

## LOW-CARBON MARTENSITIC STEELS. ALLOYING AND PROPERTIES

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Requirements on the structure of a steel with structural strength and a set of characteristics higher than those of medium-carbon steels with a structure of tempered sorbite are formulated. Principles for choosing compositions for process-adaptable low-carbon martensitic steels are presented. The combination of carbon and alloying elements providing high stability of austenite in the ranges of normal and intermediate transformations is determined, which makes it possible to obtain lath martensite in slow cooling.

**Key words:** steel, structure, austenite, martensite, phase transformations, structural strength.

### INTRODUCTION

Analysis of medium-carbon (0.20 – 0.40% C) structural steels with yield strength of 650 – 1200 MPa and weldable steels (0.12 – 0.25% C) in machine building has made it possible to determine their disadvantages where the implementation of structural strength and adaptability to manufacture is concerned. It follows from this analysis that the steels used in the machine-building cycle of production of heat hardened articles and welded assemblies should be characterized by

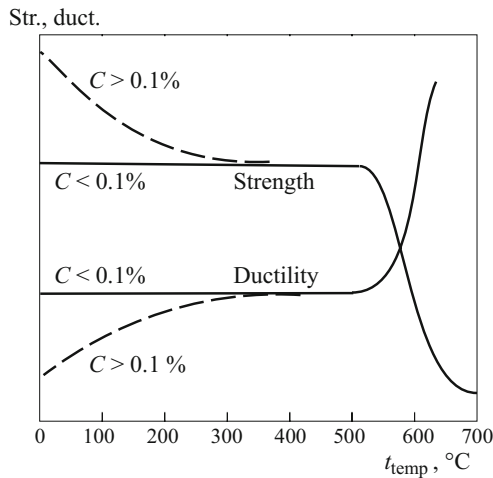
- the specified structural strength of articles and welded structures corresponding to a yield strength  $\sigma_{0.2} = 650 - 1300$  MPa;
- the required combination of strength, ductility, and toughness parameters in service in a base temperature range of  $\pm 50^\circ\text{C}$ ;
- the possibility of making the designed construction with minimum capital expenditure in new and full-scale productions;
- the possibility of the use of various process operations for making parts and welded assemblies;
- the possibility of surface hardening by thermochemical or another kind of treatment (nitriding, carburizing, etc.);
- good weldability without heating in heat-hardened and annealed conditions;
- weldability of parts over the metal of the core after surface hardening;
- minimum mass of the parts and consumption of metal; production of precision heat-treated preforms, semiproducts, parts, and welded assemblies;

- combination of hot forming with hardening without the use of liquid coolant;
- deformation-free hardening of preforms and welded assemblies without special measures for preventing deformation (facilities, special quenchants, etc.);
- creation of equal-strength welded joints;
- no constraint on the time between hardening (welding) and tempering;
- facing in annealed and heat-hardened states;
- possibility of welding of different grades of steel;
- possibility of welding of a heat-hardened steel and a thermally untreated steel in one joint;
- cold deformation with high degree of strain in annealed and heat-hardened states;
- good processibility by cutting;
- universality of application, possibility of replacement of several grades of steel by a single grade in operation under various conditions.

Traditional structural steels (with up to 0.4% C) used for heat-hardenable articles and welded assemblies with high enough yield strength (up to 1400 MPa) do not meet the listed requirements due to the elevated content of carbon. Typical steels for heat-hardened preforms (38KhNM, 38KhN3M) and welded assemblies (12Kh2NMFA, 20GNM, 20KhGSA, 12KhG2MF, etc.) contain 0.15 – 0.40% C.

