# Thermodynamic Analysis of Precipitation Process of Complex Carbonitride $Ti_xV_{1-x}C_yN_{1-y}$ in HSLA-Type Steel

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**ABSTRACT**

The paper presents a detailed analysis of the MX-type interstitial phase precipitation process and a thermodynamic analysis of the $Ti_xV_{1-x}C_yN_{1-y}$ carbonitride precipitation in austenite. The subject of research analysis was the newly developed HSLA-type steel containing 0.175% C, 1.02% Si, 1.87% Mn, 0.0064% N, 0.22% Mo, and microadditions 0.022% V and 0.031% Ti. Analysis of the process of precipitation of MX interstitial phases under thermodynamic equilibrium conditions proved that the first phase that precipitates in the austenite of the tested steel is TiN-type nitride. The onset temperature of this phase was 1450 °C. Subsequently, carbides of the TiC-type, VN-type nitrides and VC-type carbides, for which the precipitation onset temperatures were 1180 °C, 870 °C and 775 °C will be released, respectively. The analysis of the precipitation process of the complex carbonitride in austenite under thermodynamic equilibrium conditions was based on the Hillert and Staffansson model, developed by Adrian, with the use of the CarbNit computer program. The beginning of carbonitride precipitation with the stoichiometric composition $Ti_{0.985}V_{0.015}C_{0.073}N_{0.927}$ occurred at the temperature of 1394 °C. At 850 °C practically all of the Ti is bound in the carbonitride of the stoichiometric composition $Ti_{0.883}V_{0.117}C_{0.378}N_{0.622}$. At the same temperature, a significant part of microaddition V will be dissolved in austenite, which means that vanadium will have a lesser effect on the formation of a fine-grained austenite structure, but more strongly on the precipitation hardening of steel by the dispersion VN and V particles (C, N) released during the cooling of the products.

**Keywords:** carbonitride, thermodynamic model, HSLA-type steel, microstructure.

## INTRODUCTION

The increasing requirements of the recipients of steel products determine the necessity to produce grades of high strength, guaranteed ductility, susceptibility to technological deformations in cold and hot conditions, and limited anisotropy of plastic properties [1–5]. The simultaneous fulfillment of these opposing properties requires a rational selection of the chemical composition, ensuring the desired hardenability and weldability of the steel [6–11].

The group of steels that meet the aforementioned requirements in a wide range are the low-alloy HSLA-type steels. These steels contain high affinity microadditions with C and N, i.e. Nb, Ti and V, up to about 0.1%. These steels are characterized also by an increased concentration of N,

and in the case of steel for quenching and tempering also up to 0.005% B - increasing the hardenability [12–16]. Metallic microadditions in the interaction with C and N form stable MX-type interstitial phases with a NaCl network, which makes it possible to manufacture steel products with a fine-grained structure, giving them high strength and guaranteed resistance to cracking. Such a technological solution ensures a significant reduction in production costs as a result of the elimination of energy-consuming heat treatment operations or its limitation to tempering only [17–19].

The production of products with high strength properties and ductility from microalloyed HSLA steels requires the proper selection of mechanical working conditions. The conditions of the mechanical working process must be adjusted to the

temperature range of the precipitation in the austenite of MX-type interstitial phases introduced into the steel of microadditives. The solubility in austenite of a carbide or nitride is determined by the logarithm of the solubility product, expressed by the formula [20]:

$$\log([M] \cdot [X]) = B - A/T \tag{1}$$

where: [M] – mass fraction of metallic micro-additive dissolved in austenite, expressed in mass %;
[X] – mass fraction of metalloid dissolved in austenite, expressed in mass%;
T – absolute temperature;
A and B – constants related to the energy of compound formation (the constant A is proportional to the enthalpy, and the constant B to the entropy of compound formation). The values of these constant solubility products depend on the determination method, hence, in the literature, different values can be found for the same MX phases.

