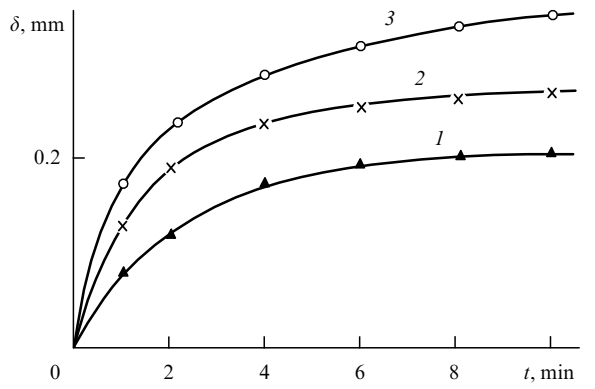

Figure 11. Dependence of the reversible strain on the exposure time for the Cu – Sn – Ga alloy at −196 °C (*1*); 0 °C (*2*), and +23 °C (*3*) [73].

temperatures at which the martensitic transformations start are formed near these particles. A martensitic transformation starts at a certain temperature in a certain region near δ-phase particles. The transformation then proceeds in the adjacent regions because of the strain generated in the transformation. The process develops in time and gradually decays.

The crystal structure of the initial and martensite phases in Cu – Sn – Ga alloys has been determined by neutron diffraction analysis [74]. In all such alloys, the initial phase has a disordered bcc structure with the lattice parameter $a = 0.297$ nm, while the martensite phase has an orthorhombic lattice whose packing type depends on the gallium content in the alloy. In the Cu – 23.5 mass% Sn – 0.5 mass% Ga, martensite with $3R$ packing is formed. As the gallium concentration increases, martensite with $2H$ packing emerges. When the Cu – 23.8 mass% Sn – 2.0 mass% Ga alloy is subjected to aging at 150 – 200 °C, martensite with a hexagonal close-packed (hcp) structure is formed.

IMTs have also been detected in Cu – Zn – Al [76 – 78], Cu – Ge [79], and Mn – Cu [80] alloys, in pure Co [81, 82], and in CsCl [83] and β-PbO_2 [84] compounds.

Studies of Cu – Zn – Al alloys [76, 77] have shown that the IMTs in these alloys are related to processes of annealing at room temperature and depend on the quenching conditions. In the process of exposure (up to 60 min), T_s rises substantially, and the observed isothermal process is athermal in nature. Such a transformation is known as pseudoisothermal. Isothermal accumulation of martensite at 284 – 290 K occurs most rapidly in the first 10 to 12 min, and then the rate decreases, but the transformation may continue for 60 to 70 min. The final product of the isothermal transformation in these alloys consists of two equilibrium phases, α and β. The transformation is fully reversible — the initial phase is restored under heating. A C-like dependence of the transformation rate on the temperature of the transformation from the supersaturated α-phase to the z-phase after annealing at high temperatures has been detected in Cu – (11.8 – 12.2) mass% Ge alloys [79]. At a fixed annealing temperature, the rate of formation of the z-phase decreases with an increase in the temperature of isothermal exposure. The researchers concluded that the formation of the z-phase is controlled by nucleation processes.

IMTs were also observed during antiferromagnetic ordering in Mn – (9 and 13.5) mass% Cu and Mn – 10 mass% Ge alloys, in which the phase with a face-centered tetragonal lattice and a lattice parameter ratio $c/a < 1$ forms [80]. At 300 K, all the alloys have the degree of magnetic order equal to 0.8 – 0.9 and are in the martensite state. It takes 20 to 40 min for reversible strain to isothermally accumulate or for the electric resistance to change. In [80], the IMT in these alloys was associated with the relaxation of stresses generated in the formation of the first martensite crystals.

Information about the possibility of IMT in pure Co can be found in Refs [81, 82]. It was reported in [81] that isothermal transformations occur near the temperature of the beginning of the fcc → hcp transformation in the interval from 417 to 340 °C. Below 340 °C, no IMTs have been observed. For the martensitic transformation to develop by the isothermal-kinetics path, the cooling rate must not exceed 5×10^3 K s^{-1} [82]. For higher cooling rates, the martensitic transformation develops by the athermal-kinetics path.

