

The Role of Molybdenum in the Kinetics of Bainitic Transformation of Steel

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ABSTRACT

When studying the kinetics of the transformation of supercooled austenite in a wide range of cooling rates for medium-carbon steels, molybdenum alloying sharply increases the stability of austenite during its diffusion decomposition, shifting the region of decomposition into pearlite and ferrite towards low cooling rates. It is shown that the region of austenite decomposition into bainite is separated from the region of decomposition into pearlite. Bainite transformation occurs over a very wide range of cooling rates in the temperature range 530–335 °C, with the formation of mainly products of decomposition of the granular structure.

Keywords: Medium-carbon steel, Molybdenum, Cooling, Diffusion decomposition, Austenite stability.

1 INTRODUCTION

Alloy steels with increased molybdenum content are widely used for the manufacture of large-sized critical components, such as wind turbine shafts, power turbine rotors and other components requiring a combination of high strength, toughness and hardenability. Molybdenum is one of the key alloying elements that increase the hardenability and suppress the temper brittleness of steels. Medium-carbon bainitic steels have higher strength but lower toughness than low-carbon bainitic steels [1].

The volume of research presented in the literature provides a comprehensive understanding of the kinetics of phase transformations in alloyed steels and the factors influencing the formation of their microstructure and properties [2]. Study [3] demonstrates the systematic influence of carbon on the temperature parameters of phase transformations: as its concentration increases, the onset temperature of martensitic transformation (M_s) decreases, which is consistent with classical ideas about the stabilizing effect of carbon on austenite. Interestingly, increased carbon content extends the stability interval of austenite in the bainite transformation region, but only up to a certain limit (0.30% C), after which other mechanisms probably begin to dominate. The obtained isothermal decomposition diagrams correspond to type IV according to the Weber and Rose classification, which is typical for alloyed steels, and the high temperature of the start of bainite transformation (about 500 °C) indicates the risk of upper bainite formation during continuous cooling.

Research [4] complements this picture by focusing on the role of structure, namely the size of the initial austenite grain. It has been established that the kinetics of austenite formation during heating are significantly accelerated with a decrease in grain size, which is explained by an increase in the area of boundaries that serve as sites of preferential heterogeneous nucleation of the new phase. At the same time, the critical temperature A_{c1} does not depend on grain size, which emphasizes the different nature of the thermodynamic and kinetic aspects of the transformation. The development of a mathematical model linking the amount of austenite formed with time, heating rate and grain size is of considerable practical value for predicting and optimizing heat treatment regimes, especially for large forgings with a gradient of properties from the surface to the core.

Research [5] delves into the details of isothermal bainite transformation and its effect on the characteristics of residual austenite. The key conclusion is that there is a trade-off between the amount of residual austenite and its carbon content depending on the isothermal holding temperature. Higher transformation temperatures promote the formation of a larger volume of residual austenite, but it is less stable due to its lower carbon content. Conversely, low-temperature bainite transformation, although producing a smaller volume, ensures its higher stability due to carbon dispersion. At the same time, it was found that the kinetics of the transformation accelerate with increasing temperature, and the morphology of the decomposition products changes: as the temperature decreases, finer bainitic

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ferrite and smaller particles of residual austenite are formed. The difference in activation energies for nucleation at different types of boundaries confirms the complex nature of bainite transformation.

Taken together, the available data clearly show that in order to control the properties of high-strength alloy steels, it is necessary to take all these factors into account simultaneously, since they are closely and complexly interrelated. The fundamental knowledge gained and the mathematical models developed form the basis for the targeted selection of heat treatment modes that allow the required set of mechanical properties to be obtained in products.

Analysis of the literature shows that the influence of various factors on the kinetics of austenite transformations has been studied in general, but systematic studies of phase transformations in such steels over a wide range of cooling rates for steels with a molybdenum content of about 0.5% remain limited. Thus, the study of transformations at high cooling rates (water quenching), characteristic of the processing of large-sized products, is of particular interest. In this regard, a study was conducted to investigate the kinetics of the transformation of supercooled austenite over a wide range of cooling rates for steel with the following chemical composition (wt. %): C - 0.36, Mn - 0.83, Si - 0.42, S - 0.004, P - 0.014%, Cr - 0.86, Ni - 0.37, Cu - 0.045, Al - 0.031, Mo - 0.55%.

