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## Abstract

## Full Text

*Physical Chemistry*

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# On the Autocatalytic Character of the Martensitic Transformation

*(Presented by Academician G. V. Kurdyumov on 13 V 1960)*

One of the most important questions in the theory of martensitic transformations at the present stage of its development is the question of the role of structural imperfections of the initial phase in the course of this transformation, and in the structure and properties of its products. Of substantial interest in this connection is the clarification of the question of the role of imperfections that arise in the initial austenitic phase not under the action of external factors (deformation, irradiation, etc.), but directly in the course of the transformation itself and that influence the further development of the process.

The appearance of distortions in austenite during the martensitic transition is inevitable by virtue of the specific features of this type of transformation, which cause the occurrence of large deformations of the austenite crystal lattice near the forming martensite crystals: the cooperative mechanism of the transformation and the strictly regular character of atomic displacements, with relatively high elastic properties of the medium <sup>(1,2,16,17)</sup>.

Under the influence of the martensitic transformation, disturbances may arise in the crystal structure of austenite that have an opposite effect on its stability <sup>(2,4,18)</sup>. Changes that exert a retarding influence on the further course of the martensitic transformation (hydrostatic pressures, fragmentation and disorientation of blocks, etc. <sup>(6,18-20)</sup>) can, evidently, become significant and play an essential role in the course of the transformation only at its later stages <sup>(1,2)</sup>. The occurrence in austenite of defects of the crystal structure that lead to activation of the transformation (large elastic distortions of a local character <sup>(22)</sup>) affects the subsequent development of the process from its very earliest stages <sup>(2,4)</sup>. The present work is devoted to consideration of the role of precisely this type of structural imperfection.

There are numerous experimental data indicating the autocatalytic character of the martensitic transformation: the phenomenon of "burst" <sup>(7)</sup>; a less active course of the process in powder <sup>(7,22)</sup>; a more intensive isothermal transformation in a specimen in which, by the beginning of the holding period, a certain amount of martensite is present <sup>(9)</sup>; activation of austenite under the influence of preliminary deep cooling <sup>(23,24)</sup>, etc. The formation, in the course of the

Figure 1

Figure 1: Figure 1

martensitic transformation, of activating changes is also confirmed by the results of theoretical investigations (3).

In the present work, the autocatalytic effect of the martensitic transformation and its role in this transformation were studied: 1) by analyzing the extensive experimental material on the kinetics of martensitic transformations previously obtained by the authors; 2) by carrying out a special experimental investigation.

We analyzed experimental data obtained over the last decade on the kinetics of the martensitic transformation during deep cooling and subsequent heating. For a number of Fe–Ni–Mn and Fe–Cr–Ni alloys, on the basis of numerous experiments, from 50 to 150 values were calculated for the ratio of the effects of heating ( $M_{\text{heating}}$ ) to the effects of the preceding cooling ( $M_{\text{cooling}}$ ). The obtained values of  $M_{\text{heating}}/M_{\text{cooling}}$  as a function of the effects  $M_{\text{cooling}}$  were plotted on a graph (Fig. 1).

The character of the curves obtained—with a sharply pronounced maximum near the ordinate axis—indicates that in all cases the martensite crystals that had formed beforehand exert a strong stimulating influence on the subsequent development of the transformation. So long as the development of the process is not limited by a shortage of sites capable of undergoing transformation, the relative intensity of transformation during heating increases sharply as the effect of the preceding deep cooling increases; of particular interest is the fact that, for a given effect  $M_{\text{cool}}$ , the effect  $M_{\text{heat}}$  is, for each alloy, a constant quantity independent of its prior treatment, i.e., of the features of the structural state of the austenite (state of plastic deformation, high annealing, phase work-hardening, etc.); in all cases, complete exhaustion of all the austenite capable of undergoing transformation (for example, 40–50%) occurs during heating even when, in the course of cooling, only about 1% martensite is formed.

**Fig. 1.** Activating action of martensite, obtained during cooling, on the transformation during subsequent heating. Alloy H24G3 (0.065% C, 23.7% Ni, 2.82% Mn).  $M_{\text{cool}}$ —cooling effect from 20 to  $-196^\circ$ ,  $M_{\text{heat}}$ —effect of subsequent heating from  $-196$  to  $20^\circ$ ; the numbers in circles are  $M_{\Sigma} = M_{\text{cool}} + M_{\text{heat}}$ .

