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# THE PHASE TRANSFORMATIONS IN HYPOEUTECTOID STEELS Mn-Cr-Ni

# PRZEMIANY FAZOWE W STALACH PODEUTEKTOIDALNYCH Mn-Cr-Ni

The results of a microstructure and hardness investigations of the hypoeutectoid steels Mn-Cr-Ni, imitating by its chemical composition toughening steels, are presented in the paper. The analysis of the kinetics of phase transformations of undercooled austenite of steels containing different amounts of alloying elements in their chemical composition, constitutes the aim of investigations.

Metallographic examinations were carried out on a Axiovert 200 MAT light microscope. Sections were etched with a 3% $HNO_3$ solution in $C_2H_5OH$.

Dilatometric tests were performed using L78 R.I.T.A dilatometer. Using dilatometer the changes of elongation (Δl) of the samples with dimensions Ø 3×10 mm as a function of temperature (T) were registered. Obtained heating curves were used to precisely determine the critical temperatures (critical points) for the tested steels, while the differentiation of obtained cooling curves allowed to precisely define the temperatures of the beginning and the end of particular transition to draw CCT diagrams.

Four CCT diagrams worked out for the tested hypoeutectoid steels (for quenching of steel) are – in the majority of steels – separated by the undercooled austenitic range and are of the letter „C" shape. However, for steels with Mn and Ni the separation of diffusive transformations from the bainitic transformation by the stable austenitic range is not observed. Hardenability of four investigated hypoeutectoid steels is similar, but still not high. To obtain martensite in the microstructure of these steels, it is necessary to apply the cooling rate higher than 25°C/s. The exception constitutes the Mn – Ni steel, in which only cooling with the rate higher than 50°C/s allows to achieve the martensitic microstructure and to avoid diffusive transformations (pearlitic and ferritic).

*Keywords*: microstructure, hypoeutectoid steel, CCT diagram, hardenability, alloying elements

W artykule zamieszczono wyniki badań mikrostruktury, twardości stali podeutektoidalnych Mn-Cr-Ni imitujących składem chemicznym stale do ulepszania cieplnego. Celem badań jest analiza kinetyki przemian fazowych przechłodzonego austenitu stali różniących się zawartością pierwiastków stopowych w składzie chemicznym.

Badania metalograficzne wykonano na mikroskopie świetlnym Axiovert 200 MAT. Zgłady wytrawiono 3% nitalem (3% roztwór $HNO_3$ w $C_2H_5OH$).

Badania dylatometryczne wykonano przy użyciu dylatometru L78 R.I.T.A. Za pomocą dylatometru rejestrowano zmiany wydłużenia (Δl) próbek o wymiarach Ø 3×10 mm w funkcji temperatury (T). Otrzymane krzywe nagrzewania posłużyły do precyzyjnego wyznaczenia temperatur krytycznych (punktów przełomowych) dla badanych stali. Z kolei, otrzymane krzywe chłodzenia różniczkowano, co pozwoliło precyzyjnie określić temperatury początków i końców poszczególnych przemian dla wykonania wykresów CTPc.

Opracowane cztery wykresy CTPc dla badanych stali podeutektoidalnych (do ulepszania cieplnego) są w większości rozdzielone zakresem trwałości przechłodzonego i mają kształt litery „C". Jednak dla stali z Mn i Ni nie obserwuje się rozdzielenia przemian dyfuzyjnych od przemiany bainitycznej zakresem stabilnego austenitu. Hartowność czterech badanych stali podeutektoidalnych jest zbliżona do siebie, ale nadal niewielka. Dla uzyskania samego martenzytu w mikrostrukturze badanych stali, niezbędne jest zastosowanie szybkości chłodzenia większej niż 25°C/s. Wyjątek stanowi stal Mn-Ni, gdzie jej hartowność jest znikoma, ponieważ dopiero chłodzenie z szybkością większą niż 50°C/s pozwoli uzyskać mikrostrukturę martenzytyczną i uniknąć przemian dyfuzyjnych (perlitycznej i ferrytycznej).