The main experimental results concerning the established laws governing IMT can be briefly summarized as follows:

1. IMTs are observed in many alloys based on iron and other metals at low temperatures (room temperature and lower).

2. IMTs can exist in combination with athermal martensitic transformations or without them.

3. The crystal growth rate in an IMT, as well as in an athermal martensitic transformation, is close to the speed of sound. This means that the thermally activated nucleation of crystals of isothermal martensite constitutes the IMT's thermally activated stage that determines the kinetics of the transformation.

4. The temperature dependence of the IMT rate, as of other phase transformations, is described by a curve with a maximum (as the temperature decreases, the transformation rate first increases, then reaches its maximum, and finally decreases). The lowest temperature at which IMTs are still observed in iron-based alloys is about 77 K. At this

temperature, IMT slowly develops over the course of several thousand hours.

5. The higher the temperature interval of the transformation (i.e., the higher the martensite point), the greater the maximum value of the IMT rate. In alloys with a high martensite point, the maximum transformation rate may happen to be so high that it becomes difficult to record it in experiments, and hence the transformation appears to be athermal.

6. At a fixed temperature, the increase in the thermodynamic driving force of transformation caused by an external magnetic field leads to an increase in the IMT rate, up to its transformation into an athermal martensitic transformation.

7. The IMT rate strongly depends on the presence of earlier formed martensite (athermal or isothermal): a small amount (up to 2%) of martensite formed at a low temperature increases (by a factor of several hundred) the rate of subsequent IMT and broadens the temperature of this transformation (the autocatalytic effect). The final amount of isothermal martensite then remains practically the same.

8. The IMT rate depends on plastic pre-strain, irradiation by neutrons, and phase hardening, i.e., on the defect structure of the initial phase.

5. Morphological features and the microstructure of isothermal martensite

Studies of the morphological and microstructural features of isothermal martensite began almost at the same time that IMT was discovered. These studies make it possible (a) to answer the question of how the amount of isothermal martensite increases: as a result of the growth of the already formed crystals or through nucleation of new crystals; (b) to detect the interaction of the crystals with each other and with the defects of the initial phase (dislocations and clusters of dislocations, stacking faults, and twins); and (c) to study the structure and state of the interphase boundaries, the substructure of martensite crystals, and the stage of crystal growth at which this substructure appears.

Through pioneering research done with a number of iron-based alloys (Fe – Ni, Fe – Mn – C, and Fe – Ni – Mn), it was found that an increase in the amount of martensite occurs primarily because of the appearance of new martensite crystals, although certain growth of the already existing crystals was also detected [85, 86]. Maksimova and Nikonorova [86] studied the N23G3 allow and found that when it was exposed to the temperature $-23\,^{\circ}$C, the martensite that formed had the shape of long, thin crystals, often parallel to each other. The crystals were small with a not very distinct relief on the surface, and somewhat increased in size under isothermal exposure.

A detailed study of the morphology and fine structure of martensite crystals formed by the athermal- and isothermal-kinetic paths was conducted in [87]. The 35 iron-based alloys that were studied, which contained 12.4 – 35.6 mass% Ni and 0.015 – 0.95 mass% C, can be divided into three groups according to the kinetic features of the transformation: those with isothermal kinetics (T_s above $-10\,^{\circ}$C), those with athermal kinetics (T_s below $-100\,^{\circ}$C), and those with mixed kinetics (T_s ranging from -10 to $-100\,^{\circ}$C). Characteristic of alloys with isothermal kinetics is the presence of irregular, strongly peaked interphase boundaries of martensite crystals. The crystals are of different shapes, differ in size, and form similarly directed groups or obtuse-angled pairs. Small plates have a high dislocation density, and sometimes inside the plates one can observe irregularly located twins of irregular shapes along the $\{112\}\langle 111\rangle_{\alpha}$ system.

Athermal martensite is formed as regular plates with distinct, straight boundaries, and the size of the plates is limited by the grain size. The density of transformation twins along the $\{112\}\langle 111\rangle_{\alpha}$ system is high inside the crystals. There are no dislocations in the plates.

In the intermediate group, 40 to 50% of martensite is formed by the explosive-kinetics path, and the martensite crystals can grow somewhat if the sample is exposed to temperatures within the transformation interval; the lower the temperature, the smaller the growth. The median part of the crystals contains parallel transformation twins along the $\{112\}\langle 111\rangle_{\alpha}$ system. On the periphery of the crystals, where the dislocation density is high, the twin density diminishes.

