

# Analysis of the kinetics of precipitation of MX-type interstitial phases in microalloyed steels

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## Materials

### ABSTRACT

**Purpose:** The paper presents analysis of the kinetics of precipitation of MX-type (M - metal, X - metalloid) interstitial phases in austenite of constructional steels microalloyed with Nb, Ti, V and B, assigned for production of forged machine elements with the use of thermo-mechanical treatment.

**Design/methodology/approach:** The analysis was conducted basing on the dependence of solubility of MX-type phases in austenite as a function of temperature. The research of influence of austenitizing temperature in a temperature range from 900 to 1200°C on grain size of primary austenite has been used to verify the analysis.

**Findings:** The kinetics of TiN, TiC and NbC precipitation as well as the temperature sequence of precipitation of these phases have been determined. The investigation of influence of austenitizing temperature on the grain size of primary austenite confirmed correctness of the analysis.

**Research limitations/implications:** The analysis was done basing on the thermodynamic model proposed by Adrian, assuming that only individual, single MX phases are soluble in austenite.

**Practical implications:** The studies provide the basis for proper design of manufacturing process of thermo-mechanical treatment of high strength forged machine parts obtained from microalloyed steels.

**Originality/value:** The kinetics of precipitation of interstitial phases in newly elaborated microalloyed steels has been compiled.

**Keywords:** Microalloyed steels; MX-type phases; Primary austenite; Thermo-mechanical treatment; Forged elements

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## 1. Introduction

Die forging is a commonly used method of production of machine parts obtained from unalloyed and alloy steels. Forged parts of unalloyed steels are usually subjected to normalizing. However, alloy steel parts forged prior to mechanical working

require application of soft annealing or high-temperature tempering, and in ready state - toughening and dimensional correction with the methods of machining processes, i.e. machine cutting or grinding. The pursuit of lower production cost is a basis for implementation of economical technologies of products made of constructional alloy steels with the methods of thermo-

mechanical treatment. These methods consist in plastic working conducted in conditions adjusted to their chemical composition and the type of introduced microadditions with consecutive direct hardening of parts from the temperature of plastic deformation finish or after particular time specified. This allows reducing expensive heat treatment of products exclusively to tempering. Desired mechanical and technological properties, i.e. high yield strength at guaranteed crack resistance, can be obtained for metallurgical products with fine-grained microstructure [1-7].

HSLA-type (High Strength Low Alloy) microalloyed steels - containing up to 0.3% C and 2% Mn and microadditions with high chemical affinity to N and C, i.e. Nb, Ti and V in the amount of about 0.1%, and sometimes also slightly increased concentration of N and up to 0.005% of B, increasing hardenability - are particularly useful for production of forged parts with fine-grained microstructure using the method of thermo-mechanical processing. In properly selected conditions of plastic deformation, metallic microadditions introduced into these steels form dispersive particles of nitrides, carbonitrides and carbides, slowing down the process of recovery and static or metadynamic recrystallization and also limit grain growth of recrystallized austenite. Dispersive particles of interstitial phases, limiting movements of grain boundaries of recrystallized austenite, create the possibility to obtain metallurgical products with fine-grained microstructure and high mechanical properties with the use of thermo-mechanical treatment - unobtainable with application of traditional methods of hot plastic working and heat treatment. Production of mass-products with desired functional properties requires proper adjustment of thermo-mechanical treatment conditions to the kinetics of precipitation of MX-type (M - metal, X - metalloid) interstitial phases of microadditions introduced into steel in austenite [8-14].

Understanding the impact of secondary interstitial phases on the processes occurring during hot plastic working and its cooling from the temperature of the end of this treatment requires the knowledge of the mechanism of their formation and their stability in austenite. Analysing the interaction of M metallic microaddition with X metalloid dissolved in austenite, it should be assumed that at a certain T temperature, they form a MX compound, in accordance with the reaction [15]:



where: [M] and [X] - portion of M microaddition and X metalloid, dissolved in a solid solution at T temperature, respectively.

Equilibrium constant for this reaction can be written as:

$$k_s = [M] \cdot [X] = a_{[M]} a_{[X]} / a_{(MX)}, \quad (2)$$

where:  $a_{[M]}$ ,  $a_{[X]}$ ,  $a_{(MX)}$  - chemical activity of M metallic microaddition, X metalloid and formed MX interstitial phase, respectively.

The dependence of MX phase solubility as a function of temperature, taking into consideration the Arrhenius equation, can be presented as follows [9]:

$$\log [M] \cdot [X] = - (Q/RT) + c, \quad (3)$$

or

$$\log [M] \cdot [X] = - (Q/2,303RT) + c/2,303, \quad (4)$$

where: Q - energy (heat) of MX phase dissolution, R - gas constant, T - temperature (K), c - constant dependent on the type of phase.

The (3) equation is usually presented in the form:

$$\log [M] \cdot [X] = B - A/T, \quad (5)$$

where: [M] and [X] - mass fraction of metallic microaddition and metalloid dissolved in austenite at T temperature, respectively, A and B - constants connected to free enthalpy of MX phase formation. The values of A and B constants in (5) equation for selected interstitial phases are set together in Table 1.

Table 1.

Values of the constants A and B in the equation (5) for selected carbides and nitrides [16,17]

MX phase	A	B
AlN	7184	1.79
VC	9500	6.72
VN	7840	3.02
TiC	10745	5.33
TiN	14400	5.00
NbC	7290	3.04
NbN	8500	2.80
ZrC	8464	4.26
ZrN	13968	3.08
TiN*	16586	5.90
BN	13970	5.24

\* - it concerns the formation of TiN in a solidification process of steel

It should be noted that the constants A and B depend on the method of determination; for this reason slightly different values for the same phase can be found in the literature.

High technical usability belongs to the diagrams of different MX phases dissolution in austenite, determined for different steels basing on the (5) equation as well as to computer programs allowing to calculate chemical composition and fraction of these phases as a function of temperature. As an example, Fig. 1 presents solubility curves of NbC carbide dissolved in austenite of steel with diversified concentration of carbon and VN nitride as a function of temperature and nitrogen concentration of steel containing 0.2% C.

According to the figure, Nb microaddition introduced in the amount of 0.05% into steel containing 0.2% C, at the temperature equal 1000°C, applied usually as the temperature of plastic working finish, is completely bound in NbC dispersive particles limiting grain growth of recrystallized austenite. However, V microaddition in the amount of 0.1% introduced into steel containing 0.2% C and 0.020% N, at the temperature of 1000°C is bound into VN nitride only in about 50% and has less significant impact on the formation of fine-grained microstructure of austenite, but influences stronger the precipitation strengthening of steel by dispersive VN and V(C,N) particles, precipitating

during cooling of parts and also VC after nitrogen is depleted. In this case, complete utilization of V to the formation of fine-grained microstructure of  $\gamma$  phase requires reduction of temperature of plastic working finish to approximately 900°C. The highest stability in austenite belongs to interstitial phases of titanium, TiN in particular, being partially formed already during crystallization in the interdendritic spaces, and successively in austenite, also in the form of Ti(C,N) and after nitrogen is depleted - in the form of TiC carbide. Giving consideration to the possibility of Ti(C,N) carbonitrides and TiC nitrides crystallizing to TiN nitrides formed before and coagulation process occurring at high temperature, precipitations of TiN interstitial phases have generally substantial sizes and less significantly limit grain growth of recrystallized austenite [15].