Carbon is the most economical element for raising the strength of a steel, but its elevated content is responsible for a number of undesirable consequences. In the presence of carbon shear cooperative transformations (martensitic, bainitic) determine a high level of internal stresses. Blocking of dislocations by atmospheres of carbon atoms or carbides hinders stress relaxation. In most cases bainitic transformation in medium-carbon structural steels develops comparatively ra-

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**Fig. 1.** Diagram of the principal dependence of the characteristics of strength (str.) and ductility (duct.) on the tempering temperature for steels containing about 0.1% C.

pidly; the presence of even a little amount of upper bainite in heat treated steels causes rapid increase in the critical brittle point [1].

Growth in the carbon content intensifies the volume effect in the transformation and thus causes warping and shrinkage of the construction, which makes it necessary to perform laborious leveling.

Welding of medium-carbon steels causes special difficulties. Untempered low-ductility martensite and upper bainite form in the welding zone due to the high cooling rate and this results in formation of cold cracks.

Since the demand for steels possessing high structural strength and processibility is high, we observe a long-term world tendency for creating steels with reduced carbon content. Attention is also devoted to the simplicity of heat treatment and the possibility of hardening without the use of liquid cooling media. After cooling at a moderate rate such steels have a structure of ferrite [2, 3], bainite [4], and martensite [5, 6].

Steels known as pearlite-free ones and bearing 0.03 – 0.1% C, 1.5 – 2.0% Mn and low (up to 0.06 – 0.08%) additives of Nb or V have been developed in the 1960s [2, 3]. As a rule, these steels are subjected to controlled rolling with subsequent accelerated cooling and have a yield strength  $\sigma_{0.2} = 400 - 500$  MPa.

Steels known as bainitic ones, which contain a comparatively low amount carbon and are alloyed in a way that results in formation of a bainitic structure in a wide range of cooling rates have been suggested as long ago as in the 1950s [4].

Bainitic transformation is connected with redistribution of carbon in the austenite in the process of the transformation (removal of carbon from the front of a growing crystal of  $\alpha$ -phase), which yields regions of retained austenite enriched with carbon to a high degree. For example, in steel 15KhNMPA the lattice parameter of the retained austenite

(hardening with decelerated cooling below  $M_i$  aimed at raising the fraction of retained austenite) is equal to 0.3542 nm; after a 5-min hold at 500°C (50% of the intermediate transformation) it is equal to 0.3572 nm. This corresponds to enrichment of retained austenite, i.e., growth in its carbon content by 0.6% on the average).

The concentration of carbon in retained austenite is quite nonuniform; a part of retained austenite with lower carbon concentration transforms into martensite in further cooling to room temperature [1, 7]. For this reason, the structure of the steel after bainitic transformation and cooling to room temperature exhibits “islands” containing retained austenite and martensite with elevated (with respect to the mean value) carbon content [1, 7 – 11]. The presence of the “islands” is responsible for growth in the yield strength and marked intensification of the susceptibility to brittle fracture.

### PRINCIPLE OF FORMATION OF COMPOSITION OF LOW-CARBON MARTENSITIC STEELS (LCMS)

LCMS basically meeting the listed requirements were developed in the 1980s [1, 6] and had a structure of lath martensite. The structure of low-carbon martensite is characterized by a twice higher toughness at a strength equal to that of the traditional medium-carbon steels [12].

Low-carbon lath martensite (about 0.11% C) in hardened (untempered) state (Fig. 1) is distinguished by strength and ductility characteristics similar to those of alloy medium-carbon steels (up to 0.40% C) tempered at 300 – 500°C, in which the solid solution preserves about 0.10% C [6] and the rest of the carbon goes to carbides. In low-carbon martensite the whole of the carbon is preserved in the solid solution and a carbide phase is virtually absent. As a result, the hardened metal possesses high ductility, toughness, and strength. Since a packet of crystals is represented by a weakly fragmented single block separated from the neighbor blocks by high-angle boundaries, it becomes a structural component entering the relations describing the strength of the steel [13]. Specifically, in the Hall – Petch formula

$$\sigma_{0.2} = \sigma_0 + kd^{-1/2},$$

relating the yield strength  $\sigma_{0.2}$  and the size parameter  $d$  the latter correlates well with the size of an individual packet rather than with an individual crystal [13]. As a rule, the sizes of a packet and of a lath change consistently. However, when it is possible to separate their effects, the hardening due to the laths is 1 – 2 orders of magnitude higher than that due to the packets [14]. Parameter  $\sigma_0$  characterizes the resistance to the motion of dislocations not only inside martensite crystals but also involves their transition through low-angle boundaries separating the crystals of one packet.