In addition, there are differences in the relief that appears on the surface of the sample undergoing a transformation. In alloys with isothermal kinetics, the relief is indistinct and gradually disappears at the martensite – austenite boundary, which may be caused by plastic strain in the initial phase. Martensite formed by the athermal-kinetics path creates a clear relief and no apparent indications of plastic strain in austenite are present. In the second group of alloys (with mixed kinetics), the relief is of an intermediate nature. We note that martensite formed by two kinetic mechanisms in a single alloy (say, Fe – 29 mass% Ni) has different morphologies and substructures.

Studies of the Fe – 28.8 mass% Ni alloy have shown that up to 60% of the martensite can be formed by the isothermal-kinetics path [88]. Martensite plates begin to grow from grain boundaries or annealing twins, growth occurs along a martensite plate and crosswise (usually on one side), and many plates grow simultaneously.

Studies of other iron-based alloys (e.g., Fe – 24.3 mass% Ni – 5 mass% Mo) have shown the same morphological features of isothermal martensite: there is almost no relief on the surface, and the interphase boundaries have indistinct outlines [89]. The crystals form rows separated by layers of the initial phase. Under subsequent exposure, the layers transform, and a large formation consisting of fragments, so to say, emerges. All the crystals are similarly oriented and have thin twins of varying thickness along the $\{112\}\langle 111\rangle_{\alpha}$ system. Alloying the Fe – (25 – 26) mass% Ni system with chromium, manganese, or molybdenum does not significantly change the morphological features and substructure of isothermal martensite. By an electron microscope study of the features of IMT in these alloys, it was found that in the interval from $+20$ to $-100\,^{\circ}$C, isothermal martensite forms rods with dislocation coils inside the crystals [90]. Some regions of the crystals are disoriented, and in the austenite regions adjacent to the martensite, the dislocation density is increased. The isothermal martensite and the initial phase were found to be linked by the Kurdyumov – Zaks orientational relation.

Light and electron microscopy methods used to study the morphology, substructure, and crystallographic characteristics of isothermal martensite forming in Fe – 23 mass% Ni – 3.8 mass% Mn have shown that temperature (77 and 143 K) has no effect on the morphological features and crystallography of IMT [91, 92]. Inside the martensite crystal, lines were discovered that pass through the interphase boundary into the austenite. The crystal consists of separate small plates that have the same orientation, but the habit of these plates differs from the macroscopic habit of the

entire crystal. A martensite crystal formed by the athermal-kinetics path consists of several martensite plates belonging to different martensite plates but joined. Such a configuration substantially reduces the shape strain of the region that underwent the transformation.

In analyzing the crystallographic characteristics of Fe – Ni – Mn alloys, it was found that the orientation of the macroscopic habit plane is close to $\{225\}_\gamma$ and that the plates inside a crystal are aligned along the $\langle 110\rangle_\gamma$ direction and have a $\{112\}_\gamma$ habit [91]. In each martensite plate (90 – 550 nm thick), there was observed a high density of the transformation twins that appeared in the early stages of the transformation, while in the region in front of the plates, the dislocation density is high. The habit's orientation does not change as the crystal grows. As in Ref. [90], the isothermal martensite and the initial phase were found to be linked by the Kurdyumov – Zaks orientational relation.

The problem of the accommodation of shape strain during the nucleation and growth of a martensite crystal was examined in [92]. It was assumed that accommodation (the relaxation if the stresses are generated in the transformation and caused by the transformation mechanism itself) occurs because of the dislocation clusters that form near the interphase boundaries (this has been corroborated by experiments), with the result that there is no need for several variants of martensite to form simultaneously (the emergence of self-accommodation groups of martensite crystals or a crystal consisting of two variants). In the case of IMT, accommodation may occur (and occurs) as a result of the formation of several plates of the same orientation. The study of the processes of growth of isothermal martensite crystals in [92] shows that a packet of slip lines emerges from each martensite plate and forms a V-shaped wedge with it. Each plate appears with a very high rate, and after a certain time, a new plate with the same habit appears near it. As a result, separate plates form a large macrocrystal (Fig. 12).

The formation of isothermal martensite in the form of plates is probably a general characteristic feature of martensite. This fact is also corroborated by the results of studies of the morphology of martensite that forms in the Fe – 15 mass% Ni alloy [93]. The researchers found that during exposure to a temperature below T_s (670 K), separate martensite plates are formed first, and only after that the plates form packets and blocks.