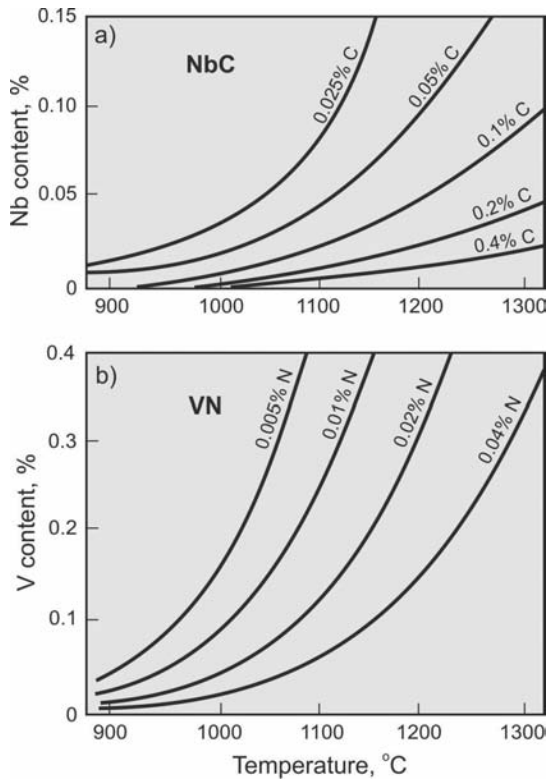


Fig. 1. Solubility curves of NbC and VN in austenite as a function of temperature and content of carbon and nitrogen in steel [15]

**A thermodynamic model for dissolution of simple carbides and nitrides in case of a single compound**

For the analysis of a single compound, calculation of undissolved <MX> compound portion and concentrations of [M] and [X] elements dissolved in austenite at T temperature is brought to solution of system of equations, which consist of the product MX compound solubility and mass balance equations of the elements included in the reaction [18]:

$$[M] \cdot [X] = k_{MX} \tag{6}$$

$$M = [M] + \frac{(M)}{(MX)} \langle MX \rangle \tag{7}$$

$$X = [X] + \frac{(X)}{(MX)} \langle MX \rangle \tag{8}$$

where:  $k_{MX} = [M] \cdot [X]$  - the product of MX compound solubility, M and X - total concentration of these elements in steel in wt%, while atomic weight of the elements is presented as symbols put in ( ) parentheses.

The following quadratic function is a solution of (6) - (8) system of equations:

$$[X]^2 + [X] \left[ \frac{(X)}{(M)} \cdot M - X \right] - \frac{(X)}{(M)} \cdot k_{MX} = 0 \tag{9}$$

with only one root of equation being its solution:

$$[X] = \frac{X - \frac{(X)}{(M)} \cdot M + \sqrt{\left( \frac{(X)}{(M)} \cdot M - X \right)^2 + 4 \frac{(X)}{(M)} \cdot k_{MX}}}{2} \tag{10}$$

The value of the second root of equation is negative and has been rejected. The equation (10) describes the amount of [X] dissolved element in the [X]<X range. If the solution meets [X]>X condition it means that considered (M, X) elements are present in the solution.

**A thermodynamic model for dissolution of simple carbides and nitrides in case of presence of two compounds**

Simultaneous presence of two compounds in austenite, which do not show mutual solubility, concerns the case in which both compounds have different crystal lattice. Carbide or nitride of IV or V group of periodic classification of elements with NaCl type cubic lattice and AlN nitride with hexagonal lattice can be listed as examples of such compounds. Thermodynamic equilibrium in austenite of steel containing M' and M'' elements and X interstitial element forming M'X and M''X compounds with M' and M'' elements, is described by the following system of equations [19,20]:

$$[M'] \cdot [X] = k_{M'X} \tag{11}$$

$$[M''] \cdot [X] = k_{M''X} \tag{12}$$

$$M' = [M'] + \frac{(M')}{(M'X)} \langle M'X \rangle \tag{13}$$

$$M'' = [M''] + \frac{(M'')}{(M''X)} \langle M''X \rangle \tag{14}$$

$$X = [X] + \frac{(X)}{(M'X)} \langle M'X \rangle + [X] + \frac{(X)}{(M''X)} \langle M''X \rangle \tag{15}$$

where:  $k_{MX} = [M] \cdot [X]$  - the product of MX compound solubility, the values in [ ] square brackets indicate concentration of an element in solution in wt%, the values in < > angle brackets indicate concentration of non dissolved compound in wt%, the values in ( ) parentheses indicate atomic weight of an element and the values without brackets indicate total concentration of the element in steel expressed in wt%.

The following quadratic function is the solution of (11) - (15) system of equations:

$$[X]^2 + [X] \left[ \frac{(X)}{(M')} \cdot M' + \frac{(X)}{(M'')} - X \right] - \frac{(X)}{(M'X)} \cdot k_{M'X} - \frac{(X)}{(M''X)} \cdot k_{M''X} = 0 \quad (16)$$

Depending on the temperature, the following cases are possible for considered Fe-M'-X configuration:

• both M'X and M''X compounds are undissolved:  
 $M' \cdot [X] > k_{M'X}$  and  $M'' \cdot [X] > k_{M''X}$ , (17)

• M'X is dissolved, while M''X is undissolved:  
 $M' \cdot [X] < k_{M'X}$  and  $M'' \cdot [X] > k_{M''X}$ , (18)

• M'X is dissolved, while M'X is undissolved:  
 $M' \cdot [X] > k_{M'X}$  and  $M'' \cdot [X] < k_{M''X}$ , (19)

• both compounds are dissolved:  
 $M' \cdot [X] < k_{M'X}$  and  $M'' \cdot [X] < k_{M''X}$ . (20)

### Solubility of complex carbonitrides

Complex interstitial phases can be present in various forms dependent on the concentration and type of elements in steel. Various variants can occur:

$M_1 - \dots - M_i - C$   
 $M_1 - \dots - M_i - N$   
 $M_1 - \dots - M_i - N - C$

where:  $M_i$  indicates an element which demonstrates chemical affinity to carbon and/or nitrogen.