## 1. Introduction

Optimal strength properties in relation to plastic properties have steel groups and alloy cast steels due to the application of the proper heat treatment, such as quenching [1]. These large groups of alloys for quenching are finding wide applications in the automotive, marine and extractive industry [2-6]. Materials made of these alloys are very often exposed to strong dynamic loads and variable climatic conditions (temperature differences: +20°C÷–60°C). Thus, a high yield strength, high YS/UTS values, high impact strength and weldability are required from them, since they are often welded to rolled or forged elements.

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TABLE 1

Chemical compositions of tested hypoeutectoid steels, % by mass

| No. | Steel symbol | C<br>% | Mn<br>% | Si<br>% | P<br>% | S<br>% | Cr<br>% | Ni<br>% | Mo<br>% | Cu<br>% | V<br>% | W<br>% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **39MnNi6-4** | 0.39 | 1.40 | 0.020 | 0.006 | 0.020 | - | 1.00 | - | 0.030 | 0.002 | 0.01 |
| 2 | **37MnMo6-3** | 0.37 | 1.47 | 0.014 | 0.006 | 0.020 | - | - | 0.27 | 0.030 | 0.002 | 0.01 |
| 3 | **36CrNi4-4** | 0.36 | 0.07 | 0.060 | 0.006 | 0.010 | 0.98 | 0.98 | - | 0.030 | 0.004 | - |
| 4 | **35CrMo4-3** | 0.35 | 0.08 | 0.060 | 0.005 | 0.010 | 0.98 | - | 0.31 | 0.030 | 0.005 | 0.01 |

Therefore, in order to obtain the proper combination of mechanical properties the right chemical composition and microstructure obtained as the result of the designed heat treatment should be selected – in practice – for each alloy individually. From this point of view, the analysis of microgradients of the chemical composition in hypoeutectoid steels with a background of alloying elements such as: Mn, Mo, Cr and Ni seems essential [7-11]. Up to now, an influence of each element was considered separately, sometimes only indicating the group of alloys in which this influence was estimated. It should be noted, that the interaction of two or more alloying elements is significantly different from the sum of effects of these elements added separately. The most important can be the common effect of: molybdenum and chromium, molybdenum and nickel, chromium and nickel, manganese and chromium, manganese and nickel, manganese and molybdenum. These mutual interactions of various elements on the effects of the others, may be the basis for the assessment of the impact magnitude of each of them on e.g. hardenability of steel under conditions of the presence of even one or several other elements in the above mentioned alloys of iron based steels.

The obtained investigation results of hypoeutectoid steels, containing: 0.35÷0.40% C and other alloying elements, are presented in the hereby paper. The assessment of the influence of the selected alloying elements on critical and austenitising temperatures and microstructures of the tested steels was performed. The kinetics of phase transformations of four hypoeutectoid steels for quenching during continuous cooling, is described in this paper.

## 2. Research material

The material for study were four hypoeutectoid steels: 39MnNi6-4, 36CrNi4-4, 37MnMo6-3 and 35CrMo4-3 (marked in accordance with PN-EN 10027-1:1994 standard). Steels in the form of model alloys were supplied as cast by Z. J. Głuchowski S. C. Kooperacja Przemysłowo-Handlowa in Gliwice, and then were reforged in INTECH – MET S. C. plant in Gliwice. The control analyses of the tested steels were performed in AGH, the University of Science and Technology in Krakow (see Table 1).

Tested steels are hypoeutectoid with a carbon content of about 0.4% and various contents of alloying elements such as: Mn, Ni, Mo and Cr. These steels imitate by their chemical compositions the group of structural steels for quenching.

The microstructures of tested steels in the state after forging is shown in Figure 1.