Chemical composition of austenite and the content of undissolved <MX> compound can be determined using the ratio of the solubility of the compound and the mass balance of the elements involved in the reaction, the product of which is the compound <MX>. A simplified thermodynamic model based on the laws of equilibrium thermodynamics, concerning the separation of the compound <MX>, describes the system of equations [21]:

$$kMX = [M] \cdot [X] \tag{2}$$

$$M = [M] + \frac{(M)}{(MX)} < MX > \tag{3}$$

$$X = [X] + \frac{(M)}{(MX)} < MX > \tag{4}$$

where: M, X – total concentration of these elements in steel in mas. %;
(M) – atomic mass of the elements;
(MX) – molecular mass of the compound.

The solution to the above system of equations is the quadratic function that allows to calculate the amount of the interstitial element dissolved in austenite [22]:

$$[X]^2 + [X]\left[\frac{(X)}{(M)} \cdot M - X\right] - \frac{(X)}{(M)} \cdot k_{MX} = 0 \tag{5}$$

If $\Delta > 0$, then equation (5) has two solutions, the negative solution is ignored, while for $\Delta \leq 0$ the austenitizing temperature is higher or equal to the dissolution temperature of the compound <MX>. The content of the interstitial element dissolved in austenite at $\Delta > 0$ is determined from the formula:

$$[X] = \frac{X - \frac{(X)}{(M)} \cdot M + \sqrt{\left(\frac{(X)}{(M)} \cdot M - X\right)^2 + 4\frac{(X)}{(M)} \cdot k_{MX}}}{2} \tag{6}$$

Models of precipitation processes in the microalloyed HSLA-type steels based on the laws of equilibrium thermodynamics also predict the formation of complex carbonitride phases during technological operations of mechanical working. Carbides and nitrides of the microadditions Nb, Ti and V show mutual solubility and as a result of this process carbonitrides are formed with a chemical composition and dissolution temperature depending on the chemical composition of steel [23–26]. Multicomponent models, considering the presence of one to three microadditions, are based on the model of regular solutions of interstitial phases proposed by Hillert and Staffansson [27]. These models are based on the following assumptions [21]:

- substitution elements (M', M'', M''') and interstitial elements (C, N) form diluted solutions in austenite, and their activities fulfill Henry's law,
- as a result of the reaction between substitution and interstitial elements, carbonitride $M'_xM''_{1-x}C_yN_{1-y}$ or $M'_xM''_yM'''_{1-x-v}C_yN_{1-y}$ is formed, showing perfect stoichiometry,
- in the formed carbonitride atoms of metals and interstitial elements occupy positions in two independent subnets,
- the possibility of vacancies in both subnets and the dissolution of iron atoms in carbonitride are ignored.

According to the Hillert and Staffansson model, the molar free energy of carbonitride is equal [27]:

$$G_{MC_yN_{1-y}} = G_m = y\,^oG_{MC} + (1-y)\,^oG_{MN} + RT[y\ln(y) + (1-y)\ln(1-y)] + y(1-y)L_{CN}^M \tag{7}$$

where: $L_{CN}^M$ – parameter of the interaction of the element M on the C-N solution.

A detailed description of the model representing the equation describing the state of thermodynamic equilibrium is presented in [27].

## MATERIALS AND METHODS

The conducted analysis concerned the newly developed HSLA type steel intended for the production of multi-phase structure forgings with retained austenite. The tested steel contains 0.175% C, 1.02% Si, 1.87% Mn, 0.0064% N, 0.22% Mo, and microadditions 0.022% V and 0.031% Ti.

Thermodynamic analysis of the $\gamma$ phase equilibrium state of structural components in terms of the g phase stability of the tested HSLA-type steel concerned the calculations of the chemical composition of austenite as well as the content and chemical composition of the MX interstitial phases introduced into the steel of microadditions as a function of the cooling temperature.

The analysis of the precipitation process of carbides and nitrides in austenite under thermodynamic equilibrium conditions was carried out with the use of the model developed by Adrian [21, 29]. The calculations were made on the basis of the logarithmic relationship (1) and the equations (2÷4) concerning the mass balance.

The analysis of the process of separation of complex carbonitrides under thermodynamic equilibrium conditions was based on the Hillert and Staffanson model [27], modified by Adrian [21, 30], allowing to calculate the chemical composition of austenite as well as the composition and content of carbonitride precipitates in the multicomponent system Fe-M'-M''-M'''-Al-C-N. A detailed description of the thermodynamic model describing the state of equilibrium in steel containing no more than three micro-additions and Al is presented in [30].

