ON THE "THERMOELASTIC" EQUILIBRIUM ON MARTENSITIC TRANSFORMATIONS

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The recently proposed theory of diffusionless or martensitic transformations [1] allowed one to explain some basic anomalies in their kinetics (the huge rates of nucleation and growth of crystals in the martensitic phases, as well as the termination of their growth), to determine conditions for these transformations to run in solids, and to predict the existence of two new phenomena at martensitic transformations: 1) a slow running of the transformation at sufficiently low temperatures and 2) the existence of the "elastic" crystals of the martensitic phases.

The first of the aforementioned phenomena was discovered with the help of the special tests on carbon and alloyed steels [2] and Cu–Sn eutectoid alloys [3]. The activation energy and the temperature dependence of the transformation rate were determined for the austenite-martensite transformation in steels.

In the present report, we are going to describe experiments, in which we succeeded to clearly show the existence of the second expected phenomenon – "elastic" crystals of the martensitic phase.

The process of transformation was directly observed with the use of an optical microscope in the alloys with the point of the martensite transformation lying below room temperature. A quenched specimen was polished, mounted onto the microscope stage, and cooled with the help of a special device [3]. Martensitic crystals appeared on cooling produced a relief on the polished surface.

Elastic crystals have not been observed in Cu–Sn (about 25% Sn) alloys: crystals formed under cooling did not disappear on heating to room temperature [3]. Cu–Al alloys containing about 14.5% Al with the nickel addition (1.0–1.5%), have shown a different picture. Specimens had the β_1-phase structure after quenching from 900 °C. The transformation of β_1 into the martensitic γ'-phase occurred under cooling below room temperature [4]. The appearance of γ' crystals started at $+10°$C in one of the alloys. It was possible to observe the gradual growth of γ' crystals at slow cooling. These crystals had shape of two kinds: ones gave long parallel strips expanding at the decrease of temperature on the surface of a polished section; others, being wedge-shaped, moved inside the grains. With decrease in the temperature, new crystals appeared and grew, until all the section's field was completely covered with a needle-type relief.

The termination of cooling induced the stop of the growth; the crystal growth continued if the cooling was renewed, until crystals were reaching neighboring martensitic crystals or the boundaries of original austenite grains. Sometimes, the crystals, while meeting others in their way, were growing at their expense, crossed them, and grew further.

On heating, γ' crystals were shrinking in size and disappeared. The decrease in size started from those regions of the crystal, where the growth stopped during the cooling. Crystals which appeared last on cooling disappeared on heating in the first turn. The whole image disappeared on heating in the same order as it was growing, but in the reverse direction. The order could be slightly broken at a fast heating. The martensite relief disappeared completely at heating just above the martensitic transition temperature ($+10°$ for this alloy).

The process of transformation can be stopped at any stage and reversed on cooling as well as on heating. The structure remained unchanged if the temperature was maintained constant. Each temperature corresponded a definite pattern of the relief — the equilibrium between the martensitic crystals and the medium, in which they grew, had been established.

The existence of such an equilibrium allowed us to easily photograph the separate stages of growth and disappearance of martensitic crystals.

In Fig. 1, we show some of the photos of the same section's place which were obtained at the stops on cooling (a, b, c) and then on heating (d, e, f) in a temperature interval of $+10$–0 °C. In Fig. 2, we present microphotographs of the different place of the same section. In this case, the initial crystals had the shape of thin bands; the photos of this place were taken
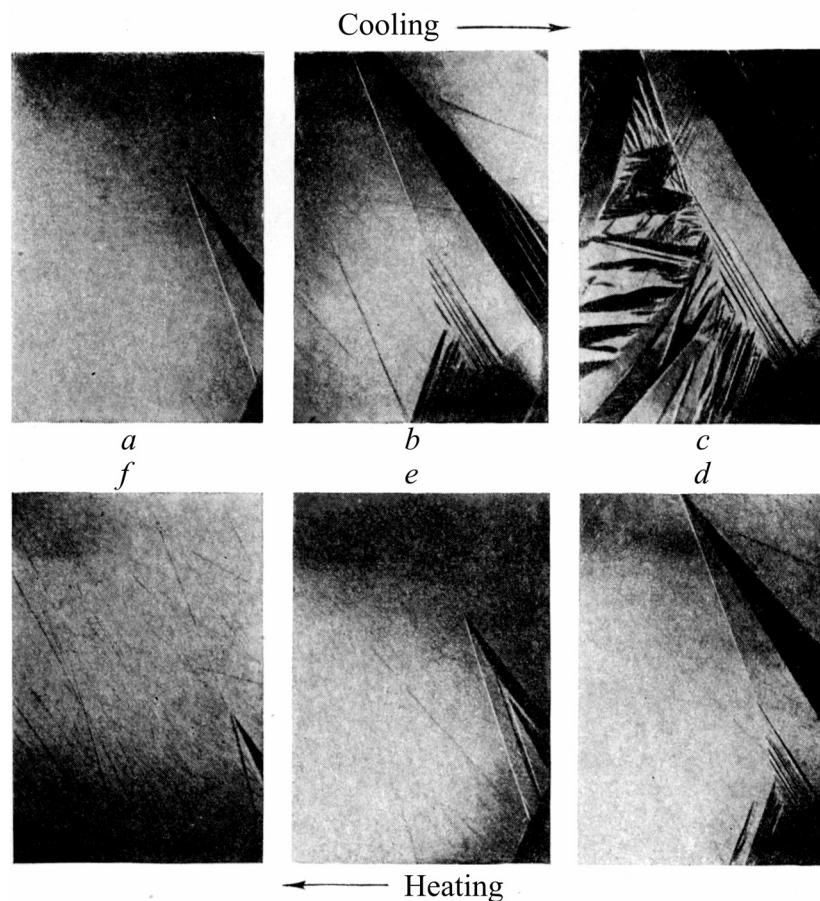
89