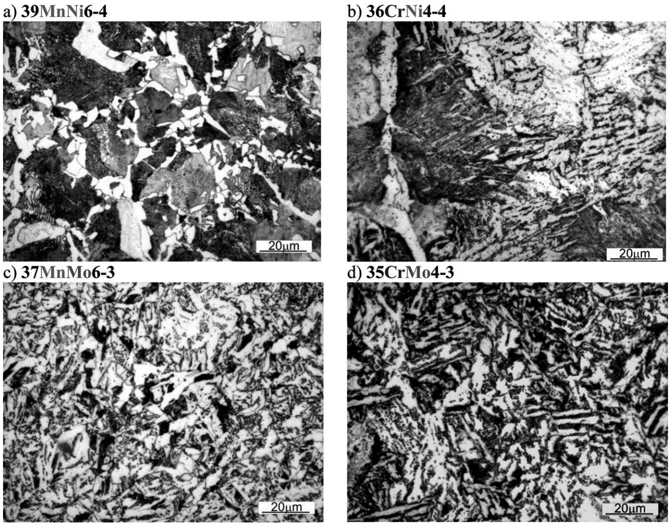


Fig. 1. The microstructure of hypoeutectoid steels in after forging state. Etched with 3% vol. $HNO_3$ in $C_2H_5OH$

As can be seen, the investigated steels in as-forged state have the pearlitic-ferritic microstructure with a small amount of bainite. The mentioned above structural components are of a different morphology. In steels containing 1% Ni, ferrite occurs on grain boundaries of prior austenite forming a network. Sometimes ferrite occurs also in the Widmannstätten system (compare Fig. 1a and b). The investigates steels containing Mo (37MnMo6-3 and 35CrMo4-3) have ferrite, pearlite and bainite in their microstructures.

In order to determine the correct critical temperatures (critical points) for four tested steels after forging the sample were heated at the rate of 0.05°C/s to a temperature of 1100°C and then cooled at the rate of 1°C/s to room temperature. Critical temperatures read are shown in Table 2.

TABLE 2

Critical temperatures determined for tested hypoeutectoid steels in a state after forging

| No. | Steel | $Ac_{1s}$ [°C] | $Ac_{1f}$ [°C] | $Ac_3$ [°C] |
|---|---|---|---|---|
| 1 | **39MnNi6-4** | 680 | 705 | 820 |
| 2 | **36CrNi4-4** | 720 | 750 | 780 |
| 3 | **37MnMo6-3** | 685 | 715 | 800 |
| 4 | **35CrMo4-3** | 740 | 765 | 820 |

Temperatures of critical points confirm the behavior of alloying elements in the studied steels. Nickel and magnesium, as an austenite creative elements lowers the critical temperatures, whereas molybdenum and chromium, which are highly ferrite creative significantly shifts the critical temperatures upward.

## 3. Experimental procedure

The chemical composition of the model alloy was designed in the Laboratory of Phase Transformations, Department of Physical and Powder Metallurgy, AGH University of Science and Technology.

The microstructure of the investigated material was examined using Axiovert 200 MAT the light microscope.

The hardness measurements were performed with the Vickers HPO250 apparatus.

The dilatometric measurements were performed with the L78R.I.T.A. dilatometer.

## 4. Results and discussion

### 4.1. Heat treatment (full annealing)

In order to obtain a microstructure similar to the equilibrium state the full annealing was performed for the tested steels. After such annealing the necessary treatment for mechanical testing and to remove the internal stress and improve the workability is easier to perform.

Full annealing was performed in a Carbolite RHF 16/19 laboratory oven. Samples were heated to a temperature by 50°C higher than the $Ac_3$ for tested steels, maintained at this temperature for 2 hours and then cooled at the rate of 3°C/min to a temperature of 500°C and further at the rate of 30°C/min to room temperature. The microstructures of four steels in state after full annealing are shown in Figure 2.

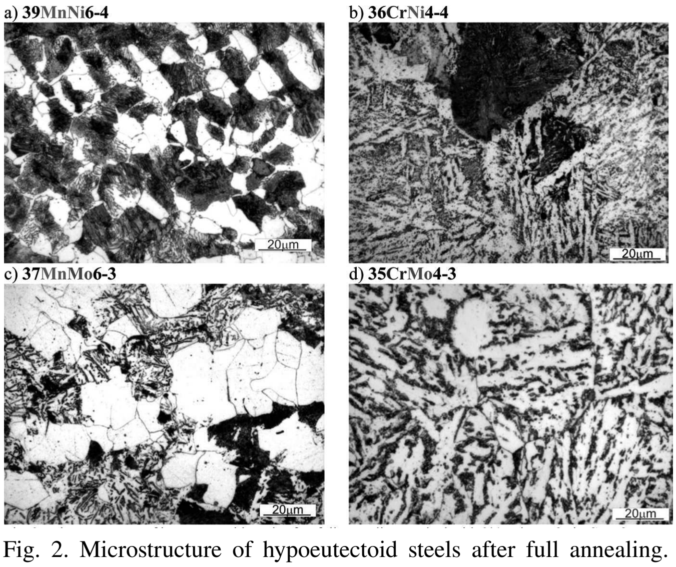


Fig. 2. Microstructure of hypoeutectoid steels after full annealing. Etched with 3% vol. $HNO_3$ in $C_2H_5OH$