Depending on considered variant, different thermodynamic models can be used for calculation of the kinetics of MX complex phases. One of them is the model presented in [21] by Adrian, basing on Hillert and Staffansson model [22] concerning stoichiometric phases. The main assumption of this model is that microadditions marked as M', M'' and M''' and (C, N) interstitial elements present in steel form dilute solutions in austenite and their activities fulfil Henry's law. This assumption is right at small concentration of microadditions and is usually fulfilled for majority of low-alloy steels. This model also supposes that  $M'_x M''_y M'''_{1-x-y} C_y N_{1-y}$  carbonitride, presenting perfect stoichiometry, what means that the total amount of metal atoms bound in carbonitride is equal the amount of atoms of carbon and nitrogen, is formed in the result of reaction between substitute and interstitial elements. Deriving equations in such complicated model is very complex, hence the final form of equations describing thermodynamic equilibrium of Fe-M'-M''-M'''-C-N configuration has been shown below [21]:

$$y \ln \frac{xy k_{MC}}{[M'a][Ca]} + (1-y) \ln \frac{x(1-y) k_{MN}}{[M'a][Na]} + y(1-y) \frac{L_{CN}}{RT} = 0 \quad (21)$$

$$y \ln \frac{vy k_{MC}}{[M''a][Ca]} + (1-y) \ln \frac{v(1-y) k_{M''N}}{[M''a][Na]} + y(1-y) \frac{L_{CN}}{RT} = 0 \quad (22)$$

$$y \ln \frac{(1-x-v)y k_{MC}}{[M'''a][Ca]} + (1-y) \ln \frac{(1-x-v)(1-y) k_{M'''N}}{[M'''a][Na]} + y(1-y) \frac{L_{CN}}{RT} = 0 \quad (23)$$

Presented system of equations consists of eight unknowns describing chemical composition of [M'a], [M''a], [M'''a], [Ca], [Na] austenite and (x, v, y) carbonitrides. Use of subsequent equations, describing the law of conservation of mass during the reaction of carbonitride formation, is necessary for solution of the equation:

$$M'a = \frac{x}{2} f + (1-f) [M'a] \quad (24)$$

$$M''a = \frac{v}{2} f + (1-f) [M''a] \quad (25)$$

$$M'''a = \frac{z}{2} f + (1-f) [M'''a] \quad (26)$$

$$Ca = \frac{v}{2} f + (1-f) [Ca] \quad (27)$$

$$Na = \frac{1-y}{2} f + (1-f) [Na] \quad (28)$$

where: f - mole fraction of carbonitride,  $k_{MX}$  - the product of MX compound solubility converted into at.%; the values in [ ] square brackets indicate concentration of an element in solution in at.%, the values in ( ) parentheses indicate atomic weight of an element and the vales without brackets indicate total concentration of an element in steel expressed in at.%.

Input data for solution of the above system of equations are: chemical composition of steel, austenitizing temperature,  $k_{MX}$  product of solubility of simple carbides and nitrides, MX, parameter of impact of M element on a C-N solution,  $L_{CN}=4260$  J/mole, R gas constant. Applying proper simplifications or modifications, this model can be used for analysis of interstitial phases in the form of  $MC_y N_{1-y}$  and  $M'_x M''_{1-x} C_y N_{1-y}$  and also for the analysis when there is an addition of Al, insoluble in the rest of MX phases [20].

Presented systems of equations are systems of nonlinear equations and therefore they can be solved only with the use of numerical methods. The examples of programs, which can be used for calculation of the kinetics of precipitation of complex phases, are: Carbnit and ThermoCalc [15,21]. Presented model can be exploited practically to solution of technological problems connected with production of microalloyed steels, in the field of design and modification of chemical composition, to calculation of such parameters as: chemical composition of austenite, chemical composition and fraction of carbonitrides and dissolving temperature of carbonitrides.

## 2. Material and methodology

The research was performed on newly elaborated microalloyed steels. Chemical composition of steel (Table 2) was designed taking into consideration the production of forged machine elements with energy-saving method of thermo-mechanical processing. Molten steels are characterized with high metallurgical purity, i.e. they have limited concentration of P and S impurities and gases.

Table 2.  
Chemical composition of the investigated steels

Alloying	Mass contents, (%)	
	Steel A	Steel B
C	0.31	0.28
Mn	1.45	1.41
Si	0.30	0.29
P	0.006	0.008
S	0.004	0.004
Cr	0.26	0.26
Ni	0.11	0.11
Mo	0.22	0.22
Nb	—	0.027
Ti	0.033	0.028
V	0.008	0.019
B	0.003	0.003
Cu	0.20	0.20
Al	0.040	0.025
N	0.0043	0.0039
O	0.0006	0.0006

Investigated steel melts, weighing 100 kg, were done in VSG-100 type laboratory vacuum induction furnace, produced by PVA TePla AG. Furnace charge consisted of ARMCO, 04JA grade iron and alloy additions, mainly in the form of pure metals (Mn, Cr, Ni, Mo, Cu, Ti and Al) and ferroalloys (FeV, FeNb and FeB) as well as non-metallic additions (C and Si). In order to modify non-metallic inclusions, mischmetal (~50% Ce, ~20% La, ~20% Nd) in the amount of 2 g/kg of steel was used. Casting was performed in atmosphere of argon through heated intermediate ladle to quadratic section cast iron hot-topped ingot mould: top - 160/bottom - 140 mm × 640 mm. In order to obtain 32×160 mm flat bars, initial hot plastic working of ingots was performed implementing the method of open die forging in high-speed hydraulic press, produced by Kawazoe, applying 300 MN of force. Heating of ingots to forging was conducted in gas forging furnace. The range of forging temperature was equal 1200-900°C, with interoperation reheating in order to prevent the temperature of the material to drop below 900°C. Ingot bodies were subjected to forging without feedheads which were cut off during forging.

Calculations of the kinetics of precipitation of MX-type interstitial phases in austenite are necessary for correct design of conditions of thermo-mechanical treatment for microalloyed steels. Depending on chemical composition of steel, and in particular on the type and concentration of introduced microadditions, plastic working of steel should be realized in a

specified temperature range. The goal of performed calculations was to determine the sequence of precipitation of interstitial phases along with the decrease of temperature. The analysis of the kinetics of MX-type interstitial phases precipitation was done basing on the thermodynamic model proposed by Adrian [18-21], assuming that only individual, single MX phases are soluble in austenite. The analysis based mainly on (5), (6) and (7) equations, regarding mass balance of elements. The constants put together in Table 1 were used for calculations.

In order to verify performed analysis, the investigation of influence of austenitizing temperature on the grain size of primary austenite was carried out. To do that, 25×20×32 mm samples were austenitized at the temperature of 900, 1000, 1100 and 1200°C for 30 min and subsequently cooled in water. With the aim to reveal grain boundaries of primary austenite, the samples were etched in saturated water solution of picric acid with addition of CuCl<sub>2</sub> at the temperature of 60°C. Metallographic observations of metallographic specimens were carried out in Leica MEF 4A light microscope applying magnification ranging from 200 to 800x. Measurements of primary austenite grain size were conducted with the use of image analyzer and Leica Qwin software cooperating with light microscope. The number of primary austenite grain size was determined in accordance with „Microscopic methods of grain size determination”, PN-84/H-04507/01 standard.

## 3. Results

The analysis of the kinetics of precipitation of MX-type interstitial phases in A steel shows that TiN nitride will be the first phase which will precipitate in austenite. The beginning of TiN precipitation occurs at the temperature equal around 1350°C. A gradual reduction of concentration of nitrogen and titanium dissolved in solid solution occurs along with the temperature lowering (Figs. 2a,b), portion of TiN increases to 100% at the temperature of 900°C (Fig. 2c), wherein concentration of titanium bound into TiN at this temperature represents about 55% of the total fraction of Ti in steel.

Another phase potentially precipitating in the A steel is AlN nitride. In reality, the presence of AlN in steel is not much probable, since chemical affinity of Ti to N is much higher than Al and its concentration has been selected in the way to bind entire N in TiN nitrides. Taking into account atomic weights of Ti and N it was calculated that the portion of titanium guaranteeing bounding of entire nitrogen in TiN is equal  $3.4 \times \% N$ . The calculation shows that 0.015% Ti is enough to bind totally N, and it's present in the steel in concentration of 0.033%, which is more than twice as much. Hence the analysis of the kinetics of AlN precipitation in austenite was omitted.