In alloys with double transformation kinetics (e.g., the 50N24G1 alloy), a somewhat different process of isothermal martensite formation was detected: large lenticular crystals of athermal martensite are overgrown with obtuse-angled girders of isothermal-martensite plates [94].

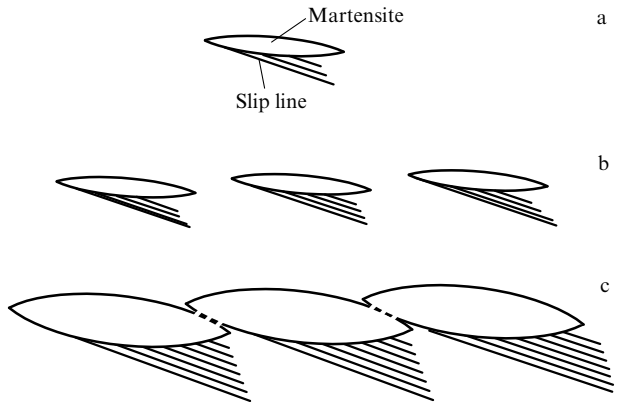

Figure 12. Consecutive stages of formation of a martensite macroplate: (a) t_1; (b) t_2; (c) t_3; $t_1 < t_2 < t_3$ [91].

A pulsed magnetic field (with the strength up to 400 kOe) applied to alloys with mixed transformation kinetics (the 60N21 alloy) initiates the nucleation of crystals with a midrib, as in athermally formed crystals, and a decrease in non-twinned regions [95].

When the N24G4 alloy with isothermal transformation kinetics is placed in a moderate dc magnetic fields (5 – 16 kOe), thin martensite plates (0.4 – 0.7 μm) with distinct straight boundaries forms, while without the field, the transformation often produces lenticular ensembles and the martensite crystals has a complex structure with irregular boundaries [69]. When the field is increased to 35 – 50 kOe, chains of thin lenses with the same midrib direction occur in addition to the thin plates. Under exposure to the temperature 140 K and a dc magnetic field, the microstructure of the martensite becomes nonuniform and more complicated: crystals of various shapes, sizes, and orientations form, and no preferred direction in the crystals is observed. Exposure to the temperature 140 K for 30 min in a 200 kOe field leads to a substantial increase in the amount of martensite.

All attempts to detect a nucleus of isothermal martensite proved fruitless (see Ref. [92]), as they did in the case of athermal martensite. In one of the first papers on this topic [96], the Fe – 29 mass% Ni – 2 mass% Mn alloy was studied and it was found that the incubation period of the transformation (the time it takes 0.2% of martensite to form) changes in inverse proportion to the cube of the grain size. The researchers then concluded that martensite nuclei are distributed evenly over the grain volume rather than located at the boundaries of the grains, as commonly assumed. Similar results were obtained in [97], the nucleation of isothermal martensite was shown to occur in different regions of the initial phase (these regions are often located far from each other), and such a situation is observed in both the early stages and the later stages of the transformation. These results contradict the experimentally established autocatalytic nature of IMT.

Isothermal martensite that forms in alloys based on copper and cobalt also exhibits characteristic features [76 – 82]. In Cu – Zn – Al alloys, which require special treatment for IMT to proceed, isothermal martensite forms in thin plates resembling those that are formed in alloys that underwent a thermoelastic martensitic transformation. Under isothermal exposure, the amount of martensite changes because the plates become longer and thicker (the elongation rate here is higher than the thickening rate) and because of formation of new martensite pates, as is the case with isothermal transformation in iron-based alloys.

The crystallography of isothermal martensite in a Cu – Zn – Al alloy was studied in [78] using the electron microscopy and electron diffraction methods. The researchers found the following orientational relation linking the martensite (2*H*) and initial (2*B*) phases: $(001)[010]_{2H}||(110)[001]_{B2}$.

The transformation of an fcc structure to an hcp structure under isothermal conditions (at 300 – 800 °C) was studied in [79] in Cu – (10.5 – 12.2) mass% Ge alloys by an optical microscope. The hcp phase forms at constant temperature as thin (5 – 30 nm), long plates. The amount of this phase increases because new plates appear near the already existing ones. This results in the formation of 'thick' plates. Inside the plates, one can observe stacking faults limited by partial

Shockley dislocations. Under thermal cycling, the hcp phase appears in the same places. The places where this phase is formed are microstructural defects, such as grain boundaries, twin boundaries, and intersections between the hcp plates that have already formed.