Microstructure of the tested steels do not differ significantly from the microstructure in as-forged state. The only difference constitutes the austenite grain size which in case of three steels (except Mn-Ni steel) is slightly larger.

After full annealing the critical points of tested steels were determined for the second time. The treatment parameters were the same as before - steels were heated at a rate of 0.05°C/s up to a temperature of 1100°C, and then cooled at a rate of 1°C/s to room temperature. An example of dilatometric curve, from which the critical temperatures were read, is presented in Figure 3 for 35CrMo4-3 steel.

The critical temperatures determined for tested steels after full annealing are presented in Table 3.

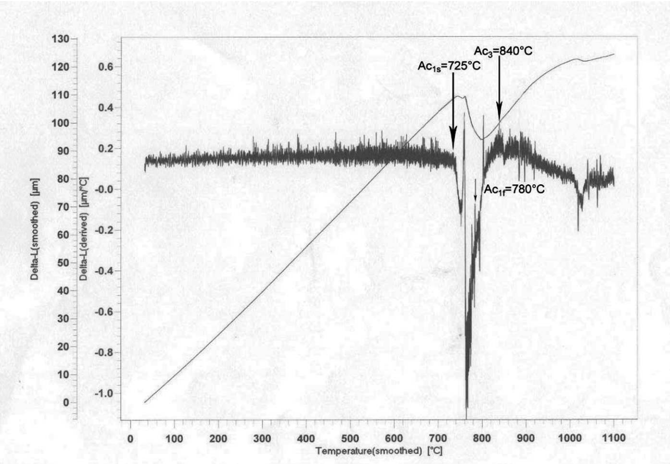


Fig. 3. Heating curve of 35CrMo4-3 steel after full annealing up to the temperature of 1100°C and the corresponding differential curve with marked critical points

TABLE 3

Critical temperatures determined for four tested hypoeutectoid steels in state after full annealing

| No. | Steel | $Ac_{1s}$ [°C] | $Ac_{1f}$ [°C] | $Ac_3$ [°C] |
|---|---|---|---|---|
| 1 | **39MnNi6-4** | 690 | 705 | 790 |
| 2 | **36CrNi4-4** | 720 | 750 | 780 |
| 3 | **37MnMo6-3** | 688 | 780 | 830 |
| 4 | **35CrMo4-3** | 725 | 780 | 840 |

The critical temperatures of the tested hypoeutectoid steels determined by the dilatometric method undergo transformation as compared with transformation points determined for the steel after forging. This is due to the application of the appropriate heat treatment for the tested steel. As already mentioned, the full annealing was performed which was aimed at obtaining the tested steels so. equilibrium, that is, one or two-phase microstructure.

It was decided, on the bases of the determined critical temperatures, that the analysis of the phase transformations kinetics of undercooled austenite – for each tested steel – will be performed for the austenitising temperature higher by 50°C than the $Ac_3$ temperature. It should be added that the austenitising temperature should be constant for all tested steels and the austenite size similar (the same).

### 4.2. Analysis of the kinetics of undercooled austenite phase transformations of hypoeutectoid Mn-Cr-Ni steels

On the basis of determined critical temperatures of tested steels hypoeutectoid austenitizing temperatures were chosen and the kinetics of undercooled austenite was analyzed. Samples of tested steels, were cooled at different rates from the austenitizing temperature within different ranges (for 39MnNi6-4 steel 94÷0.17°C/s, 36CrNi4-4 steel 49÷0.33°C/s, and 37MnMo6-3 steel 47÷0.17°C/s and for 35CrMo4-3 steel in the range 50÷0.16°C/s). Then the temperatures of beginnings and ends of each transformation was read from obtained dilatometric curves. An example of dilatometric curve for 39MnNi6-4 steel is presented in Figure 4.