Fig. 1. Magnification ×72, reproduced at 4:5

during different heating-cooling cycles. The pattern was repeated during many heating-cooling cycles. A change in the pattern for the alloy under investigation took place if the specimen was heated above room temperature. After that, the crystal growth upon cooling below the martensitic transition temperature occurred at different centers.

The behavior of the alloy at the martensitic transformation described above is extremely unusual. Based on the numerous investigations of the transformation of austenite into martensite, it was considered to be firmly established that martensitic crystals are always formed in a very short time period (smaller than 10^{-3} s), the appeared crystals do not grow, and a further transformation takes place only due to the formation of new crystals [1, 5]. The inverse martensitic transformation observed in a number of alloys was characterized by the same kinetics, and it occurred always with a large temperature hysteresis (about dozens or hundreds of degrees) [1].

In the case described above, we observed a gradual growth and were able to control the growth rate, to stop the growth, and to force the process to run into the reverse direction with a desirable rate. The hysteresis was practically absent. The inverse transformation of the martensitic phase occurred below the martensitic temperature, i.e. at temperatures, at which the low-temperature modification of the solid solution must be more stable.

The possibility for the existence of such a phenomenon follows from our idea of the mechanism of the formation of martensite crystals. According to this idea, the growth of martensite can take place if the structural coupling ("coherency") between the lattices of both phases and the order and the correspondence of the positions of atoms on both sides of the growing crystal are preserved. The growth ceases when elastic deformations induced by such ordered growth exceed the elastic limit. In this case, a plastic deformation with the relaxation of stresses takes place. As a result, the elastic
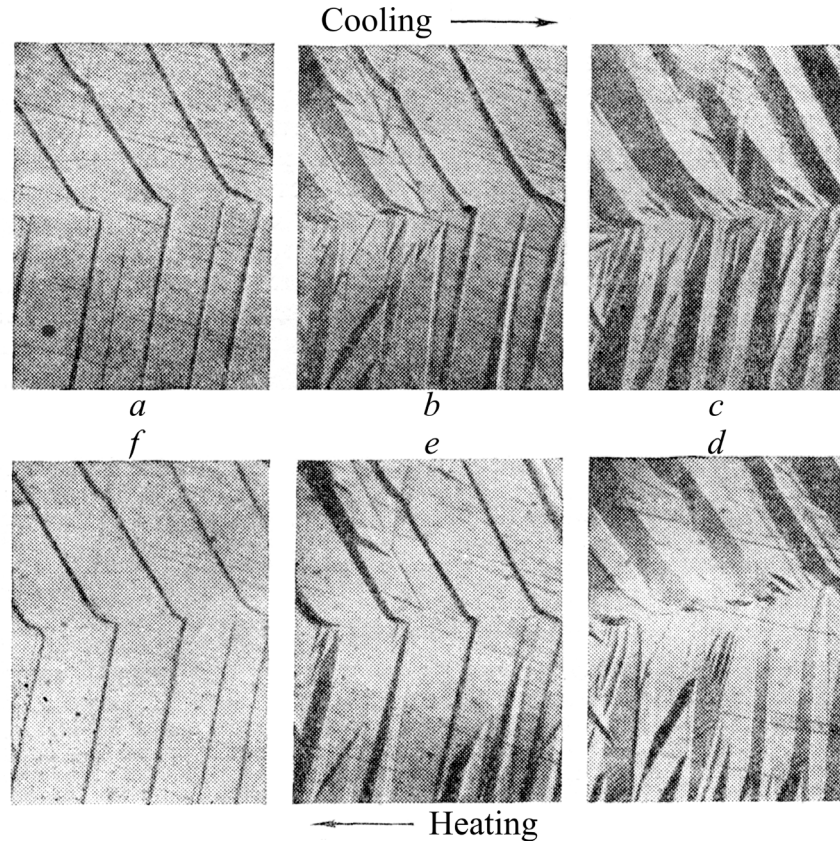
Cooling ——→