The subsequent experimental study of the autocatalytic character of the martensitic transformation was carried out with the aid of a specially designed apparatus possessing high sensitivity. The subject of the investigation was the study of the change in the course of the isothermal transformation in an Fe–Ni–Mn alloy ( $T_M = -30^\circ$ ) at a definite temperature ( $-90^\circ$ ) as a function of the amount of martensite previously accumulated at  $-196^\circ$ ,  $M_{-196}$ .\*

As a result of the investigation performed, direct experimental data were obtained showing that the martensitic transformation possesses a clearly pro-

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

nounced autocatalytic character (Figs. 2, 3). The presence of martensite previously accumulated at  $-196^\circ$  leads to a considerable increase in the intensity of the subsequent transformation. This is evidenced both by the regular rapid increase in the initial rate of the isothermal transformation with increasing  $M_{-196^\circ}$  (for example, at  $M_{-196^\circ} = 4.4\%$  the initial transformation rate increases by more than 700 times—from 0.02 to 14.3%  $\text{min}^{-1}$ ), and by the regular increase in the transformation effect from the accumulation temperature ( $-196^\circ$ ) to the control temperature ( $-90^\circ$ ) as  $M_{-196^\circ}$  increases.

The following regularities in the development of the autocatalytic effect have been established: a very rapid increase in the activation effect is observed when  $M_{-196^\circ}$  increases approximately up to 5%; as  $M_{-196^\circ}$  increases further,

\* Such a low temperature of preliminary accumulation was chosen in order to obtain the greatest possible distortions of the crystal structure of austenite and, insofar as possible, to preserve them more completely.

$M_{-196^\circ}$  to 10%, the autocatalytic effect increases somewhat further, and then gradually decreases (apparently owing to the exhaustion of regions of the initial phase capable of transforming at the given temperature).

**Fig. 2.** Activation of the isothermal transformation at  $-90^\circ$  under the influence of martensite preliminarily accumulated at  $-196^\circ$  (the amount of accumulated martensite is indicated at the curves). Alloy N23G4 (0.05% C, 23.0% Ni, 4.00% Mn). *I* —total effects; *II* —isothermal effects

The initiating action of preliminarily accumulated martensite on the further course of the transformation is manifested most clearly in the initial stages of the isothermal process (Fig. 3b); as the duration of the isothermal hold increases, the action of the stimulating changes rapidly weakens. The latter indicates the occurrence of relaxation

**Fig. 3.** Course of the development and elimination of the activation effect. Alloy N23G4. *I* —character of the change in the transformation rate at  $-90^\circ$ , as a function of  $M_{-196^\circ}$ ; *II* —decrease of the activation effect during isothermal holding

Fig. 4

Figure 4: Fig. 4

**Fig. 4.** Increase of the rate of isothermal transformation at  $-196^\circ$  with time. Alloy N23G4

processes already in the course of the transformation itself (at  $-90^\circ$ ), i.e., of the very low temperature stability of the structural disturbances that have arisen.

The autocatalytic character of the martensitic transformation is also clearly manifested in the course of the isothermal transformation itself, observed in a number of alloys under conditions where the transformation rate is very small (at very small or very large supercoolings); in the course of the transforma-

nucleation with a rate increasing with time. Such a course of transformation was established in the present work at  $-196^\circ$  (Fig. 4); the rate of transformation in this case increases over the course of more than 3 hours. The occurrence of an isothermal transformation with acceleration—so usual for normal phase transformations (when, in the course of the transformation, both the formation of new crystals and the growth of those already formed take place)—in the case of martensitic transformations (which proceed practically only through the formation of new crystals) can be explained only on the basis of the concept of the stimulating influence of the transformation products that have arisen on the subsequent course of the reaction.

Further study of the autocatalytic effect inherent in martensitic transformation should apparently most expediently be carried out in parallel with the study of the directly related phenomenon of thermal stabilization of austenite—one of the most important features of martensitic transformation. The totality of the available data on the regularities of martensitic transformation indicates the validity of the idea of the phenomenon of thermal stabilization of austenite as a process of gradual relaxation of those austenite-activating distortions that arise in it as a result of partial transformation. This relaxation process, apparently, should be regarded not only as a process of eliminating austenite-activating disturbances, but also as the formation (as a result of atomic displacements occurring during relaxation) of structural imperfections of a kind that can exert an inhibiting influence on martensitic transformation.

The autocatalytic effect of martensitic transformation and the phenomenon of thermal stabilization of austenite are directly connected with the heterogeneous character of the nucleation of the new phase in this type of transformation. The latter also determines the major role played in martensitic transformation by changes in the crystal structure of the initial phase, occurring both during the transformation itself (formation of defects) and during subsequent holding (processes of their gradual healing).

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