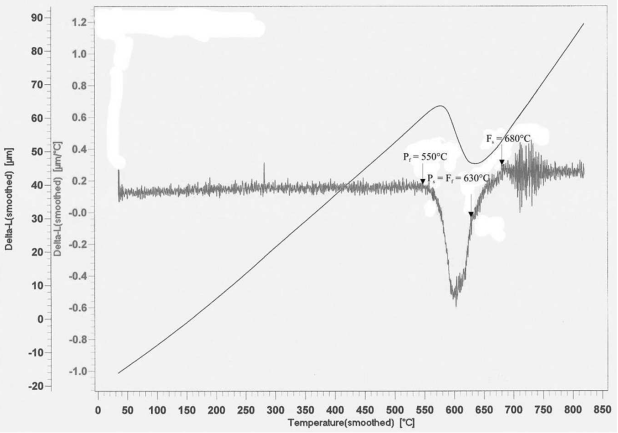


Fig. 4. Dilatometric curve of cooling of the test samples of steel 39MnNi6-4 form the austenitizing temperature $T_A$ = 820°C with corresponding differential curve, with marked start and finish temperatures of phase transformations

### 4.3. CCT diagrams for tested hypoeutectoid steels

Figures 5÷8 present CCT diagrams for tested hypoeutectoid steels: 39MnNi6-4 steel after austenitizing at the temperature $T_A$ = 820°C (Fig. 5), 36CrNi4-4 steel after austenitizing at the temperature $T_A$ = 830°C (Fig. 6), 37MnMo6-3 steel after austenitizing at the temperature $T_A$ = 830°C (Fig. 7) and for 35CrMo4-3 steel after austenitizing at the temperature $T_A$ = 890°C (Fig. 8).

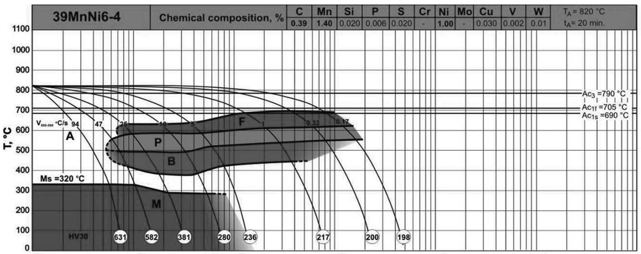


Fig. 5. The CCT diagram for 39MnNi6-4 steel after austenitizing at the temperature $T_A$ = 820°C

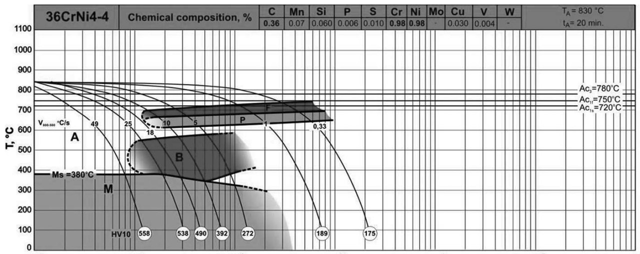


Fig. 6. The CCT diagram for 36CrNi4-4 steel after austenitizing at the temperature $T_A$ = 830°C

Analysing the CCT diagrams of the investigated steel of a carbon content app. 0.4%, a certain similarity for two steels with Mn and for successive two steels with Cr can be noticed. Thus, that is in the CCT diagrams of steels with Mn (39MnNi6-4 and MnMo6-3) the start and finish transformation curves are of a continuous character (compare Fig. 5 and 7). Maxima of diffusive transformations rates (ferritic and pearlitic) are not separated from the intermediate transformation (bainitic) by the undercooled austenite range (for the 39MnNi6-4 steel in the whole range of cooling rates: 47 ÷0.17°C/s, while for the 37MnMo6-3 steel in the range: 1 ÷0.17°C/s). Austenitising temperatures are very similar and equal app. 825°C. The temperature of the martensitic transformation start equals 320°C for the Mn-Ni steel and is 30°C lower than Ms for the Mn-Mo steel.