Low-carbon martensite does not contain twin boundaries impenetrable for moving dislocations. The temperature range of formation of packet (lath) martensite is high enough

(360–420°C). This promotes removal of stresses in slow cooling. Special features of packet martensite are its insusceptibility to formation of cold cracks, relaxation of residual quenching and welding stresses, and a lower factor of strain hardening.

The structure and the composition of a steel, where the stresses are distributed uniformly, determine the structural strength in a wide range of operating conditions. Consequently, an optimum structure should promote relaxation of local stress peaks and a hardening mechanism in which dislocations are mobile and are generated easily enough. The mentioned conditions are met by a structure where the ratio of the rate of stress relaxation to the rate of strain hardening is the highest, which requires fulfillment of the following conditions:

- (1) the structure should be represented by lath low-carbon martensite;
- (2) the carbon content in the solid solution should be about 0.1%;
- (3) the intermediate structures formed due to diffusion (pearlite, bainite) and hence due to creation of concentration and other kinds of inhomogeneity should not arise in cooling of the austenite in the hardening process independently of the cooling rate;
- (4) the second phase (carbides, etc.) should be contained in an amount not causing complete locking of dislocations and loss of their mobility;
- (5) the presence of martensite of other types (lamellar, branched, mixed, high-temperature lamellar), in which relaxation of stresses is difficult, is undesirable;
- (6) the accumulated residual stresses of production or operation nature should be the lowest.

## PRINCIPLES OF ALLOYING OF LCMS

The task of creation of high-technology LCMS with yield strength of 650–1000 MPa has been solved with allowance for the special features of the kinetics and mechanism of polymorphic  $\gamma \rightarrow \alpha$  transformation [15–17].

Depending on the alloying, the temperature, and the cooling rate the transformation can develop by two mechanisms, i.e., a “normal” (disordered, self-diffusion) one, which yields polyhedral ferrite with low dislocation density, and a martensitic one with dislocation density exceeding  $10^{10} \text{ cm}^{-2}$ .

The stability of the austenite can be elevated by lowering the temperature of the phase transition (a thermodynamic method) or extending the incubation period in the range of normal and bainitic transformations (a kinetic method).

**Thermodynamic Method.** It is known that in order to raise the stability of austenite in a temperature range of 600–500°C we should use a considerable amount of nickel and manganese (about 18–25%) required for lowering the temperature of the  $\gamma \rightarrow \alpha$  phase transformation, which would eliminate self-diffusion of iron atoms. This makes only a

martensitic transformation possible. The method is well known and employed for creating maraging steels [18].

However, the use of such steels is commercially expedient only in aircraft and rocket building, because the steels are alloyed with scarce elements in high amounts, namely, 18% Ni, 4–9% Co, 5% Mo, and 12–18% Cr.

**Kinetic Method.** Our studies have shown that martensite can be obtained in low-carbon iron by another method. Elevation of the activation energy of iron and carbon atoms by complex alloying of low-carbon austenite may raise substantially its stability and cause martensitic transformation by a shear mechanism in slow cooling without lowering the temperature of the  $\gamma \rightarrow \alpha$  transformation.

The rate of “normal”  $\gamma \rightarrow \alpha$  transformation will change substantially due to complex alloying. The features of the kinetics of  $\gamma \rightarrow \alpha$  transformation in alloy iron have made it possible to create a new class of low-carbon low-alloy martensitic steels with rupture strength  $\sigma_r = 1000–1400 \text{ MPa}$ .