The CarbNit computer program was used to evaluate the process of precipitating complex carbonitrides [32].

## RESULTS

A necessary condition for the correct design of the conditions of thermomechanical treatment of microalloyed HSLA-type steels is a detailed analysis of the separation process of MX interstitial phases, which allows to determine the temperature range of the precipitation of these phases in austenite. First, an analysis of the precipitation of single nitrides and carbides introduced into the steel of microadditions was carried out as a function of temperature, which was based mainly on the dependence (1) and equations (2–4) concerning the mass balance of elements. The following values of the constants from equation (1) were used for the calculations: for the TiN phase – A = 19800, B = 7.78; for the TiC phase – A=10745, B = 5.33; for the VN phase – A = 7840, B = 3.02; for the VC phase – A = 9500, B = 6.72 [14, 20, 28, 31–35].

The performed calculations show that the first precipitate of TiN-type nitrides will occur in the austenite of the analyzed steel containing 0.175% C, 0.0064% N, 0.031% Ti and 0.022% V. The beginning of the separation of this phase in austenite takes place at a temperature of about 1450 °C (Fig. 1a). As the temperature decreases, the content of nitrogen and titanium dissolved in the solid solution gradually decreases (Fig. 1a and Fig. 1b), while the proportion of undissolved TiN phase increases (Fig. 1c). The complete binding of titanium to nitrides of the TiN-type takes place at a temperature of about 1100 °C.

The next phase that may precipitate in the austenite of the analyzed steel is the TiC-type carbide. The temperature of the onset of the precipitation of TiC carbides is about 1180 °C. Lowering the temperature causes a decrease in the content of titanium and carbon dissolved in a solid solution (Fig. 2a and Fig. 2b) with a simultaneous increase in the share of TiC-type carbides undissolved in austenite (Fig. 2c). The performed calculations showed that under the equilibrium conditions, the titanium microaddition will be completely bound into TiC-type carbides at the temperature of about 900 °C.

Another microaddition that can form MX-type interstitial phases in the austenite of the analyzed steel is vanadium. The process of the evolution of VN-type nitrides begins at a temperature of about 870 °C (Fig. 3). As a result of lowering the temperature, the content of vanadium and nitrogen dissolved in austenite decreases (Fig. 3a and Fig. 3b), while the amount of undissolved VN phase increases (Fig. 3c). The data presented in Fig. 3 show that the vanadium microaddition introduced into the analyzed steel at a concentration of 0.022% at 800 °C is bound to VN nitrides only in about 50% and will have a lesser effect on the formation

of fine-grained austenite structure, but more strongly on the formation of austenite. precipitation hardening of steel by the dispersion VN and V(C,N) particles evolving during the cooling of the products.

The next phase that may precipitate in the austenite of the analyzed steel is the VC-type carbide. The performed calculations showed that the temperature of the beginning of the VC carbide precipitation is about 775 °C (Fig. 4). As a result of lowering the temperature, the share of VC-type nitrides in the solid solution increases

(Fig. 4c), while the content of vanadium microaddition and carbon dissolved in austenite decreases (Fig. 4a and Fig. 4b). Under equilibrium conditions, practically all vanadium is bound to VC carbides at a temperature of about 600 °C.

In fact, in steels with Ti and V microadditions there are complex Ti(C,N) and (Ti,V)(C,N) carbonitrides as a result of the mutual solubility of TiN nitrides, TiC carbides and V(C,N) carbonitrides [14, 28, 36].