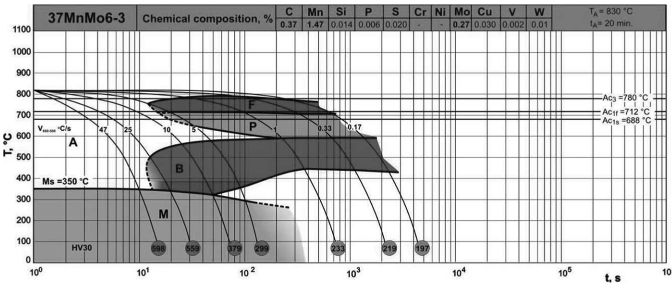


Fig. 7. The CCT diagram for 37MnMo6-3 steel after austenitizing at the temperature $T_A$ = 830°C [12]

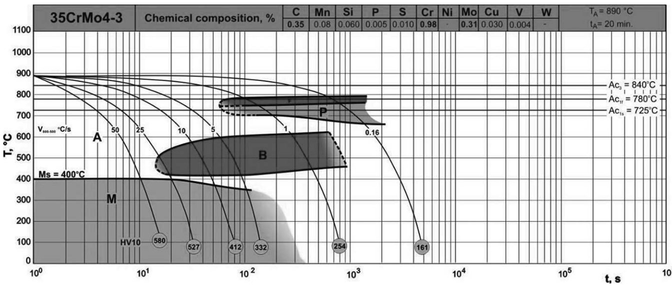
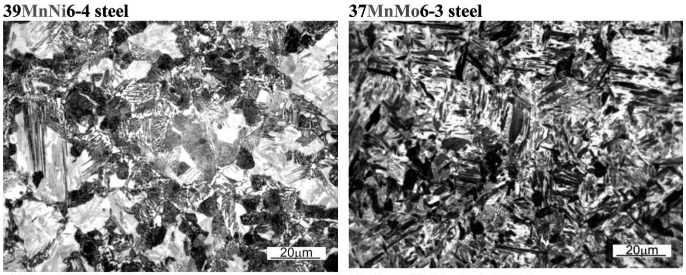


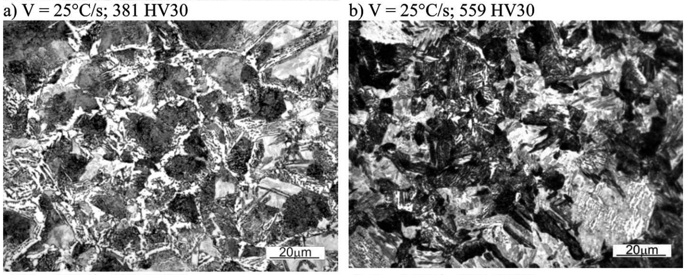
Fig. 8. The CCT diagram for 35CrMo4-3 steel after austenitizing at the temperature $T_A$ = 890°C

The CCT diagrams of steels containing Cr have also similar character as well as steels with Mn (compare Fig. 6 and 8). Curves of the start and finish of transformations are continuous. This means that the ”noses” of pearlite and ferritic transformations (diffusional transformations) converge at single point. Between the diffusional transformations and bainite transition there is a stability range of stable austenite. For 36CrNi6-4-4 steel austenitized at the temperature $T_A$ = 830°C the beginning of ferrite precipitation is observed between 25°C/s and 10°C/s cooling curves. Temperature of the beginning of martensitic transition for test steel with nickel is Ms = 380°C. In case of 35CrMo4-3 steel, which was austenitized at $T_A$ = 890°C, the beginning of ferrite precipitation was not observed until between 5°C/s a 1°C/s cooling curves. The bainitic transition begins, alike in case of steel with nickel, at the cooling rate of 25°C/s. The of the beginning of martensitic transition for 39MnCrMo6-4-3 test steel is Ms = 400°C. On both CCT diagrams of test hypoeutectoid steels one may observe separation of areas of diffusional transformation from intermediate one of super cooled austenite range. For 35CrMo4-3 steel the separation of pearlite range from bainitic one is much more broader than for 36CrNi6-4-4 steel. This is caused not only by the presence of 1%Cr but also the content of 0.3%Mo in the chemical composition of 39MnCrMo6-4-3 steel. Mo and Cr are ferrite creative elements, which limit the presence of $\gamma$ solid solution (austenite) in iron alloys.