The duration of the incubation period of the normal transformation can be measured by hours in the case of alloying of the steel with chromium, nickel, manganese, and molybdenum. Below some temperature  $M_i$  a martensitic  $\gamma \rightarrow \alpha$  transformation develops and is accompanied by the appearance of a typical microtexture.

The effect of alloying on the stability of austenite is evaluated in terms of the characteristics of self-diffusion. The parameters of the self-diffusion are determined by an adsorption method [19] using radioactive a  $\text{Fe}^{59}$  isotope.

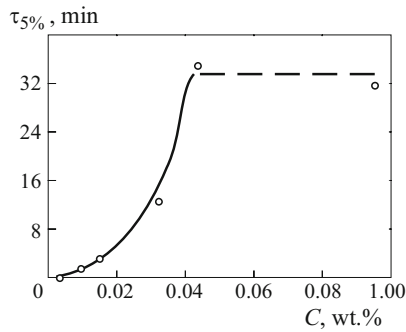
The duration of the incubation period and of the time of half-transformation of austenite at the temperature of “normal” transition agrees qualitatively with the characteristics of boundary self-diffusion of iron. The activation energy of boundary self-diffusion of iron bearing 0.04% C is equal to 26 kcal/(g · atom); in the case of alloying with 7% Cr and 2% Ni the value is 40 kcal/(g · atom); the time of 5% transformation of the  $\alpha$ -phase is less than 1 and 720 sec, accordingly.

On the other hand, in the case of the same alloying (7% Cr and 2% Ni) the activation energy of boundary self-diffusion of iron amounts to 33 kcal/g · atom at 0.003% C and to 40 kcal/(g · atom) at 0.04% C [20, 21].

These regular features and the necessity for eliminating bainitic transformation determine the permissible range of carbon concentration in low-carbon martensitic steels, which is 0.04–0.12% in most cases. The upper limit of the carbon content is still amended.

The combination of the alloying elements has been chosen so as to ensure stability of austenite in the range of “normal” transformation and to eliminate bainitic transformation.

The low content of carbon in the solid solution (0.04–0.12%) keeps the dislocations mobile (the concentration of carbon is too low for their locking); stress relaxation is promoted (another factor of stress relaxation is the comparatively high temperature of the start of martensitic trans-



**Fig. 2.** Effect of carbon concentration on the stability of austenite at the temperature of its minimum stability in the “normal” range for a steel bearing 5% Cr, 2% Ni, and 0.8% Mo (the austenization temperature is 950°C) ( $\tau_{5\%}$  is the time of 5% development of the transformation).

formation  $M_i$ ). It has been shown in [22] that complete locking of dislocations in martensite is attained at less than 0.20% carbon in the composition. The results of a study of the effect of carbon on stability of austenite (Fig. 2 [23]) show that the minimum content of carbon in the steels in question should not be lower than 0.04%.

Below, we present data characterizing the stability of austenite in the range of “normal” (austenite-ferrite) transformation (at 650°C) in various steels upon changes in the alloying system.

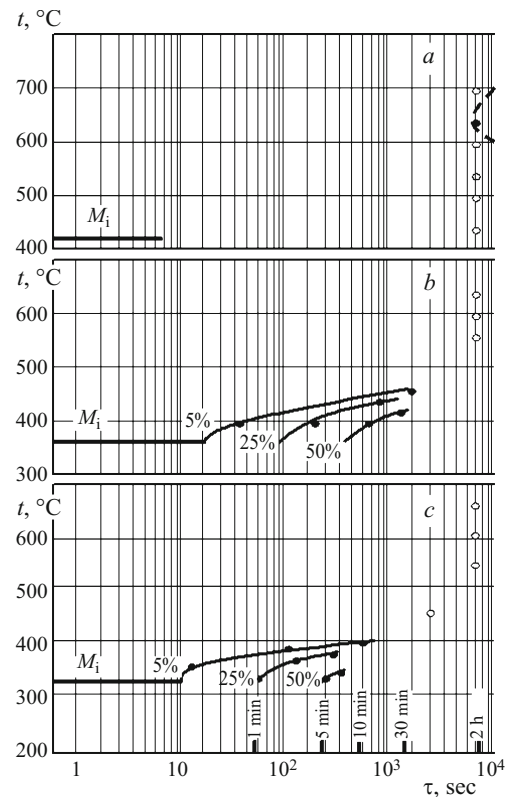
Steel	Time of attainment of 5% transformation of austenite, min
10Kh2G2.5	50
06Kh2G3.	120
11Kh4N1	20
11Kh3N2.	140
11Kh4N2	30
11Kh3N2M	120
08Kh7G2.	120
08Kh7G2D2.	180

