

J. PACYNA\*

## INTERPRETATIONS OF COOLING DILATOGRAMS IN THE RANGE OF THE BAINITIC AND MARTENSITIC TRANSFORMATIONS

### INTWERPRETACJA DYLATOGAMÓW CHŁODZENIA W ZAKRESIE PRZEMIANY BAINITYCZNEJ I MARTENZYTYCZNEJ

The method of interpretation of cooling dilatograms of undercooled austenite during its transformation into upper and lower bainite (UB and LB) and into martensite (M), applied in the Laboratory of Phase Transformations of AGH University of Science and Technology in Krakow, is presented in the hereby paper. The relation of the mechanism of the mentioned above transformations to places on the dilatometric curve where transformations start and where they are continued was indicated. An appeal for the unified, correct interpretation of dilatograms of phase transformations, in all laboratories of the world, was formulated. This will allow the formation of equally accurate diagrams of the kinetics of phase transformation of undercooled austenite at its continuous cooling (CCT). In consequence, this could provide a development of more advanced heat treatment technologies. Such approach will also allow for the correct assessment of the influence of the alloying elements on the stability of austenite and phase transformation temperatures at its cooling.

*Keywords:* cooling dilatograms, undercooled austenite, CCT diagrams, upper and lower bainite, martensite

W pracy opisano sposób interpretacji dylatogramów oziębiania przechłodzonego austenitu w zakresie przemiany w bainit górny (UB) i dolny (LB) oraz w martenzyt (M), stosowany w Laboratorium Przemian Fazowych Akademii Górniczo-Hutniczej w Krakowie. Wskazano na związek mechanizmu każdej z ww. przemian z miejscem na krzywej dylatometrycznej (temperaturą), gdzie przemiany startują i miejscem gdzie są kontynuowane. Sformułowano apel o jednolitą, poprawną interpretację dylatogramów przemian fazowych we wszystkich laboratoriach świata. Umożliwi to tworzenie jednakowo precyzyjnych wykresów kinetyki przemian fazowych przechłodzonego austenitu przy chłodzeniu ciągłym (CTPc) i w konsekwencji – tworzenie bardziej doskonałych technologii obróbki cieplnej. Pozwoli także na poprawną ocenę wpływu pierwiastków stopowych na stabilność austenitu i temperatury przemian fazowych przy jego oziębianiu.

### 1. Introduction

Undercooled austenite of eutectoid steel can transform into:

- coarse pearlite,
- fine pearlite,
- very fine pearlite (called previously troostite<sup>1)</sup>)
- upper bainite,
- lower bainite,
- martensite.

In addition, in hypoeutectoid steels preeutectoidal ferrite can also precipitate, while in hypereutectoid steels preeutectoidal cementite, called secondary cementite.

The formation or precipitation of the mentioned above structural components and phases from undercooled austenite in dependence of a temperature and time, is the most often investigated by the dilatometric method and presented as diagrams: time – temperature – transformation. These diagrams are, in reality, sets of lines indicating starts and finishes of individual transformations. It would seem, that indication of

the beginning of the transformation (point of the determined temperature and time coordinates), for the determined cooling rate, should only depend on the accuracy of the measuring device and the resolution ability of a numerical or analogue notation of the parameter, which was chosen for this assessment. However, in the majority of laboratories investigating transformations of undercooled austenite, such far-reaching freedom is – in this range – applied, that the continuous cooling transformations CCT diagrams of the same steel (the very similar chemical composition) often differ from each other in an unacceptable way. This makes difficult utilising “other’s” diagrams for the precise development of the heat treatment technology of the given steel grade and forces the preparation of “own” diagrams. Sometimes, the published CCT diagrams indicate even a lack of knowledge concerning the mechanisms of phase transformations, which are described by these diagrams.