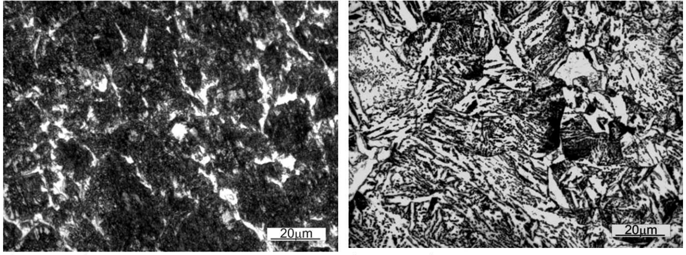
Comparing the CCT diagrams for test steels, one may state that addition of molybdenum in amount of 0.3% increases the hardenability of steel significantly more than addition of nickel in amount of 1%. Namely, the elements forming their own carbides (among others Mo, Cr) postpone the beginning of transformation, especially diffusional ones, allowing to lower the critical cooling rate (increasing the hardenability of the steel). According to CCT diagram for steel with molybdenum (Fig. 7 i 8), the postponing time of the beginning of phase transformations is almost three times longer than in case of steels with nickel (compare with Fig. 5 i 6). One should note that nickel (as well as manganese) is an austenite creative element and its addition does not change the characteristics of “C” curves but only shifts them towards longer times.



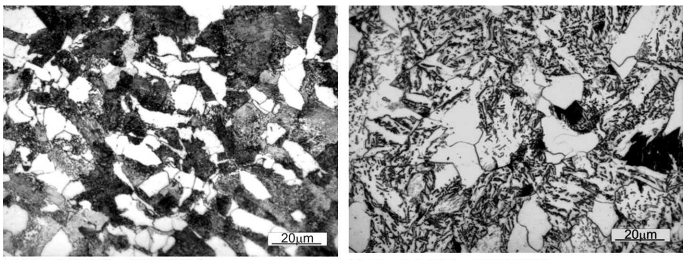
a) V = 25°C/s; 381 HV30 b) V = 25°C/s; 559 HV30



c) V = 10°C/s; 280 HV30 d) V = 10°C/s; 379 HV30



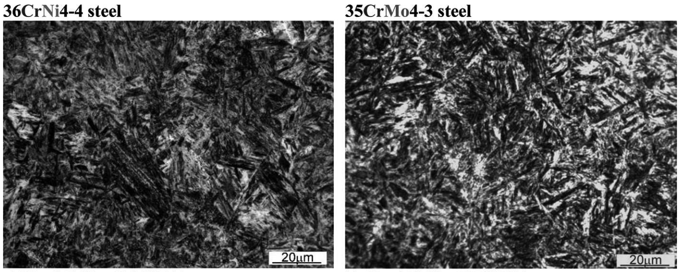
e) V = 1°C/s; 217 HV30 f) V = 1°C/s; 233 HV30



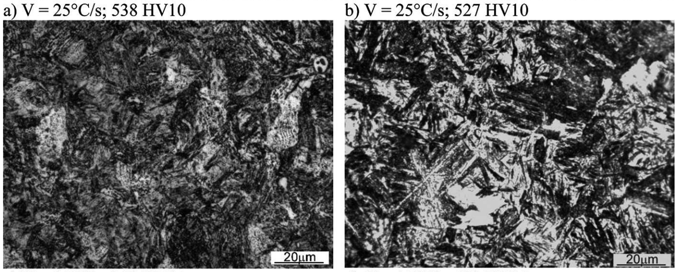
g) V = 0.17°C/s; 198 HV30 h) V = 0.17°C/s; 197 HV30

Fig. 9. Microstructure of dilatometric of selected samples used for drawing of CCT diagrams of two tested steels with Mn: 39MnNi6-4 (a, c, e, g) and 37MnMo6-3 (b, d, f, h)