The next phase precipitating in A steel is TiC carbide. Performed calculations have indicated that the start of precipitation of TiC takes place at the temperature of about 1190°C (Fig. 3).

At the temperature of 950°C practically all titanium is bound into TiC (Fig. 3a), while the concentration of carbon dissolved in solid solution at this temperature is equal 97.5% of total carbon content in the steel.

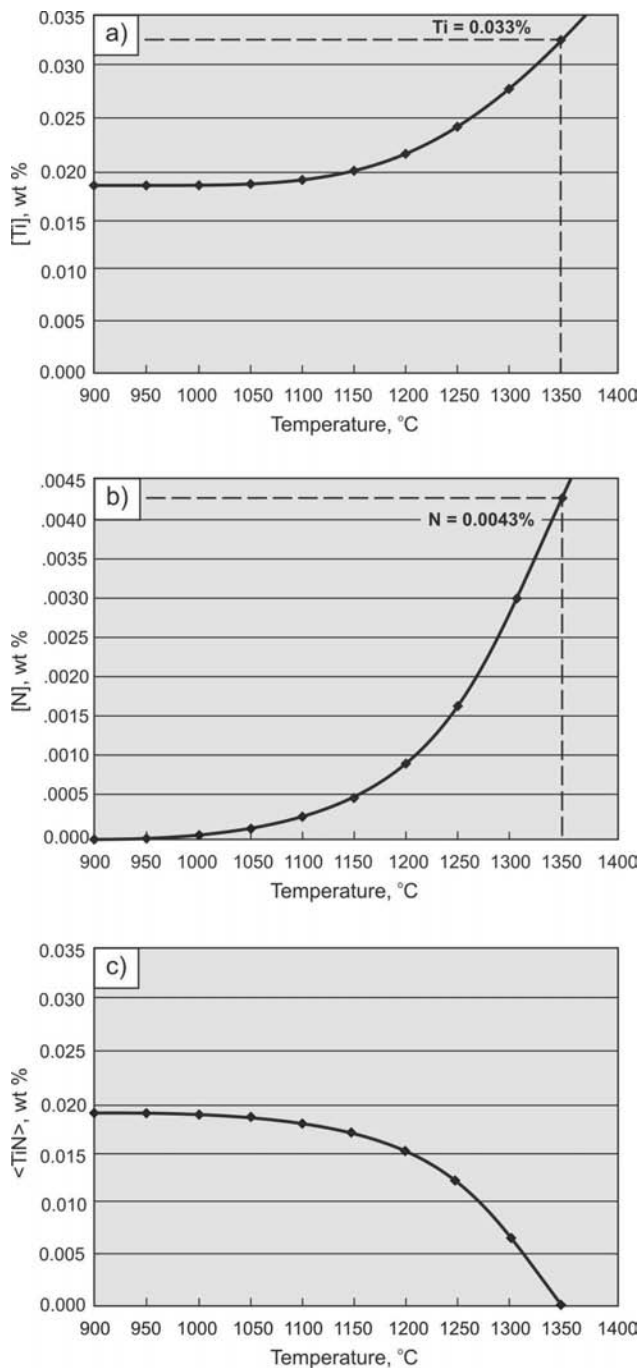


Fig. 2. The kinetics of precipitation of TiN in austenite of A steel, containing 0.033%Ti and 0.0043%N as a function of temperature: a - concentration of titanium  $[Ti]$  dissolved in austenite, b - concentration of nitrogen  $[N]$  dissolved in austenite, c - fraction of  $\langle TiN \rangle$  phase undissolved in austenite

Vanadium is another microaddition that is able to form MX-type phases in A steel. Performed analysis revealed that microaddition of vanadium is completely dissolved in solid solution, even below 750°C. Hence vanadium microaddition introduced into A steel in a concentration of 0.008 wt% shall not affect the formation of fine-grained austenite microstructure through VC dispersive particles precipitating on the grain boundaries of this phase, but it'll influence increase of strength of the steel through solution hardening.

The analysis of the kinetics of precipitation of MX-type interstitial phases in B steel showed - as in case of A steel - that TiN is the first phase which will precipitate in austenite. The beginning of precipitation of this phase occurs at the temperature of about 1330°C. This temperature is slightly lower than it is in case of A steel because of lower concentration of Ti and N in the steel. A gradual decrease of concentration of nitrogen and titanium dissolved in solid solution (Figs. 4a,b) and an increase of TiN fraction (Fig. 4c) occur along with temperature lowering. Complete binding of titanium in TiN is present at the temperature of approximately 1000°C (Fig. 4c). Just as in A steel, chemical composition of B steel was designed so that all nitrogen was bound into TiN nitride by Ti microaddition. Therefore, the analysis of the kinetics of precipitation of remaining interstitial phases with nitrogen has been omitted.

The next MX-type phase precipitating in B steel austenite is TiC. Performed analysis revealed that the temperature of the beginning of precipitation of titanium carbides in the steel is slightly lower than the temperature of the beginning of precipitation of TiC in A steel, and is equal approximately 1160°C. A gradual decrease of concentration of carbon and titanium dissolved in solid solution occurs along with a decrease of temperature (Figs. 5a,b). However, the fraction of TiC increases along with temperature lowering (Fig. 5c).

Niobium carbide is the phase which is third in terms of temperature of the beginning of precipitation, which is formed in B steel. The beginning of NbC precipitation occurs at the temperature of about 1135°C. The portion of NbC carbides in solid solution increases along with lowering the temperature and at the temperature of 1050°C is equal approx. 0.0175 wt%. (Fig. 6c), at the temperature of 900°C the fraction of the phase reaches its maximum and is equal approx. 0.0275 wt%. Increase of NbC fraction is accompanied by simultaneous decrease of Nb and C concentration in solid solution (Figs. 6a,b). At the temperature of 900°C practically all Nb is bound into NbC (Fig. 6a), while the concentration of C dissolved in solid solution at this temperature is equal approx. 99% of the total carbon content in steel, what is connected to high concentration of this element in the steel.

Similarly as in A steel, V microaddition will be completely dissolved in B steel austenite in a range of hot plastic working. VC carbides begin to precipitate at the temperature much below  $A_{c3}$ . Analysis of single interstitial phases in solid solution does not reflect the real situation satisfactorily, because in fact all of these phases precipitate in steel according to the temperature sequence, overlapping and absorbing elements dissolved in austenite, thereby altering their kinetics of precipitation.