2. MATERIALS AND METHODS

The kinetics of austenite transformation after separate heating were studied in a wide range of cooling rates on DIL 805A/D dilatometers, which allowed the martensitic transformation to be identified at different cooling rates [6]. Samples with a diameter of 4 mm were heated to 900 °C and held for 20 min. They were then cooled at rates ranging from 16.4 °C/s to 0.02 °C/s. The thermogram was used to determine the average cooling rate in the temperature range between A_{c3} and M_s . The inflection points on the dilatograms were used to determine the start and end temperatures of the phase transformation. The structure of the decomposition products was studied using a microstructural method on dilatometric samples after various cooling rates. The sections were etched with a 4% solution of nitric acid in alcohol. The percentage content of structural components was determined under a microscope using a computer image analysis system. The results of the study of the kinetics of phase transformations during continuous cooling are summarized in the form of a thermokinetic diagram of the decomposition of supercooled austenite of the given chemical composition of steel (Fig. 1).

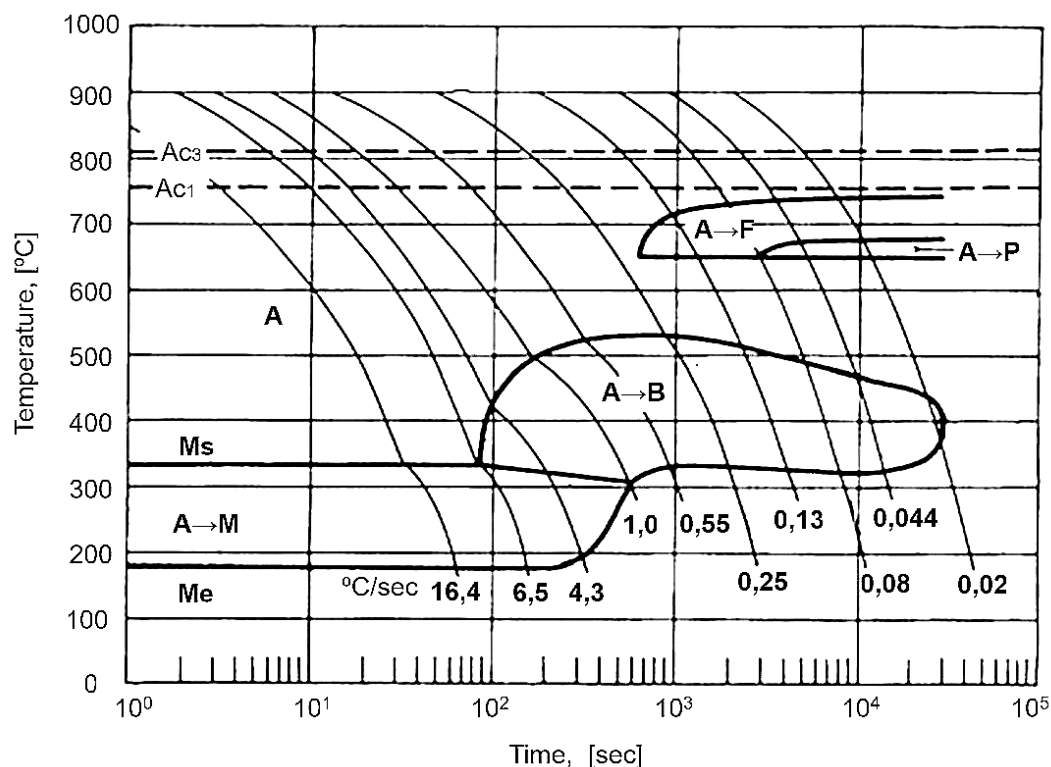


Figure 1: The CCT diagram of steel with C - 0.36, Mn - 0.83, Si - 0.42, Cr - 0.86, Ni - 0.37, Cu - 0.045, Al - 0.031, Mo - 0.55%.

3. RESULTS AND DISCUSSIONS

Critical points were determined during heating at a rate of 200° C/hour and are equal to: A_{c1} – 755 °C and A_{c3} – 810 °C. The increased temperature A_{c1} is due to the increased dissociation energy of molybdenum-doped cementite [7].