The morphologies of isothermal and athermal martensite in pure cobalt are different [82]: isothermal martensite appears in the form of thin faceted plates matching the initial phase along the $\{111\}_{\mathrm{fcc}}$ planes and containing stacking faults with a high density, while athermal martensite appears in the form of fragments of slanted orientation or groups of almost parallel plates with twins along $\{11\bar{2}\,0\}_{\mathrm{hcp}}$.

6. Theory of isothermal martensitic transformation

The theory of isothermal martensitic transformations has been developed by many researchers and can be found in a number of original works (see Refs [101, 106–113]). A detailed coverage of the results of these works can be found in a number of review articles [7, 99, 114, 115] and monographs [4, 9]. In view of this, we here mention only the very general aspects.

In contrast to the mechanism of nucleation and growth of the crystalline phase from a melt, when there is a phase transformation in a solid, in addition to the competition between two contributions to the free energy (a reduction in energy related to the appearance of a new, more stable, phase and a rise in energy caused by the appearance of an interface between the nucleus and the initial phase), we must allow for the energy of the elastic interaction of the new-phase crystal and the surrounding matrix. The requirement that the elastic energy of the system incorporating the crystal and the initial phase be minimal [111, 114] leads to a change in the shape of the growing crystal (nucleus) and to a change in its internal structure, with the result that a description of crystal nucleation becomes more complicated. In the case of high-temperature transformations in the solid state, when the thermal mobility of atoms plays a decisive role, classical theory provides a satisfactory description of the kinetic features of such transformations, in particular, the C-like temperature dependence of the transformation rate.

As soon as an IMT with the temperature dependence of its rate described by a curve with a maximum (just as in other phase transformations) was discovered, attempts were made to describe the IMT kinetics by theoretical means within the classical theory of phase transformations (with allowance for the transformation occurring in an elastic medium).

The difficulty of describing the IMT kinetics stems from the fact that an IMT is a thermally activated process, and hence in describing it we must use the standard ideas of the kinetics of overcoming energy barriers in the 'path' of the transformation via thermal activation. Another factor is that the data on experimental investigation of the effect of a magnetic field on IMT kinetics show that as the thermodynamic driving force, the magnetic field drives the IMT rate up and that when a critical value of the magnetic field is reached, the transformation becomes athermal and may proceed at a low temperature [66, 69]. There is no way in which the classical approach can be used to describe the complete disappearance of the energy barrier in the transformation at a large thermodynamic force and the emergence of an athermal transformation mode.

This contradiction can be resolved by the nonclassical theory of martensitic transformation kinetics, proposed in [33] and developed in [37, 98, 99]. According to these ideas, a martensitic transformation proceeds heterogeneously at prepared places distributed according to their readiness to transform. The heterogeneous nature of martensite crystal nucleation has a number of direct experimental corroborations [85, 98]. As the thermodynamic driving force of transformation increases (due to supercooling or an external field), the critical value of this force is attained, and at this point, the most prepared nucleus proves capable of growing spontaneously and athermally. In [100, 101], it was shown that the possibility of such athermal growth of crystals under substantial supercooling is real. Further supercooling initiates the least prepared nuclei. This description lacks the fluctuation stage of nucleus formation, which is a common topic in classical theory.

At temperatures close to the absolute zero, only one variant of transformation is possible, and that is an athermal realization of the existing spectrum of nuclei, or athermal transformation. At a higher temperature, another process is possible, and that is the thermally activated growth of 'almost critical' nuclei to the size at which they become capable of growing athermally. This is the thermally activated process responsible for IMT.

The effective energy barrier of an IMT is a function of the thermodynamic driving force of the process and is determined by the proximity of the real driving force to its critical value at which the transformation becomes athermal. When the critical value of the thermodynamic driving force is reached, the energy barrier disappears.