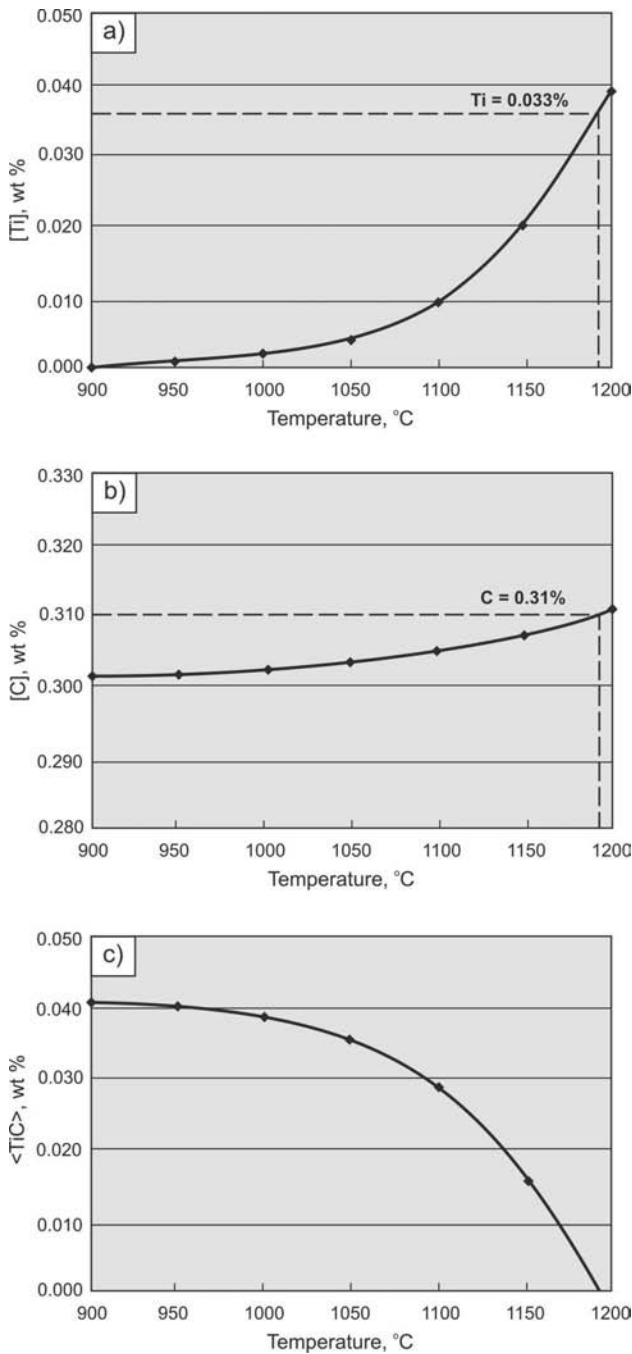


Fig. 3. The kinetics of precipitation of TiC in austenite of A steel, containing 0.033% Ti and 0.31% C as a function of temperature: a - concentration of titanium [Ti] dissolved in austenite, b - concentration of carbon [C] dissolved in austenite, c - fraction of <TiC> phase undissolved in austenite

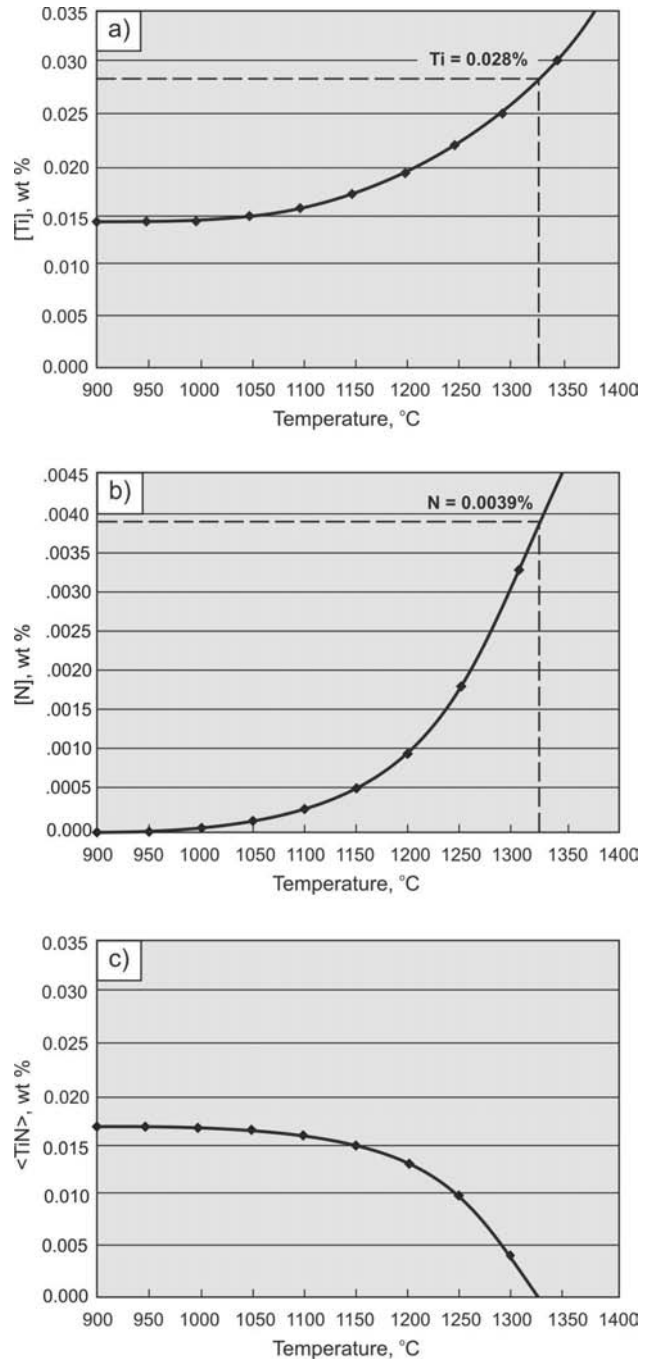


Fig. 4. The kinetics of precipitation of TiN in austenite of B steel, containing 0.028% Ti and 0.0039% N as a function of temperature: a - concentration of titanium [Ti] dissolved in austenite, b - concentration of nitrogen [N] dissolved in austenite, c - fraction of <TiN> phase undissolved in austenite