a   *b*   *c*

f   *e*   *d*

←——— Heating

Fig. 2. Magnification ×72, reproduced at 2:3

coupling between two lattices is broken, the new lattice "separates" from the old one, the correspondence disappears, and the disorder in atomic positions on the interface comes into existence.

The preservation of the structural coupling during the growth of a martensite crystal leads to the appearance of the elastic energy, whose value depends on the ratio of the interatomic distances in both lattices, values of their elastic constants, and the way of a structure reconstruction at the growth. On reaching a certain size by the crystal, the total change of the thermodynamic potential of the system will be written as

$$R = -\Delta\Phi + E_\mathrm{s} + E_\mathrm{el},$$

where $\Delta\Phi$ is a decrease of the thermodynamic potential due to the transition into the new modification, and E_s and E_el are, respectively, the surface and elastic energies. It was supposed that the function R can have a minimum at a certain size of the growing crystal [1]. Then, in the case where this minimum will take place at sizes less than those which induce the stresses

sufficient for the break of the structural coupling, the "thermoelastic" equilibrium has to be established. The crystal growth must stop not because the structural coupling is broken, but because R will increase at the further growth. However, the growth termination is not final in this case, as it was in the case of breaking the structural coupling. The preservation of the coupling must lead to the situation where the crystal may change its size both in the directions of its increase and decrease, by depending on the direction of a change of the quantity $\Delta\Phi$ and, therefore, the temperature: "an increase in the temperature must lead to a shrinkage of the crystal, while a decrease – to its enlargement until the coherency is broken" [1].

In this case, a martensitic crystal must behave itself like the elastic twin [6]; a change of the temperature plays the role of a mechanical load.

The above-described observations of both the "hysteresisless" reversibility of the martensitic transformation in Cu–Al alloys and the equilibrium shifting with variation in the temperature are in full correspondence

with conclusions of the theory. Truth to tell, we were not able to obtain "residual" martensitic crystals in these alloys, i.e. to achieve the breaking of the elastic coupling, even at considerable amounts of the martensitic phase. Apparently, in the same original grain, the structural correspondence is preserved not only on the interface between the old and new phases, but also on the boundaries between martensitic crystals. This conclusion is supported by, first, the strong order characterizing the disappearance of crystals on heating (this order is inverse to the order of their appearance on cooling) and, second, the opportunity for a growing martensitic crystal to consume other crystals already present.

The existence of the thermoelastic equilibrium and "elastic" crystals of martensite discovered in the present paper confirms the correctness of our ideas of the mechanism of martensitic transformations.

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3. G.V. Kurdyumov and L.G. Khandros, Zh. Tekhn. Fiz. **19**, No. 5 (1949).

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5. S.S. Shteinberg, Metallurg. No. 9–10, 58 (1937).

6. R.I. Garber, Zh. Eksp. Teor. Fiz. **17**, 63 (1947).

KURDYUMOV GEORGII VYACHESLAVOVYCH (14.02.1902–06.07.1996)

Georgii Vyacheslavovych Kurdyumov was the outstanding physicist of the XX century, a true member of the Academy of Sciences of USSR and National Academy of Sciences of Ukraine (Kurdyumov G.V. *Selected papers* (Akademperiodyka, Kyiv, 2002), 775 p.). Due to him, the martensitic transformation, as compared with other phase transitions, appeared as a separate phenomenon, while its studies were transformed into an independent area of contemporary science. The first scientific review on martensitic transformations (Zh. Tekhn. Fiz., **18**, 999 (1948)) came from Kurdyumov's pen. This paper is one of the most cited ones amongst the broad bibliography devoted to martensitic transformations. In this review, G.V. Kurdyumov predicted the thermoelastic phase equilibrium which was found experimentally later on, in 1949, by G.V. Kurdyumov and L.G. Khandros (1914–1993) who was the closest disciple of G.V. Kurdyumov and led the Department of Phase Transformations for many years at the institute founded by Kurdyumov (G.V. Kurdyumov Institute for Metal Physics of the National Academy of Sciences of Ukraine). The scientific paper proposed to your attention is the first description of the thermoelastic phase equilibrium (Dokl. Akad. Nauk SSSR **66**, 211 (1949)).