Analysis of the thermokinetic diagram and microstructural studies of the samples showed the following: at cooling rates above $6.5\text{ }^{\circ}\text{C/s}$, supercooled austenite transforms with the formation of martensite. The start temperature of the martensitic transformation at a cooling rate of $16.4\text{ }^{\circ}\text{C/s}$ is $330\text{ }^{\circ}\text{C}$, and the end of the decomposition is recorded at a temperature of $180\text{ }^{\circ}\text{C}$. The release of a significant amount of heat during the formation of martensite leads to a slowdown in the cooling rate of the sample. The second feature of the decomposition of supercooled austenite is the uneven rate of martensite formation during cooling. Thus, when cooling at a rate of $6.5\text{ }^{\circ}\text{C/s}$, 50% of martensite is formed when cooling to $280\text{ }^{\circ}\text{C}$. With further cooling, the rate of decomposition of supercooled austenite into martensite decreases, and the decomposition of austenite ends only at a temperature of $180\text{ }^{\circ}\text{C}$. The martensitic structure of samples cooled at rates of $16.4\text{ }^{\circ}\text{C/s}$ and $6.5\text{ }^{\circ}\text{C/s}$ has, for the most part, a rack structure.

In the cooling rate range from $6.5\text{ }^{\circ}\text{C/s}$ to $1.0\text{ }^{\circ}\text{C/s}$, supercooled austenite decomposes into bainite and martensite. The temperature at which bainite begins to form at a cooling rate of $4.3\text{ }^{\circ}\text{C/s}$ rises to $420\text{ }^{\circ}\text{C}$, and at a cooling rate of $1\text{ }^{\circ}\text{C/s}$ it is already $490\text{ }^{\circ}\text{C}$. At the same time, the degree of decomposition into bainite increases and at a cooling rate of $1\text{ }^{\circ}\text{C/s}$ is 90-95%. The microstructure of steel after cooling at a rate of $4.3\text{ }^{\circ}\text{C/s}$ consists of 20% bainite and 80% martensite, and after cooling at a rate of $1\text{ }^{\circ}\text{C/s}$, the martensite content decreases to 3-5%. In this case, mainly lower bainite is formed in the form of dark stripes (Fig. 2a). The mechanism of formation of such structures is described in [8]. The decomposition of supercooled austenite only into bainite is observed in a wide range of cooling rates from $1\text{ }^{\circ}\text{C/s}$ to $0.2\text{ }^{\circ}\text{C/s}$. At the same time, the temperature at which austenite begins to decay into bainite increases from $490\text{ }^{\circ}\text{C}$ to $530\text{ }^{\circ}\text{C}$. The temperature at which austenite decay ends also increases from $305\text{ }^{\circ}\text{C}$ to $335\text{ }^{\circ}\text{C}$.