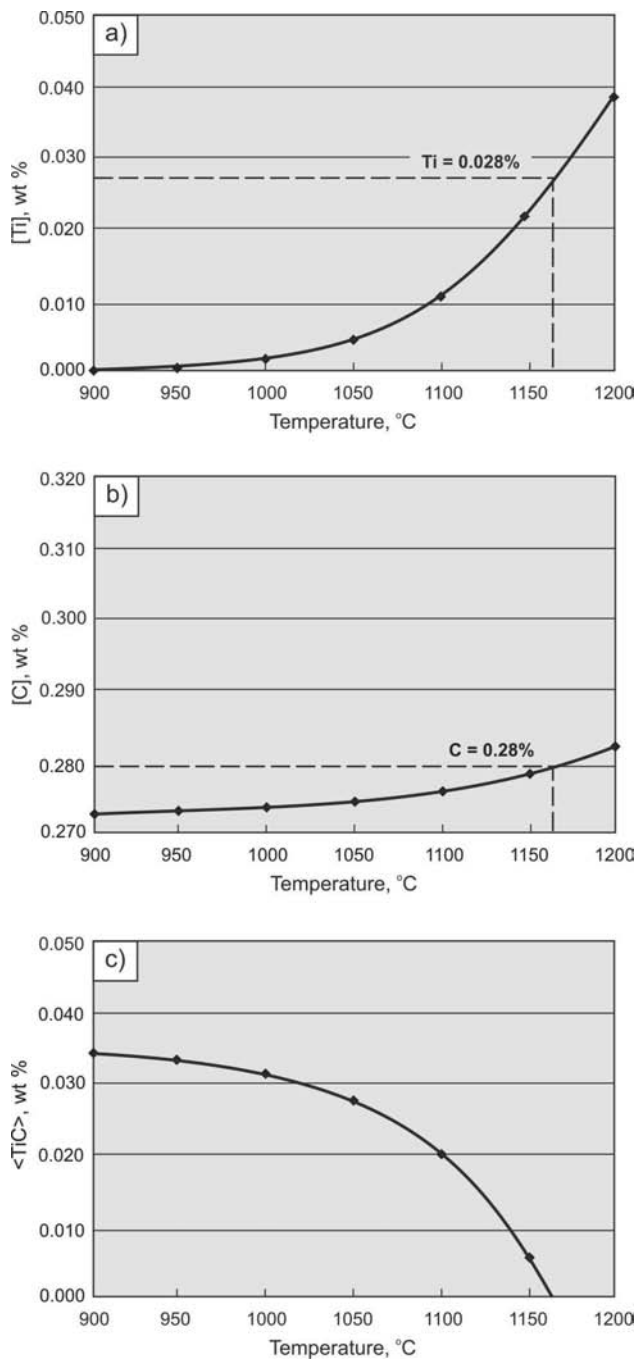


Fig. 5. The kinetics of precipitation of TiC in austenite of B steel, containing 0.028% Ti and 0.28% C as a function of temperature: a - concentration of titanium [Ti] dissolved in austenite, b - concentration of carbon [C] dissolved in austenite, c - fraction of <TiC> phase undissolved in austenite

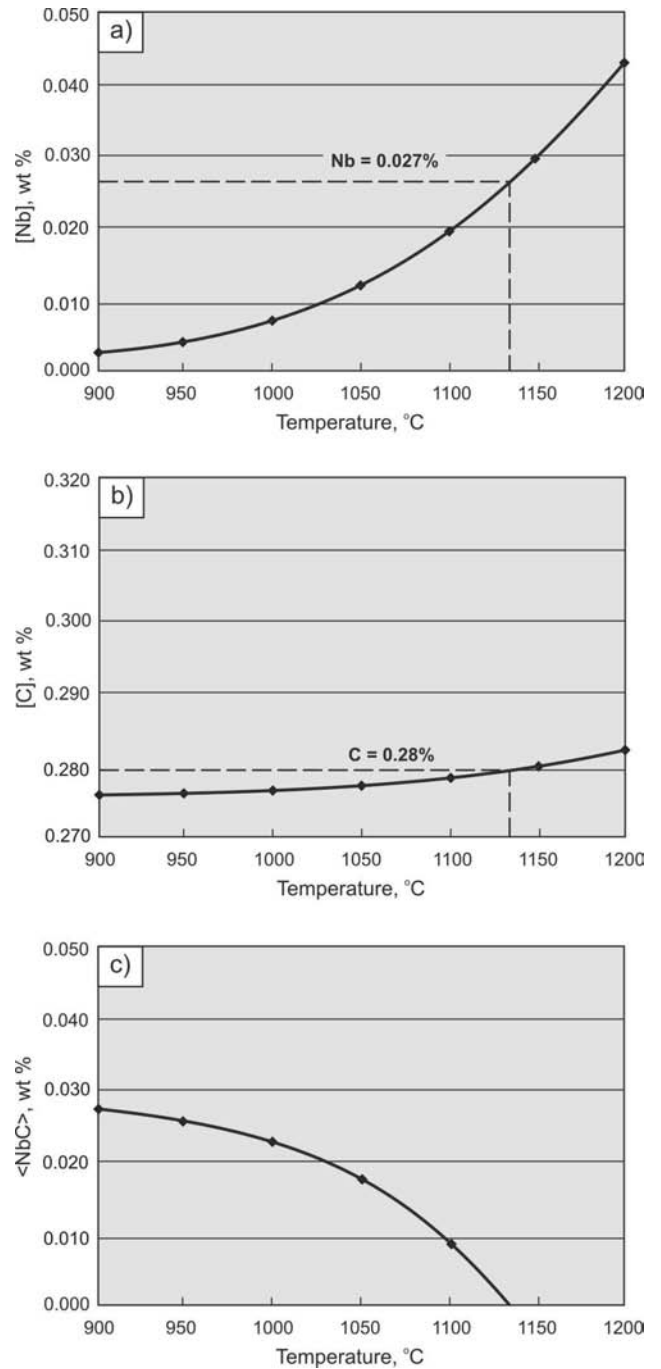


Fig. 6. The kinetics of precipitation of NbC in austenite of B steel, containing 0.027% Nb and 0.28% C as a function of temperature: a - concentration of niobium [Nb] dissolved in austenite, b - concentration of carbon [C] dissolved in austenite, c - fraction of <NbC> phase undissolved in austenite



The consequence of such situation may be the change of the beginning and finish temperature of precipitation of analyzed phases as well as the change of their fraction in solid solution. Nevertheless, analysis of individual interstitial phases is crucial for elaboration of effective temperature of precipitation sequence of carbides and nitrides in examined steels, providing a basis for further analysis.

The next step during the analysis of the kinetics of precipitation of interstitial phases is to consider the presence of several compounds in a solid solution simultaneously. During such analysis isomorphism of particular phases should be taken into account. This is very important because phases which are mutually soluble are considered in a different way than those, which are present together in solid solution and do not interact. Slightly different approaches to isomorphism of MX-type phases can be found in the literature. Some authors, particularly for calculating purposes, assume complete dissolution of all MX-type phases [9,16], while others conduct the analysis assuming the isomorphism of particular phases [15,23]. However, the temperature range for the presence of given phases is essential for proper design of the technological process of rolling or forging of microalloyed steels. Determination of precise chemical composition of specific phases - from the technological point of view - has a limited significance. It should be taken into account that the presence of MX-type complex phase can arise from mutual isomorphism of individual particles or one single precipitation can be a crystallization nucleus for another in a lower temperature range. It is particularly probable in case of phases, which temperatures of precipitation in solid solution differ significantly.

Obtaining the final sequence of precipitation of MX-type phases is reduced to confronting together the results of calculations of the kinetics of precipitation of TiN and TiC in A steel austenite (Fig. 7) and TiN, TiC and NbC in B steel (Fig. 8). It arises from data compiled in Fig. 7 that only TiN phase is present in solid solution in a temperature range from 1350°C to 1190°C. TiC begins to precipitate at the temperature of 1190°C. At the temperature of 900°C Ti microaddition is entirely bound in TiN and TiC. Approximate mass fraction of all phases present in steel can be determined on the basis of a comprehensive sequence of the precipitation of interstitial phases in austenite. Summing up mass fractions of TiN and TiC it can be concluded that overall fraction of interstitial phases present in A steel is equal approx. 0.06 wt% at the temperature of 900°C. The data set together in Fig. 8 shows that TiN begins to precipitate in B steel austenite at the temperature of about 1325°C. Up to the temperature of approx. 1165°C, TiN nitride is the only interstitial phase in the steel. TiC begins to precipitate at this temperature and at the temperature of about 30°C lower - NbC. By summing up mass fractions of TiN, TiC and NbC it was revealed that the total fraction of interstitial phases present in B steel is equal approximately 0.079 wt%.