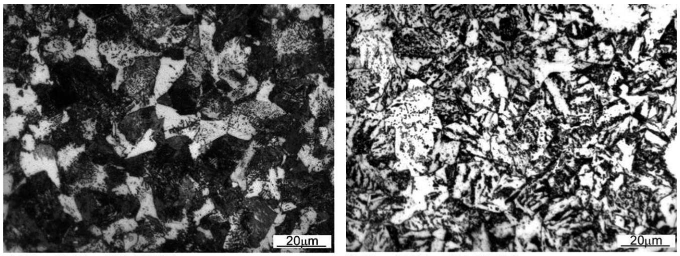
Figures 9 and 10 present the microstructure of dilatometric samples of four tested hypoeutectoid steels used for drawing of CCT diagrams.



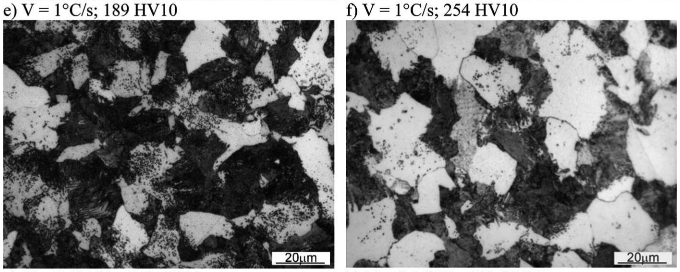
a) V = 25°C/s; 538 HV10 b) V = 25°C/s; 527 HV10



c) V = 10°C/s; 392 HV10 d) V = 10°C/s; 412 HV10



e) V = 1°C/s; 189 HV10 f) V = 1°C/s; 254 HV10



g) V = 0.33°C/s; 175 HV10 h) V = 0.16°C/s; 181 HV10

Fig. 10. Microstructure of dilatometric of selected samples used for drawing of CCT diagrams of two tested steels with Cr: 39CrNi4-4 (a, c, e, g) and 35CrMo4-3 (b, d, f, h)

Metallographic analysis of steels with Mn reveals that the microstructure of the sample cooled at a rate of 25°C/s is martensite, bainite, ferrite and pearlite for 39MnNi6-4 steel (Fig. 9a) and is martensite with a trace of bainite for 37MnMo6-3 (compare Fig. 9b). The application of even lower cooling rates (1°C/s and 0.33°C/s) results in that the microstructure of Mn-Ni steel is ferrite-pearlitic one (Fig. 9g), but for Mn-Mo steel is ferrite, pearlite with bainite (compare Fig. 9h).

The microstructure of steels with Cr within the range of cooling rate at 50÷0,16°C/s looks similar to the one of steels with manganese. At cooling rate of 50 and 25°C/s the microstructure of hypoeutectoid steels with Cr contains martensite and trace amount of bainite (Fig. 10a, b). For the lower cooling rate the microstructure of test steels is ferrite-pearlitic (compare Fig. 10g, h).

## 5. Summary and conclusions

The study included evaluation of the kinetics of phase transformations of undercooled austenite in four hypoeutectoid steels, wherein the CCT diagrams were developed for the respective austenitizing temperatures, which was supplemented with metallographic documentation and hardness measurements. This research allowed to formulate the following conclusions:

- Developed CCT diagrams have the diffusional transformations separated by a stability range of the supercooled austenite and have the shape of the letter "C".
- Bainite formed in cases of examined steels was created above 350°C, which means that it is probably the upper bainite, which is dangerous because of the low resistance to cracks propagation. Upper bainite is composed of ferrite strips with precipitated cementite along grain boundaries, what significantly weakens the boundaries.
- The hardenability of tested steels is similar, but molybdenum acts much more effectively than nickel. Molybdenum occupies the I-st place among the effectiveness of alloying elements for the steels designed for low tempering, where the "background" of other elements is weak [11].
- Hardenability of four investigated hypoeutectoid steels is similar, but still not high. To obtain martensite in the microstructure of these steels, it is necessary to apply the cooling rate higher than 25°C/s. The exception constitutes the Mn – Ni steel, in which only cooling with the rate higher than 50°C/s allows to achieve the martensitic microstructure and to avoid diffusive transformations (pearlitic and ferritic).

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