The laboratories investigating the kinetics of undercooled austenite are the most often applying the dilatometric method. A macroscopic sample length is very sensitive to dilatation effects accompanying the austenite transformation into ferrite

\* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF METALS ENGINEERING AND INDUSTRIAL COMPUTER SCIENCE, AL. A. MICKIEWICZA 30, 30-059 KRAKOW, POLAND

<sup>1)</sup> In the European Standard PN-EN 10052:1999 concerning „Terms in heat treatments of ferrous alloys” the name troostite does not occur.

or martensite. Therefore, already the first visible deviation of the dilatogram from the monotonic pathway should be treated as the start of the undercooled austenite transformation.

On the other hand, the dilatometric method is not very sensitive (in contrast to e.g. calorimetric method), to chemical composition changes in the undercooled austenite volume during the preparation to the transformation period. Precipitations of carbides from austenite are also accompanied by very small dilatation effects. Therefore lines of the beginning of the secondary carbides precipitation are only marked in the CCT diagrams developed in the best laboratories, or limited to such steel grades in which this precipitation is very intensive.

Standards of some countries, including the Polish Standard PN 68/H-04500, indicate in what way the critical temperatures marked A (called sometimes transformation temperatures) can be determined from the heating or cooling dilatograms, recorded as: elongation  $\Delta L$  – temperature T. These standards also indicate in what way temperatures of beginnings and ends of individual transformations should be indicated. These are temperatures at which the dilatometric curve starts to bend back from the monotonic waveform (in reality: from the line slightly bended ‘down’ – in accordance with the coefficient of thermal expansion change with a temperature). Unfortunately, several researchers, dealing with the transformations kinetics, ignore these recommendations, using e.g. the point of intersection of tangents to the line before and after the transformation start, for the determination of the transformation beginning. The similar procedure is applied in determining the transformation end. Such proceedings cause, that two CCT diagrams made for the same steel grade in different research institutions differ from each other so much that they are completely useless for the heat treatment technologists.

The numerical recording of the elongation, temperature and time changes, provides the possibility of a mathematical treatment (differentiation) of the recorded temperature changes with time, elongations with time and elongations in dependence of a temperature. The most useful, for the determination of temperatures of beginnings and ends of various transformations of undercooled austenite, are dilatograms written primarily in the system: elongation  $\Delta L$  – temperature T, and after differentiating in the system:  $d(\Delta L)/dT/L_0 = f(T)$ . If  $L_0$  is the sample length at the beginning of the differentiation range the dependence:  $d(\Delta L)/dT/L_0 = f(T)$  is, really, the dependence of the coefficient of linear expansion on a temperature. It is much easier to point out the beginning (or end) of the transformation in such curves, if only the differentiation parameters are properly selected.

## 2. Determination of the bainitic start Bs transformation temperature

The bainitic transformation is the intermediate (diffusionless – diffusive) austenite transformation, between the transformation into martensite (usually supersaturated with carbon) and the transformation into ferrite and carbides (usually cementite  $M_3C$ ). It is always accompanied by the positive di-

latation effect. Upper bainite is formed (acc. [1]) at temperatures lower than the temperature of forming very fine pearlite (troostite), i.e. app. 500°C, but higher than 350°C. Within the range from app. 350°C to the temperature of the martensite transformation start,  $M_s$ , lower bainite is formed.

With the cooling rate increase the temperature of the bainitic transformation start  $B_s$ , due to its partially diffusive character, is decreasing. This is its distinctive feature differing it from the temperature of the martensite transformation start  $M_s$ , which does not depend on the cooling rate in steels containing the amount of interstitial elements. Thus, positive dilatation effects in the dilatograms of austenite cooling, recorded at temperatures in between 500°C and  $M_s$ , originate from the bainite formation <sup>2)</sup>.

According to R.J. Entin [2], natural fluctuations of carbon content occurring in undercooled austenite favour the bainitic transformation. The majority of authors, among others [1-4], is of the opinion that the bainitic transformation is started by the martensite laths formation in spaces of a decreased carbon content (higher  $M_s$  temperature). A priority of carbides precipitations, from undercooled austenite, in places of an increased carbon concentration should be rather excluded due to too low temperature (below 500°C precipitations of carbides stops) and the necessity of obtaining locally at least 6.67% of carbon. An the growth of the martensite laths additionally enriches neighbouring spaces in carbon, favouring carbides precipitations. Then these carbides precipitations impoverish neighbouring spaces in carbon, which - in turn - facilitates the martensite formation and the cycle of similar transformation sequences, as the described above, is repeated.