Quantitatively, the relation between the effective activation barrier and the thermodynamic driving force can be derived from the temperature dependence of the hysteresis of pressure-induced transformations [102]. The hysteresis ΔP increases linearly as the temperature drops,

$$\Delta P = \Delta P_{\mathrm{k}}\,\frac{T_{\mathrm{a}} - T}{T_{\mathrm{a}}}\,, \tag{1}$$

where ΔP_{k} is the size of hysteresis as $T \to 0$ and T_{a} is the temperature corresponding to $\Delta P = 0$. Equation (1) implies that

$$T = \frac{\Delta P_{\mathrm{k}}\,T_{\mathrm{a}} - \Delta P T_{\mathrm{a}}}{\Delta P_{\mathrm{k}}} = \frac{T_{\mathrm{a}}\,(\Delta G_{\mathrm{k}} - \Delta G)}{\Delta G_{\mathrm{k}}}\,, \tag{2}$$

because for pressure-induced transformations, the difference of the Gibbs energies of the initial and final phases is $\Delta G = \Delta P \Delta V$ (where ΔV is the bulk transformation effect).

On the other hand, the line on which a thermally activated transformation begins is described by the condition

$$v = v_0 \exp\left(-\frac{G^*}{RT}\right) = \mathrm{const}\,, \tag{3}$$

where v is the transformation rate and G^* is the height of the energy barrier (the activation energy) or, because v_0 and R are constants,

$$\frac{G^*}{T} = \mathrm{const} = a\,. \tag{4}$$

Substituting (2) in (4), we obtain

$$G^* = a T_{\mathrm{a}}\,\frac{\Delta G_{\mathrm{k}} - \Delta G}{\Delta G_{\mathrm{k}}}\,. \tag{5}$$

At $\Delta G = 0$, we have $G^* = aT_a = G_0^*$, and finally,

$$G^* = G_0^* \frac{\Delta G_k - \Delta G}{\Delta G_k} = G_0^* - \left(\frac{G_0^*}{\Delta G_k}\right) \Delta G \,. \tag{6}$$

A similar relation follows immediately from the linear dependence of the IMT activation energy in Fe–Ni–Mn obtained in [103] (Fig. 13),

$$G^* = G_0^* - k\Delta G = 242 - 98\Delta G \,, \tag{7}$$

where all the quantities are measured in units of kJ mol^{-1}. The data in [103] show that for a $\gamma \to \alpha$ transformation to occur in Fe–Ni–Mn alloys, we must have $G_0^* = 242$ kJ mol^{-1} and $k = G_0^*/\Delta G_k = 98$. This means that the athermal transformation regime can be achieved with a driving force equal only to roughly 2.4 kJ mol^{-1}.

Thus, the height of the energy barrier of a martensitic transformation strongly depends on the thermodynamic driving force of the process and vanishes when this force reaches its critical value. The transformation from a thermally activated transformation regime (IMT) to an athermal transformation regime (athermal martensitic transformation) occurs at moderate values of the thermodynamic driving force.

Many kinetic features of IMT are determined by the dependence of the height of the energy barrier on the driving force. Among these features is the high sensitivity of the IMT kinetics to various factors — external stresses, magnetic field, and martensite that formed before the transformation. Another characteristic feature of martensitic transformation related to changes in the thermodynamic conditions that occur during a transformation is the decay of the transformation in isothermal conditions in the presence of the initial phase [10, 62].