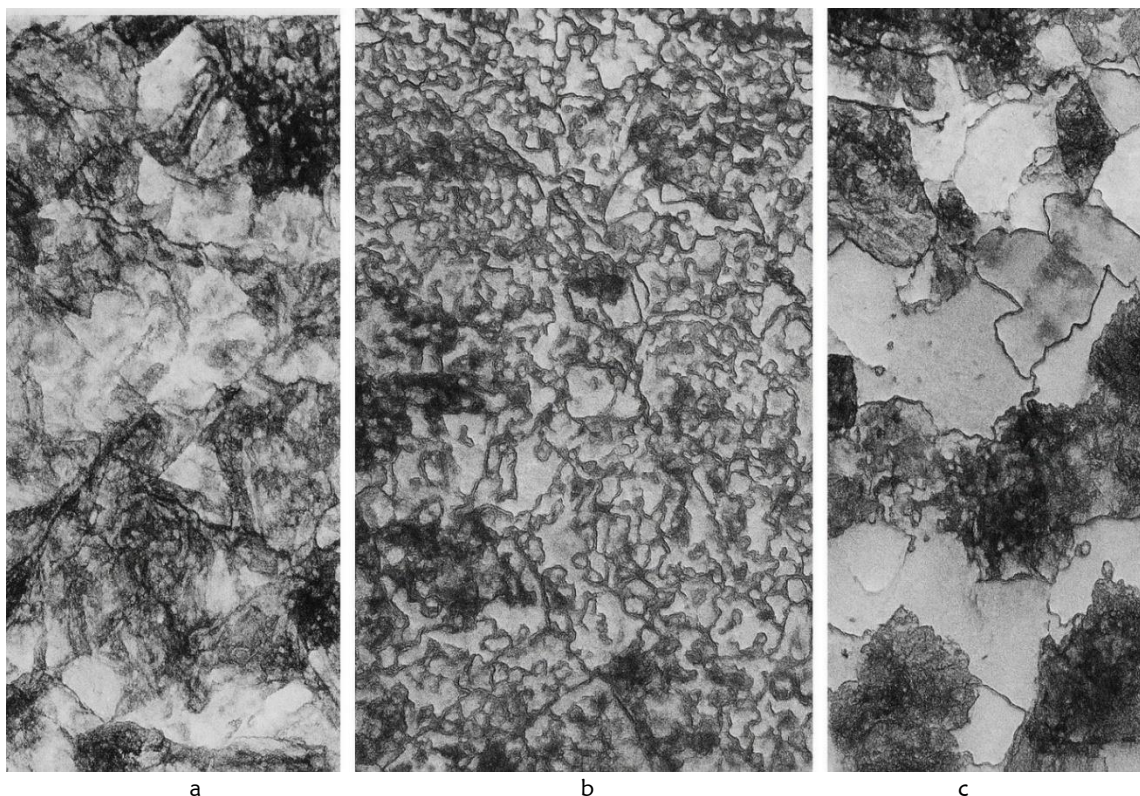


Figure 2: Microstructure of steel after heating to $900\text{ }^{\circ}\text{C}$ for 20 minutes and cooling at a rate of: a – $4.3\text{ }^{\circ}\text{C/s}$, b – $2.7\text{ }^{\circ}\text{C/s}$, c – $0.16\text{ }^{\circ}\text{C/s}$ $\times 500$.

Bainite has a heterogeneous granular structure (Fig. 2b). The mechanism and kinetics of granular bainite formation are described in [9, 10]. At the same time, the rate of austenite decomposition into bainite at temperatures below $530\text{ }^{\circ}\text{C}$ decreases due to a decrease in the carbon diffusion coefficient. The maximum rate of austenite decomposition occurs at temperatures above $450\text{ }^{\circ}\text{C}$. When the temperature drops to $380\text{ }^{\circ}\text{C}$, 95% of bainite is formed. The remaining 5% of residual austenite decomposes only during cooling to $335\text{ }^{\circ}\text{C}$. Similar kinetics of austenite decomposition into bainite are described in [11].

Ferrite-pearlite structures in steel are formed at cooling rates below $0.25\text{ }^{\circ}\text{C/s}$. In the cooling rate range from $0.20\text{ }^{\circ}\text{C/s}$ to $0.08\text{ }^{\circ}\text{C/s}$, supercooled austenite begins to decompose into ferrite according to diffusion kinetics. The first small ferrite grains are found at the grain boundaries in samples cooled at a rate of $0.20\text{ }^{\circ}\text{C/s}$. As the cooling rate decreases to $0.13\text{ }^{\circ}\text{C/s}$, the austenite decomposition starts temperature rises to $715\text{ }^{\circ}\text{C}$, and the degree of decomposition increases to 5-10%. At a cooling rate of $0.08\text{ }^{\circ}\text{C/s}$, the ferrite decomposition starts temperature rises

to 735 °C, and the degree of decomposition to 20%. When cooled to a temperature of 650 °C, the decomposition of supercooled austenite into ferrite stops. The remaining austenite decomposes into bainite during further cooling. At the same time, the temperature at which decomposition into bainite begins decreases from 530 °C to 490 °C as the cooling rate decreases from 0.25 °C/s to 0.08 °C/s, and the temperature at which austenite decomposition ends is in the range of 330–340 °C. Ferrite is mainly equiaxed, while bainite is formed only in fine grains of residual austenite and has a light, uniform grain size without signs of fragmentation.

The pearlite structure is formed from supercooled austenite at cooling rates below 0.08 °C/s (500 °C/hour). The first pearlite zones in the cooling process at a rate of 0.08 °C/s are formed at a temperature of 650 °C. With a decrease in the cooling rate to 0.044 °C/s, the temperature at which austenite begins to decompose into pearlite rises to 670 °C and continues during cooling to 650 °C. The degree of austenite decomposition into ferrite and pearlite according to diffusion kinetics is 70%. The microstructure of the steel consists mainly of equiaxed ferrite grains, dark-coloured pearlite grains, and bainite at cooling rates of 0.044 °C/s and below, which forms only in small grains of residual austenite and has a light, uniform colour without signs of fragmentation (Fig.1c). At a minimum cooling rate of 0.02 °C/s (75% decay) in the temperature range of 740–675 °C, large ferrite grains are formed. With further cooling in the temperature range of 675–650 °C, supercooled austenite decomposes with the formation of large and equiaxed pearlite grains. The total degree of decomposition is 95%. The remaining austenite decomposes into bainite with further cooling. The temperature at which decomposition into bainite begins decreases from 490 °C at a cooling rate of 0.08 °C/s to 445 °C at a cooling rate of 0.02 °C/s. The end temperature of austenite decomposition into bainite increases from 330 °C to 370 °C. The microstructure of the steel consists of large grains of ferrite and pearlite, with bainite present in the form of separate, slightly grainy areas. At cooling rates below 0.02 °C/s, supercooled austenite decomposes only according to diffusion kinetics with the formation of large grains of equiaxed ferrite and pearlite. Thus, in the studied steel, after heating to 900 °C and holding for 20 minutes, the following structures are formed depending on the cooling rate.