However, it should be clearly stated, that during the bainitic transformation only carbides precipitations are of a diffusive character and that these carbides are precipitated from austenite, regardless of the fact that the transformation temperature is usually below 500°C. Of course, self-tempering of martensitic laths causes the precipitation of additional cementite, which is not forming their own nuclei but nucleates on the already existing cementite, it means on the one which precipitated previously from austenite.

If the bainitic transformation temperature is high (in the range: 500°C – 350°C),  $M_3C$  precipitates are relatively large of a shape of short plates. They are mainly arranged on boundaries of martensite laths, which according to the formation temperature are self-tempering. Such microstructure is called upper bainite.

The essential feature of the upper bainite morphology, differing it from lower bainite, is a continuity of the interphase boundary of tempered martensite laths (supersaturated ferrite) and precipitated carbides. Having in mind the continuity of transformations to which undercooled austenite is subjected, it can be stated that upper bainite is such pearlite, in which an increase of cementite plates was interrupted (it was not completely finished) and ferrite plates are supersaturated with carbon.

In case of lower bainite, which is formed from undercooled austenite in the temperature range: app. 350°C –  $M_s$ , the transformation mechanism is identical. The only difference

<sup>2)</sup> Small positive dilatation effects can be found in cooling dilatograms of steels of a high tendency for precipitation of secondary carbides from undercooled austenite. However, they are of a continuous character and occur in the range from the austenitising temperature to app. 500°C.

is such that martensite laths formed at lower temperatures are wider and more supersaturated with carbon. They also occupy spaces of higher carbon content and due to that they feed the neighbouring spaces with this element to a lower degree. In effect, carbides formed in their vicinity are very fine and the most often covered by martensite laths. Thus, they mainly occur within the volume of bainitic martensite laths. Martensite of lower bainite is also subjected to self-tempering and carbides precipitating from it nucleate on carbides present in the martensite laths volume (which precipitated previously from austenite). The lower bainite morphology, observed in the microscope, constitutes, first of all, broad laths of tempered martensite, and at their background very fine precipitated (mainly from austenite) carbides are seen, at a high magnification.

In this case a continuity of the interphase boundary between carbides and tempered martensite laths (supersaturated ferrite) does not exist. Thus, there is no morphological similarity of lower and upper bainite and lamellar pearlite.

### 3. Determination of the temperature of the martensitic transformation start, Ms

When the austenite transformation temperature is more lowered, then due to still existing carbon content fluctuations in austenite, the martensite laths formation (plates in higher carbon steels) starts (at the Ms temperature) – of course – in places of a lower carbon content and gradually – as the temperature decreases – also in spaces of a higher carbon content. Formed very fast laths or plates are unable to push out satisfactory amounts of carbon to the front of transformation (even in places of a higher carbon content), so as to cause the carbide precipitation from austenite. The carbon concentration in austenite, at a temperature  $T \leq M_s$ , is not reaching the equilibrium value for carbide precipitation. Then, solely martensite (of a diversified supersaturation with carbon) is formed from austenite and carbides can precipitate already from martensite – in its whole volume – during self-tempering or tempering which occurs after quenching. In respect of a morphology, lower bainite and tempered martensite are very much alike. The only difference being, that in lower bainite carbides are precipitating mainly from austenite, while in tempered martensite they precipitate from martensite.

The martensite transformation is always accompanied by the strong positive dilatation effect and pointing out its beginning in the dilatogram (Ms temperature) should not cause any doubts, especially in view of the generally known one of its principles, that the Ms temperature in steels does not depend on the cooling rate.