The research of influence of austenitizing temperature in a temperature range from 900 to 1200°C on primary austenite grain size has been used to verify the analysis of the kinetics of precipitation of MX-type phases. Results of the research are presented in Figs. 9-15, while points in Fig. 15 represent the average diameter of austenite grains at a given temperature.

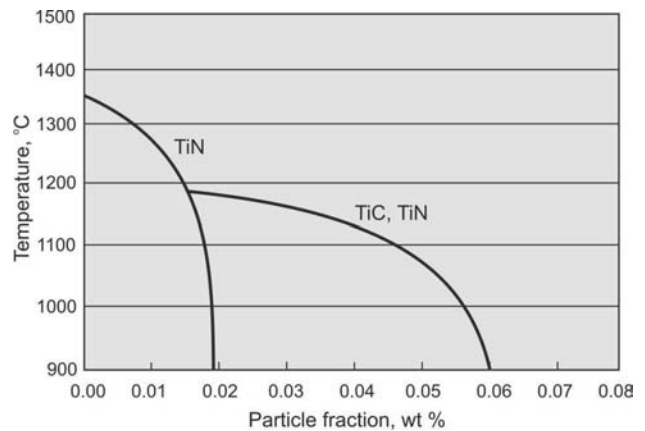


Fig. 7. Temperature sequence of precipitation the TiN and TiC in the austenite of the steel A containing 0.31% C, 0.033% Ti and 0.0043% N

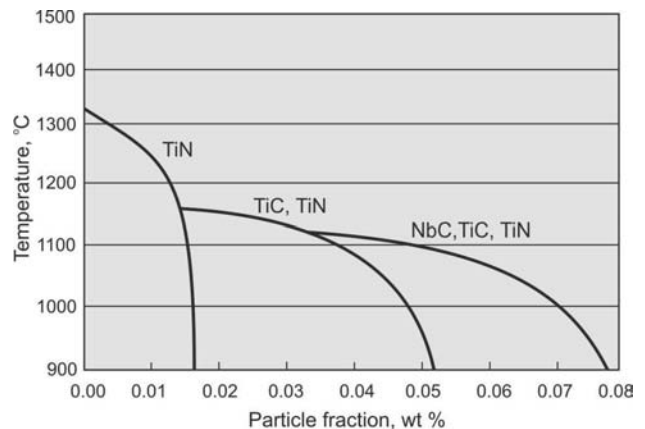


Fig. 8. Temperature sequence of precipitation the TiN, TiC and NbC in the austenite of the steel B containing 0.28% C, 0.028% Ti, 0.027% Nb and 0.0039% N

The samples austenitized in a temperature range from 900-1050°C are characterized with very fine grains of primary austenite. The size of primary austenite grains in the austenitizing temperature from 900 to 1000°C ranges from 11 to 18  $\mu\text{m}$  in case of A steel and from 8 to 12  $\mu\text{m}$  for B steel. This fine-grained microstructure is a result of the presence of a significant portion of TiN, TiC interstitial phase particles and in the case of B steel, additionally NbC, which effectively inhibits the growth of austenite grains. The increase of austenitizing temperature causes gradual growth of austenite grains dependent on the kinetics of dissolution of MX-type phases and their total fraction in the steel. The average diameter of austenite grains after austenitizing at the temperature of 1200°C increases to approx. 66 and 62  $\mu\text{m}$ , for A and B steel, respectively. The analysis of data compiled in Fig. 15 indicates that the changes of the austenite grain size as a function of austenitizing temperature is similar for both steels; however, somewhat smaller particle sizes of  $\gamma$  phase are noted in case of B steel.

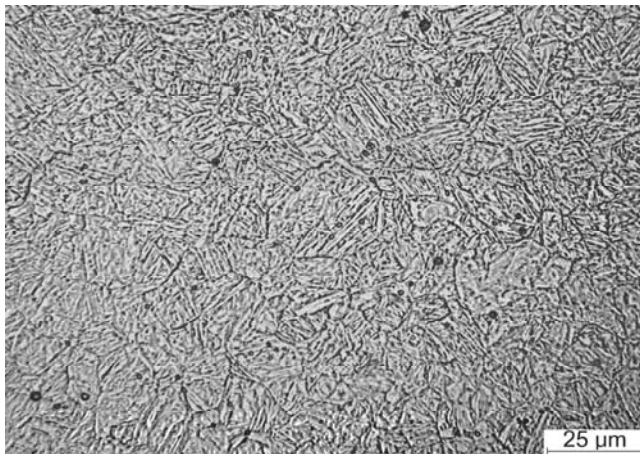


Fig. 9. Grain boundaries of primary austenite of the steel A; austenitizing temperature of 900°C

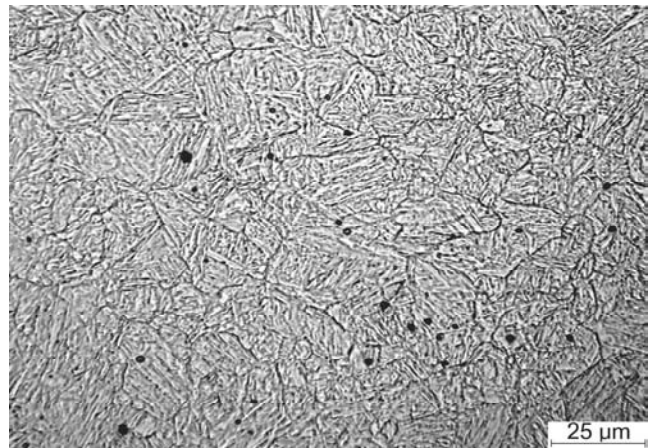


Fig. 12. Grain boundaries of primary austenite of the steel B; austenitizing temperature of 900°C

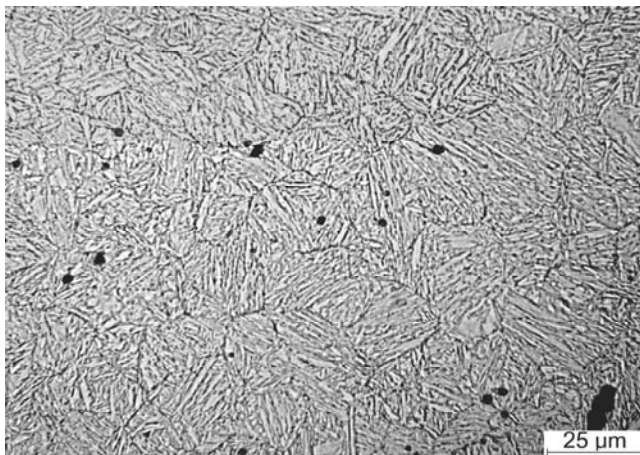


Fig. 10. Grain boundaries of primary austenite of the steel A; austenitizing temperature of 1000°C