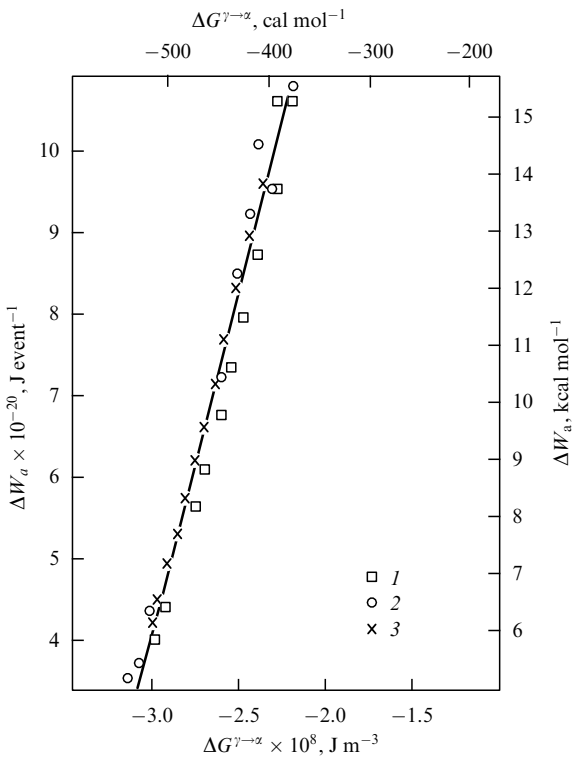

Figure 13. Dependence of the IMT activation energy in Fe–Ni–Mn alloys on the thermodynamic driving force (the difference in the Gibbs energies of the initial and martensite phases: (*1*) Fe–(23–25)% Ni–(2–3)% Mn; (*2*) Fe–22.4% Ni–3.6% Mn; and (*3*) Fe–23.3% Ni–3.6% Mn [103].

For classical phase transformations, the decrease in the rate at low temperatures (the descending branch of the C-like curve) is determined by the existence of the growth activation energy that is independent of the thermodynamic driving force of the process. In an IMT, the effective activation energy strongly depends on the thermodynamic driving force and rapidly decreases as the force becomes stronger, with the result that this activation energy cannot determine the decrease in the IMT rate at low temperatures. The birth of a crystal of the new phase means that a certain amount of work has been done inside the initial phase, an amount needed to create an interface and to inject the new-phase crystal into the matrix of the old phase. All this expenditure of energy must be compensated by the difference in the Gibbs energies of the phases, which is determined by the deviation from the equilibrium point. The smaller the phases differ in structure, the lower the energy of the interface and the smaller the second term, or the work done to inject the new-phase crystal into the matrix. In the limit of second-order phase transformations, when the phases are indistinguishable at the transformation point, the transformation hysteresis is nil. As the difference becomes bigger, the hysteresis increases. If the difference in the lattices is small and the accommodation of new-phase crystals in the matrix is not accompanied by irreversible plastic strain, the transformation may be reversible, or (more precisely) thermoelastic. The hysteresis between the direct and reverse transformations in this case is moderate; because of the reverse transformation, the structure of the initial phase and the initial shape of the sample are restored. The small elastic modulus and the high elastic limit of the initial phase (in addition to the small difference in the lattices of the initial and final phases) facilitate the reversible nature of this transformation. This ensures elastic accommodation of the intrinsic transformation strain ε_0.

If the difference between the lattices is large and the elastic interaction does not result in accommodation, the transformation is accompanied by plastic strain and the related dissipation of energy. In this case, the energy needed for the transformation and, respectively, the transformation hysteresis must be proportional to the yield point, a situation observed in experiments [10]. The straight lines describing the experimentally obtained dependence of the hysteresis on microhardness pass through the origin [10]. This means that the resistance to lattice transformation and to the motion of the interphase boundary is nil, and hence the transformation proceeds without hysteresis.

The results of calculations and the direct experimental data show that at low temperatures (below 50 K), the thermodynamic driving force ceases to increase as the temperature decreases [104]. On the other hand, it is in the low-temperature region that the yield point, which determines the resistance to lattice transformation, rapidly increases [62]. The interplay of these two factors leads to a decrease in the real thermodynamic driving force of the transformation. As a result, the martensitic transformation stops at low temperatures (the existence of the point T_f at which the transformation ends; below this point, the transformation does not develop), the IMT rate drops, and a descending branch appears in the temperature dependence of the IMT rate. Thus, the descending branches of the C-like diagram in

'normal' high-temperature transformations and in IMT have different origins [105].

7. Isothermal martensitic transformation and other thermally activated processes in solids

The results of IMT studies lead to the following important conclusions. First, they show that at low temperatures, there can be the spontaneous development of prolonged processes that lead to significant, and often dramatic, changes in the structure and properties of the material. Also, it occurs that the rate at which these processes develop and their kinetics strongly depend on the material's history and external factors, such as strain, irradiation, pressure, and magnetic field. Finally, analysis of the experimental data suggests that in describing the kinetics of low-temperature transformations, one should take the strong dependence of the activation energy on the thermodynamic driving force into account.

The IMT process is a special but not unique example of processes that can develop in materials at low temperatures because of internal factors. In accordance with the third law of thermodynamics, a stable state of two- or multicomponent substances is either a stoichiometric compound or an ordered solid solution of stoichiometric composition. In reality, such substances are usually in a metastable state and have a thermodynamic 'stimulus' to transform them into a more stable state. This fact leads to the development in these materials of processes that change the properties (degradation), which in many cases limits the possibility of using such materials for a long time.