However, the determination of the Ms temperature in steels containing – in undercooled austenite – carbide forming elements such as e.g. Mo, Cr, Mn, constitutes a serious problem. These elements have a strong tendency for the segregation to grain boundaries and to precipitate there carbides in a form of the continuous (in case of Mn and Cr) or the broken network (in case of Mo). Apart from the influence of this precipitation on the character of fractures and mechanical properties of heat treated products, this effect significantly influences the dilatograms interpretation, especially within the range of the martensite transformation.

Carbon and alloying elements impoverished zones of grain boundaries of a width depending on the advancement degree of the secondary precipitations, have quite different (higher) temperature of the martensite transformation start than spaces inside grains. This higher temperature, characteristic for zones along grain boundaries is marked as Ms', while the temperature of grain interiors (which usually dominates) is traditionally marked as Ms. With an advancement of the secondary precipitation the Ms' temperature always increases and the Ms temperature can be also increasing, especially when cooling rates are slower. Steel X153CrMoV12 (1.2379) constitutes the typical grade, in which the described above effects occur. Its CCT diagram and cooling curves are presented in Fig. 1 and 2. The modus operandi at the determination of the Ms' and Ms temperatures is the same, it means that these are

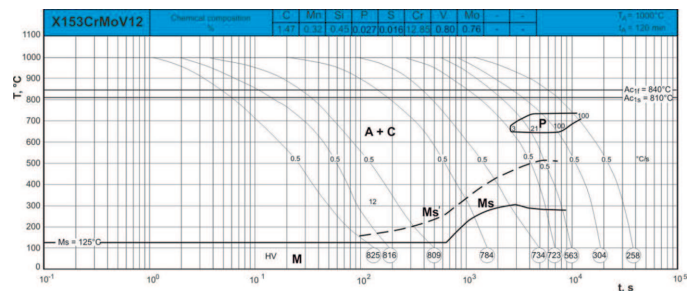


Fig. 1. CCT diagram for X153CrMoV12 (1.2379) grade steel, acc. [5]

temperatures, at which the dilatometric curve starts bending back indicating the beginning of the sample volume increase. In such steels as X153CrMoV12, bainite was not found metallographically.

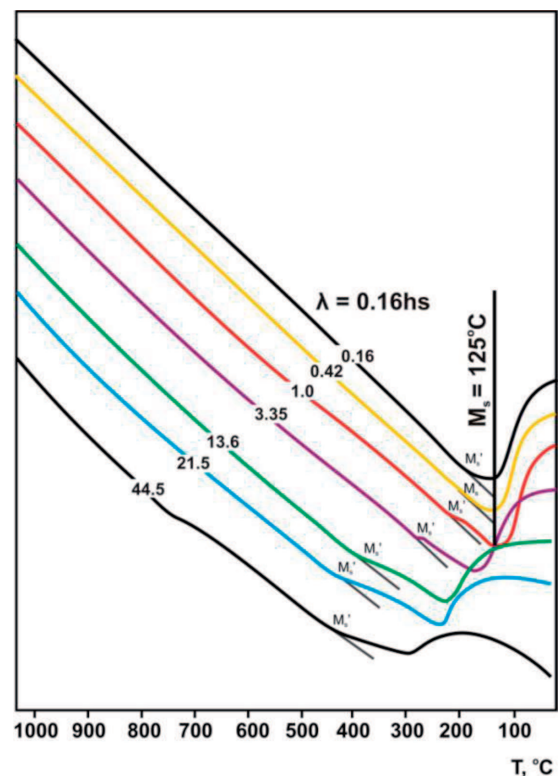


Fig. 2. A set of cooling dilatograms of X153CrMoV12 (1.2379) grade steel samples, on which the Ms' temperature, characteristic for zones along prior austenite grain boundaries, is marked, acc. [5]

#### 4. Guidelines for the cooling dilatograms interpretation in the range of the start of the bainitic and martensite transformations

The observations, which constitute the bases of the cooling dilatograms interpretation in the range of the beginning of the bainitic transformation, are given below:

- The bainitic transformation starts by forming martensite laths in places of a fluctuating lower carbon content but nearly simultaneously (due to a high growth rate of martensite laths) carbon is additionally pushed out (by the martensite laths front) to neighbouring austenite (of a fluctuating higher carbon content). As the results the austenite stability (lifetime) grows and after a properly long holding – followed by the next cooling – such austenite can remain as the stable phase (nanosteels), mechanically metastable phase (TRIP type steels) or M3C carbide can precipitate from it by the diffusive mechanism (bainitic steels).
- A strong positive dilatation effect accompanies always the austenite transformation into martensite (also bainite). However, when the beginning of the bainitic transformation is accompanied by small sample elongations (which the most often occurs in case of upper bainite) this means, that the transformation is slowly progressing but the  $B_s$  temperature of its start – is the temperature of even a small increase of the sample length.
- With an increase of austenite undercooling, the first laths of bainitic martensite cover more and more broad zones of austenite (of a diversified carbon content). Due to that the strong positive dilatation effect is observed from the very beginning. It should not raise any doubts that this is the  $B_s$  temperature and the structure formed is lower bainite.
- The carbides precipitation from austenite, also from bainitic austenite, is accompanied by a weak positive dilatation effect, which value additionally decreases with the undercooling increase pursuant to the decreasing fraction of these carbides.
- With the cooling rate increase the  $B_s$  temperature decreases since bainitic martensite laths cover more carbon rich austenite spaces, and in their front carbides are precipitating from austenite. When this precipitation stops, the martensite transformation starts and this temperature is called the start temperature of the martensite transformation,  $M_s$ .
- The fact of carbides precipitation from austenite during the lower bainite formation has a fundamental meaning in the dilatograms interpretation, when it should be decided whether the given effect originates still from lower bainite or already from martensite. The basic observation is then, whether the interesting for us point in the dilatogram lowers with the cooling rate increase as it happens in the diffusion partially transformations (at the bainite formation), or it remains without changes as it happens in the diffusionless transformations (carbon austenite into martensite).
- The positive dilatation effect of the martensite transformation is the largest.
- If the carbides precipitation from austenite is not preceded by martensite laths, it is usually a secondary precipitation,

which has nothing in common with the bainitic transformation. It usually occurs at temperatures above  $500^\circ\text{C}$ .

#### 5. Selected examples of the cooling dilatograms

The dilatogram containing the effect originated from the bainitic transformation, in the range of the upper bainite formation, is shown in Fig. 3.

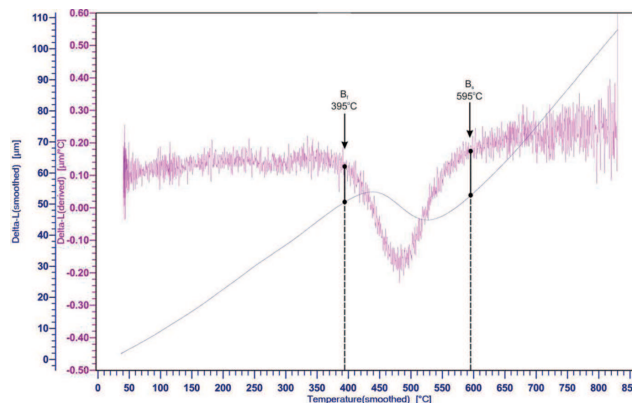


Fig. 3. Cooling dilatogram of 38MnCrNi6-4-4 steel in the range of the upper bainite formation and the differential curve

The characteristic feature of this dilatogram is a slow growth of the positive dilatation effect, especially in the initial phase of its formation. The higher the bainite formation temperature, the lower growth rate of its volume fraction in the initial phase (positive dilatation effect growth rate). The most probably this transformation rate (intensity) in its initial phase is the higher, when the higher is the austenite undercooling.

The dilatogram with the effect originated from lower bainite is shown in Fig. 4. Omitting the fact that the lower bainite formation occurs at lower temperatures, it is clearly visible that the start of the austenite transformation into lower bainite is more distinctly shown than it was in case of upper bainite (see Fig. 3).