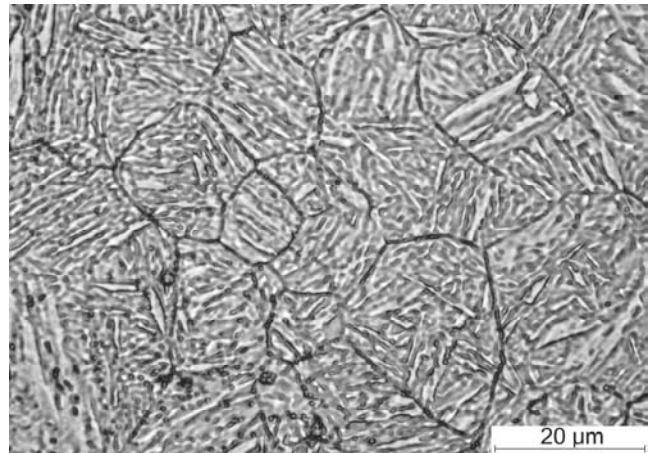


Fig. 13. Grain boundaries of primary austenite of the steel B; austenitizing temperature of 1000°C

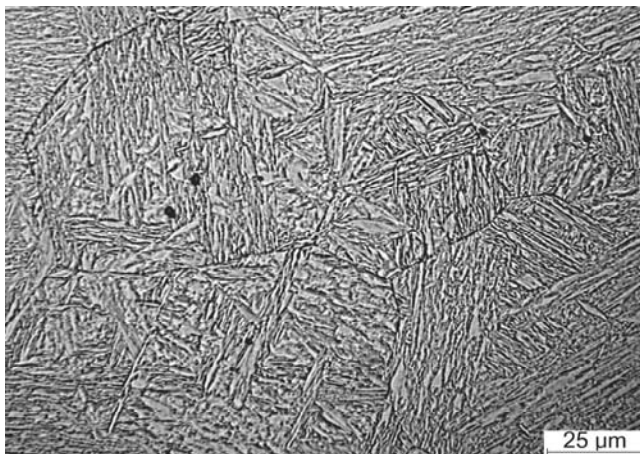


Fig. 11. Grain boundaries of primary austenite of the steel A; austenitizing temperature of 1100°C

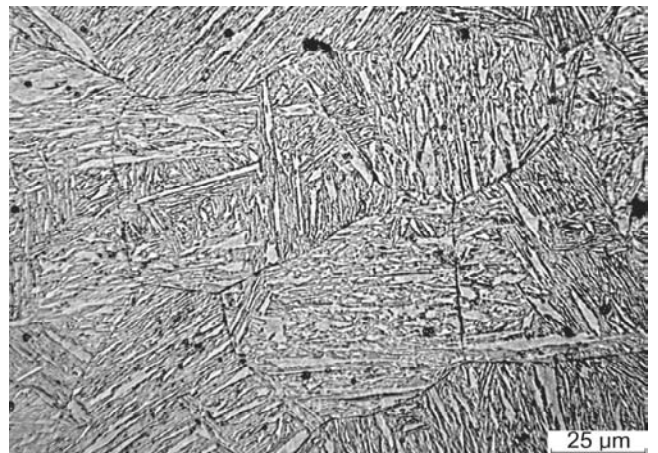


Fig. 14. Grain boundaries of primary austenite of the steel B; austenitizing temperature of 1100°C

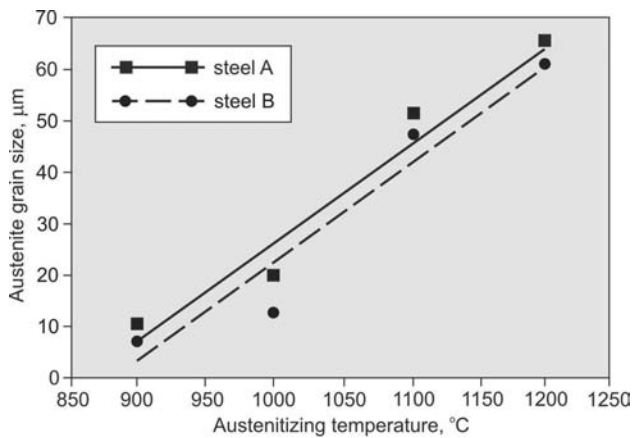


Fig. 15. Influence of the austenitizing temperature on the grain size of austenite

Slightly lower growth of austenite grains in B steel is related to the presence of NbC carbides, which complete dissolution occurs at the temperature of around 1135°C and with a slightly larger volume fraction of all particles as compared with A steel. Studies of grain size of primary austenite confirm the correctness of performed theoretical analysis of the kinetics of precipitation of interstitial phases in studied steels. Temperature range for the presence of individual MX-type phases, resulting from performed analysis, is comparable with obtained results of growth of austenite grains in the examined temperature range.

## 4. Conclusions

The research was carried out on newly elaborated steels assigned for production of forged machine elements with the method of thermo-mechanical processing. Designed chemical composition of studied steels takes into consideration interaction of boron microaddition increasing hardenability of fine-grained steels. Therefore, A and B steels have been microalloyed with titanium in a concentration guaranteeing complete binding of nitrogen into TiN, being an effective shield for boron against binding of this element in BN nitrides, which are stable in austenite.

The analysis of the kinetics of precipitation of interstitial phases in A steel revealed that TiN will be the first phase which would precipitate in austenite. The beginning of TiN precipitation occurs at the temperature equal around 1350°C. TiC is another phase precipitating in this steel and begins to precipitate in solid solution at the temperature of 1190°C. At the temperature of 900°C, the fraction of both phases is close to 100%.

Apart from TiN and TiC, also NbC starts to precipitate at the temperature of about 1135°C in B steel. Similarly as in case of A steel, almost all interstitial phases of B steel are bound in 100% at the temperature of 900°C.

The analysis of the kinetics of precipitation of MX-type interstitial phases in austenite allows to select a proper temperature range of forging for studied steels, which should correspond to the temperature range of precipitation of these

phases. High mechanical properties of forged parts can be achieved by appropriate selection of forging conditions, i.e. temperature of charge heating and plastic deformation, since the distribution of deformation and strain rate during production of die forgings with a complex shape is difficult to adjust. The conditions of charge heating for forging should not lead to total dissolution of interstitial phases of microadditions introduced into steel in solid solution, because it causes disadvantageous grain growth. Hence the charge for A and B steel forging can be heated up to the temperature of 1200°C without worrying about growth of austenite grains. The temperature of the beginning of precipitation of TiN in A and B steel, equal 1350 and 1330°C respectively, indicates that at the temperature of 1200°C significant fraction of Ti microaddition (60% in A steel and 67% in B steel) will be bound in TiN nitrides, effectively inhibiting growth of austenite grains. However, the temperature of the end of forging was assumed to be 900°C; at the temperature the portion of interstitial phase particles will be the highest and microaddition of vanadium dissolved in solid solution will result in an improvement of hardenability.

The investigation of influence of austenitizing temperature on grain size of primary austenite confirmed correctness of the analysis of the kinetics of precipitation of interstitial phases in studied steels. The presence of TiN, TiC particles in the microstructure, and in case of B steel, additionally presence of NbC, effectively limiting grain growth of the  $\gamma$  phase, determines that examined steels retain fine-grained microstructure of primary austenite, which is beneficial prior to successive hardening.

Performed analysis of the kinetics of precipitation of MX-type interstitial phases provides the basis for proper design of manufacturing process of thermo-mechanical treatment of high strength forged machine parts obtained from microalloyed steels.

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