Elevation of the content of chromium increases considerably the stability of supercooled austenite; at a specific content of chromium (from 1 to 5 – 7%) alloying with nickel, manganese and copper also raises markedly the stability of austenite.

Figure 3 presents diagrams of transformation of austenite in steels bearing 2% Cr and 3% Mn with carbon content of 0.04, 0.09, and 0.13%. In the steels with 0.09 and 0.13% C we observe an well-manifested temperature range of bainitic transformation.

The enhancement of the stability of austenite in the region of normal austenite-ferrite transformation upon growth in the carbon concentration from 0.006 to 0.04% seems to be connected with the decrease in the mobility of metallic atoms during self-diffusion due to their interaction with vacancies.

Analysis of diagrams of isothermal transformation of austenite in the studied steels allows us to infer that the car-



**Fig. 3.** Diagrams of isothermal transformation of austenite in steels bearing 2% Cr, 3% Mn and different contents of carbon, i.e., 0.04% C (a), 0.09% C (b), and 0.13% C (c). The austenization temperature is 900°C.

bon-to-chromium proportion influences the appearance of a region of bainitic transformation.

At  $Cr/C \geq 35$  (the concentrations of the elements are taken in mass percent) or  $Cr/C \geq 8$  (in atomic percent) bainitic transformation does not occur. The elimination of the temperature range of bainitic transformation at specific alloying seems to be connected with deceleration of the processes of diffusion redistribution of carbon, which is an inseparable part of the transformation [24]. The deceleration is a result of the fact that alloying, for example with chromium or molybdenum, lowers considerably the thermodynamic activity of carbon in the austenite [25] and this effect is intensified upon growth in the chromium-to-carbon proportion.

### CONCLUSIONS

Thus, a specific combination of alloying elements and carbon has made it possible to create steels with required stability of austenite, which provides formation of martensitic structure at low cooling rates, in air in the first turn.

The composition of such a steel is also determined by the conditions of its service and by the process requirements connected with the method of hardening used for obtaining the specified combination of physical and mechanical pro-



erties. These factors determine the main principles of the alloying.

(1) The sum of the alloying elements at carbon content below 0.12% should provide stability of the austenite in the “normal” range of the transformation (hardenable) with allowance for the rate of cooling in air hardening of specific preforms and welded assemblies and absence of bainitic transformation.

(2) The steel should contain molybdenum if it is welded in a heat hardened condition and should not bear molybdenum if it is not welded or if the welding is followed by a hardening treatment. Molybdenum is necessary for preventing temper brittleness and elevating the hardenability.

(3) If the steel is to be used at low temperatures (up to  $-50^{\circ}\text{C}$ ), nickel becomes a necessary additive.

(4) The composition of a steel used for making parts subjected to thermochemical treatment should contain chromium, vanadium, molybdenum and other elements in specific combinations with carbon in order to provide high surface hardness and strength of the core.

LCMS possessing elevated processibility are used for precision heat hardened preforms, rolled articles, sheets, and stampings including those hardened right after hot pressure treatment without application of liquid cooling media, composite welded heat hardened constructions, and parts subjected to thermochemical treatment (carburizing, nitriding, etc.).

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