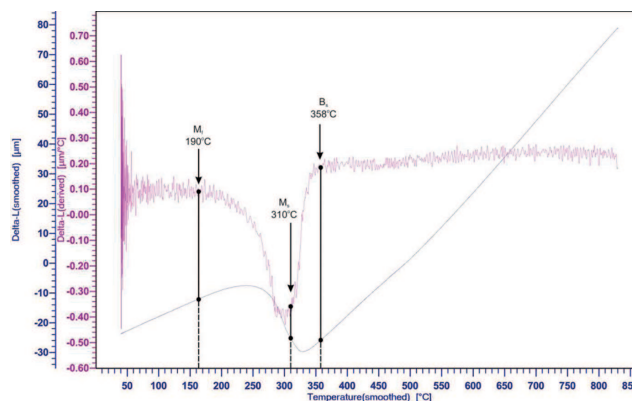


Fig. 4. Cooling dilatogram of 37MnNiMo6-4-3 steel in the range of the lower bainite and martensite formation and the differential curve

If, during cooling, both bainites are formed the lower bainite formation temperature should be looked for near  $350^\circ\text{C}$ . Usually near this temperature an increased positive dilatation effect can be seen. The beginning of this increase corresponds to the start of the lower bainite formation. The differentiation



of the basic dilatogram  $\Delta L/L_0 = f(T)$  (if its notation was numerical) and then drawing it – at the background of the basic dilatogram – in the system:  $(\Delta L)/dT/L_0 = f(T)$  can be helpful (Fig. 5).

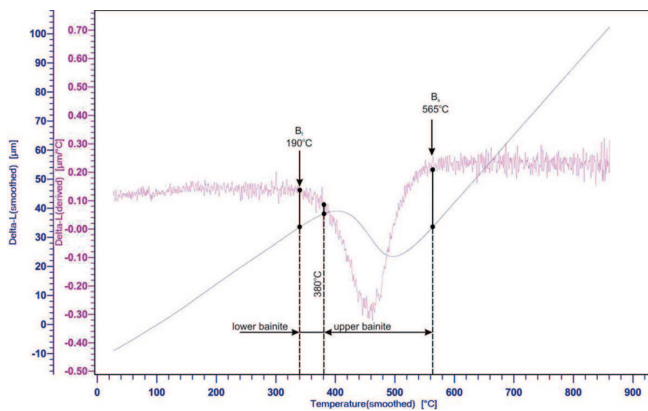


Fig. 5. Cooling dilatogram of 38MnCrNi6-4-4 steel in the range of the upper and lower bainite formation and the differential curve

The most errors at the determination of CCT diagrams are made when the  $M_s$  temperature is to be determined, under conditions when the martensite formation is preceded by the lower bainite formation and the  $B_s$  temperature is not much higher than the  $M_s$  temperature. Such case is illustrated in Fig. 6.

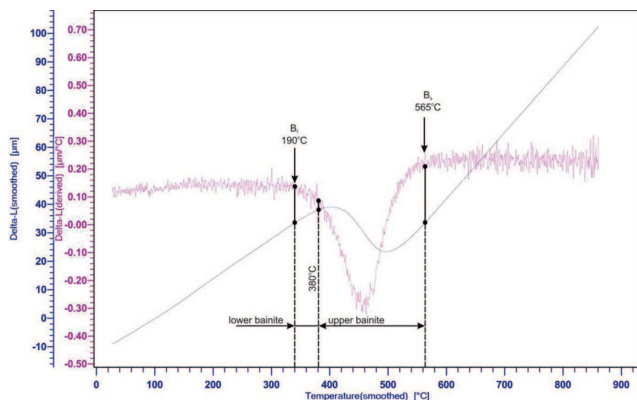


Fig. 6. Cooling dilatogram of R260 grade steel in the range of the lower bainite and martensite formation and the differential curve