The question is: How fast does the degradation proceed? Theoretical estimates of the admissible (guaranteed) time of operation of materials in a metastable state are usually made, in accordance with classical kinetics theory, on the basis of an exponential relation with the activation energy determined for high temperatures, where the rate of the processes is significant. The results of IMT studies show that the kinetics of low-temperature processes strongly depends on the thermodynamic driving force, and the processes run very intensively for large values of this force.

The idea that describing the kinetics requires taking the dependence of the height of the energy barrier on the thermodynamic driving force into account is, probably, a very general one and can be applied to all thermally activated low-temperature processes in solids. As an example, we mention low-temperature amorphization and crystallization under high pressure.

Estimates of the rate of crystallization at room temperature yield, in agreement with experimental data, vanishingly small values. However, modern data (see the reviews in Refs [116, 117]) show that under high pressure, both amorphization and crystallization may occur at room or even lower temperature. The explanation of this phenomenon, in accordance with what we have said earlier, is as follows. If the specific volumes of the crystalline and amorphous phases are very different, the critical value of the thermodynamic driving force can be reached at high pressure (this force is defined as the deviation from the pressure of stable or metastable phase equilibrium), and this corresponds to the disappearance of the energy barrier. Under these conditions, both crystallization and amorphization can run athermally at any temperature, which has been observed in experiments [116, 117].

Other examples of thermally activated processes for which the dependence of the activation energy on the value of the thermodynamic driving force has been established are also known. For instance, in Ref. [118], it is shown that the larger the internal energy accumulated under cold strain, i.e., the greater the thermodynamic stimulus to recrystallization, the lower the recrystallization activation energy. As the stresses grow, the dislocation motion activation energy decreases [119]; under small stresses, the motion of dislocations is a thermally activated process, while under large stresses, the process is athermal, without a barrier. As the stresses grow, thermally activated delayed disintegration becomes athermal. Ionic conductors placed in a strong electric field experience an electric breakdown. As the field strength grows, thermionic emission of electrons becomes field emission. In an iron–nickel alloy with a rectangular magnetic hysteresis loop, the speed with which domain boundaries directed along the field and in the opposite direction move varies from zero to the critical value of the field and rapidly increases (to values close to the speed of sound) with the field strength [120].

The strong dependence of the height of the activation barrier on the thermodynamic driving force probably also explains such phenomena as structural transformations in shock waves [121], the formation of solid solutions from pure components after treatment in mills (mechanical alloying) and in shear under pressure, anomalous diffusion under pulsed loading, etc. If we assume that in all cases athermal processes are related to the attainment of a certain (critical) value of the thermodynamic driving force, then we must explain the origin of the high thermodynamic stimulus for each of the above processes. Additional stimuli can be of several types: for phase transformations in shock waves and for amorphization under high pressure, it is the deviation from the line of stable or metastable phase equilibrium, while for the other processes, it is the excessive (stored) energy generated under strong strain.

8. Concluding remarks

The present review has covered a very interesting physical phenomenon, the isothermal martensitic transformation. Such a transformation develops for a long time in the low-temperature region, and in this it differs from 'normal' phase transformations, which develop only at high temperatures, or at a high thermal mobility of the atoms.

The evolution of the ideas about the isothermal martensitic transformation is as instructive as the evolution of the ideas about the martensitic transformation proper. Not so long ago, the martensitic transformation was considered a unique phenomenon, characteristic only of steel and of interest only to specialists in physical metallurgy. Today, it is clear that the martensitic transformation is one of the main types of phase transformation in solids.

In the same way, only a short time ago, IMP was regarded as something very exotic, a spurious phenomenon related to the martensitic transformation, which is a purely athermal process. As a result of investigations done in the last few decades, it was found that IMP is a regular and common phenomenon, just as the martensitic transformation proper is. It is one of the main kinetic variants of low-temperature phase transformations in solids.

Moreover, IMT is a representative of a broad class of processes whose characteristic feature is that when the driving force is at its critical value, the processes develop athermally,

while for a weaker driving force and a finite temperature, there may be thermally activated processes with an activation energy that strongly depends on the driving force (and that vanishes when the driving force is critical). Examples of such processes abound. The study of IMT with its high sensitivity to external and internal factors makes it possible to establish the general laws governing the entire class of such phenomena.

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