A martensitic structure is formed from supercooled austenite at cooling rates above 6.5 °C/s in the temperature range of 330–180 °C. A mixed structure consisting of bainite and martensite in various percentages is formed from austenite at cooling rates ranging from 6.5 °C/s to 1 °C/s and temperatures ranging from 490 to 180 °C. A bainitic structure is observed in samples cooled at cooling rates ranging from 1 °C/s to 0.20 °C/s and temperatures ranging from 530 to 330 °C. A mixed structure consisting of ferrite and bainite is observed in the studied steel after cooling at cooling rates ranging from 0.20 °C/s to 0.08 °C/s. At the same time, with a decrease in the cooling rate to 0.08 °C/s, the bainite content decreases to 75% due to partial decomposition into ferrite. A mixed structure consisting of ferrite, pearlite and bainite is observed in the studied steel after cooling at cooling rates ranging from 0.08 °C/s to 0.02 °C/s. At a cooling rate of 0.02 °C/s, 95% ferrite and pearlite and 3-5% bainite are formed. A structure consisting only of ferrite and pearlite is formed at all cooling rates below 0.02 °C/s.

The critical points of the studied steel are: A_{c1} – 755 °C, A_{c3} – 810 °C. The temperature of the start of martensitic transformation at cooling rates above 6.5 °C/s is 330 °C, and martensitic transformation ends at 180 °C. The increased molybdenum content in the studied steel, equal to 0.55%, caused high stability of supercooled austenite, which led to a significant shift to the right in the region of decomposition into ferrite and pearlite, and the formation of high austenite stability in the temperature range 650–530 °C. According to [8, 12], this is due to the fact that molybdenum significantly reduces the rate of nucleation and growth of pearlite colonies by lowering the diffusion coefficient of carbon and the self-diffusion of iron atoms. However, molybdenum has little effect on the kinetics of the transformation of supercooled austenite, which proceeds according to non-diffusive kinetics with the formation of martensite [12], since it has little effect on the elastic deformation energy of the α phase. This has made it possible to obtain martensite-bainite structures over a wide range of cooling rates. Similar kinetics of austenite decomposition into bainite were also found in earlier work [13]. It has been shown that in complex alloy steels with 0.39% C and 0.51% Mo, pearlite transformation is separated from bainite transformation in the temperature range of 420–540 °C. In addition, it has been shown that bainite and martensite transformations occur in a narrow range of cooling rates. The possibility of austenite decomposition in a wide range of cooling rates with the formation of 100% bainite in complex alloy steel with C-0.28%, Mo-0.49% was shown in [13]. At the same time, bainite transformation also occurs in a very wide range of cooling rates.

4 CONCLUSIONS

This study shows that a fully bainitic structure can be obtained over a very wide range of cooling rates (from 1 °C/s to 0.20 °C/s) due to the addition of molybdenum, which is a technologically significant aspect when choosing the heat treatment regime for steel. It has been established that in the cooling rate range of 1 – 0.20 °C/s, supercooled austenite below 530 °C decomposes 100% with the formation of only bainite. The bainite transformation is separated from the pearlite transformation by a temperature range of high stability. In a mixed decomposition scheme with a decrease in the cooling rate, the temperature at which austenite begins to decompose into bainite decreases from 530 °C to 430 °C. The critical points due to molybdenum and chromium are higher than those for carbon steel and are equal to A_{c1} – 755 °C and 810 °C. During cooling below 530 °C, the rate of austenite decomposition into bainite has a damping effect. The maximum rate of austenite decomposition into bainite is observed in the temperature range of 530–450 °C. At the same time, 95% of bainite is formed when cooled to a temperature of 350 °C. The end temperature of the bainite transformation with mixed austenite decomposition kinetics is above the start temperature

of the martensite transformation. Microstructural studies have established that ferrite has a mainly polyhedral shape, pearlite has a sorbite-like structure, bainite has a structure close to granular with varying degrees of dispersion of decomposition products, and martensite has a weakly pronounced needle-like structure. Thus, an increased molybdenum content of up to 0.55% in medium-carbon steel contributes to the formation of a bainite structure over a wide range of cooling rates, which allows it to be used for the manufacture of parts in the mechanical engineering, metallurgical, transport and construction industries with a high complex of mechanical and operational properties.

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