The majority of scientists, dealing with CCT diagrams, treats this low  $B_s$  temperature as an increasing (with a cooling rate decrease)  $M_s$  temperature. The most probably they assume, that this is the effect of the secondary precipitation of carbides from austenite, as it was described in relation to Fig. 1 and 2 for X153CrMoV12 (1.2379) steel. Such case, as shown in Fig. 1 and 2, occurs only when in austenite of cooled steel there is a lot of carbon and carbide-forming elements of a strong tendency to segregate to grain boundaries. Then, along grain boundaries martensite of a lower carbon content is formed and due to rather fast cooling it is not satisfactorily self-tempered and difficult to etching. Whereas lower bainite, due to a diffusive precipitation of carbides from austenite (supported by carbon pushed out from spaces of the

martensite laths formation) is etched easily and occurs not only along prior austenite grain boundaries but in the whole volume of cooled steel. Therefore in such cases it is necessary to distinguish the  $M_s$  temperature – of martensite and  $B_s$  – of lower bainite. The set of points, corresponding to the  $B_s$  temperatures of lower bainite, forms – in the CCT diagram – the rising up line, which starts from the  $M_s$  temperature line. The example of the CCT diagram with the distinguished lines:  $B_s$  for lower bainite and  $M_s$  for martensite is shown in Fig. 7.

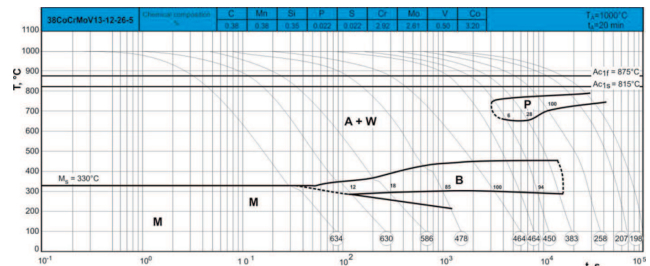


Fig. 7. CCT diagram of 38CoCrMoV13-12-26 steel with the distinguished lines of the  $B_s$  temperature – for lower bainite and the  $M_s$  temperature – for martensite, acc. [6]

However, more often it happens that beginning from the cooling rate at which bainite, especially the upper one, starts forming the  $M_s$  temperature is decreasing (see also Fig. 7). Such case occurs when the laths of bainitic martensite are pushing out a lot of carbon into austenite and bainitic carbides have no time to precipitate fully from this austenite, e.g. due to the presence of elements which delay the carbides precipitation. This effect is utilised, among others, in nanosteels and the TRIP type steels [7-11].

## REFERENCES

- [1] J. Pacyna, Designing of chemical composition of steels Ed. Metallurgy and Materials Engineering Dept., Academy of Mining and Metallurgy, Kraków (1997).
- [2] R.J. E n t i n, Transformations austenite in steels', Metallurgizdat, Moscow (1960).
- [3] L.A. D o b r z a ń s k i, Engineering of materials and its designing. Ed. WNT, Warsaw (2006).
- [4] H.K.D.H. B h a d e s h i a, Bainite in steels, 2nd edition, Institute of Materials, Cambridge (2001).
- [5] M. K a r a m a r a, A. M a z u r et al., Metallurgy and casting 7, 329-340 (1981).
- [6] J. Pacyna, Computer designing of steels and alloys. Ed. AGH Academy of Mining and Metallurgy, Kraków (2011).
- [7] W. Ś w i ą t n i c k i, K. P o b i e d z i ń s k a et al., Mater Eng 33, 6, 524-529.
- [8] J. M a h i e u, J. M a k i et al., Metall Mater Trans A 33A, 2573-2580 (2002).
- [9] C. G a r c i a et al., Application of dilatometric analysis to the study of solid-solid phase transformations in steels, Materials Characterization 48, 101-111 (2002).
- [10] T. S o u r m a i l, V. S o m a n i o, Determination of  $M_s$  temperature: methods, meaning and influence of "slow start" phenomenon, MST 29, 883-888 (2013).
- [11] Discussion with the above paper by H.K.D.H. Bhadeshia: MST 30, 510 (2014).