The results of calculations of the austenite chemical composition of the analyzed steel, and
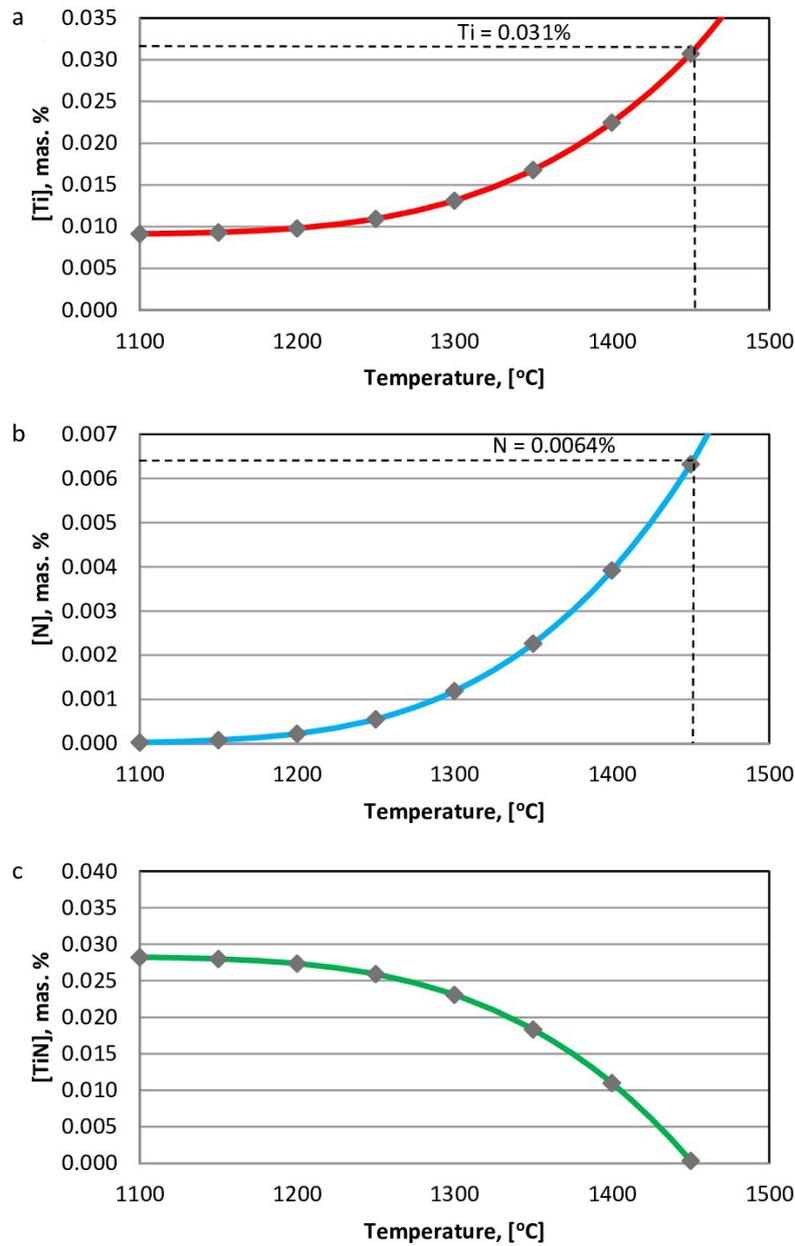


**Fig. 1.** The results of calculations of the precipitation of the TiN interstitial phase in the austenite of the tested steel containing 0.031% Ti and 0.0064% N: a) change in the concentration of Ti dissolved in austenite depending on the temperature, b) change in the concentration of N dissolved in austenite depending on the temperature, c) change in the proportion of TiN phase undissolved in austenite depending on the temperature

in particular the determination of the temperature dependence of the content of metallic and non-metallic elements, as well as the chemical composition of the complex carbonitride along with the specific volume fraction of the analyzed phase are shown in Figure 5. The process of precipitation of the complex carbonitride of the (Ti,V) (C,N) type begins at the temperature of 1394 °C. At this temperature, from the austenite is released a complex carbonitride with the chemical composition $Ti_{0.985}V_{0.015}C_{0.073}N_{0.927}$. As the temperature decreases in the range from 1394 °C to 850 °C

in the analyzed carbonitride, the concentration of vanadium increases from 0.015% at. up to 0.117% at. In the same temperature range, the carbon concentration in the carbonitride increases from 0.073 at.% to 0.378 at.%, while the nitrogen concentration decreases from 0.927 at.% up to 0.622% at. (Fig. 5a). At the temperature of 850 °C, the volume fraction of carbonitride with the composition $Ti_{0.883}V_{0.117}C_{0.378}N_{0.622}$ is 0.132%. The data presented in Fig. 5c shows that at 850 °C practically all of Ti is bound in carbonitride, while a large part of the microaddition V is still
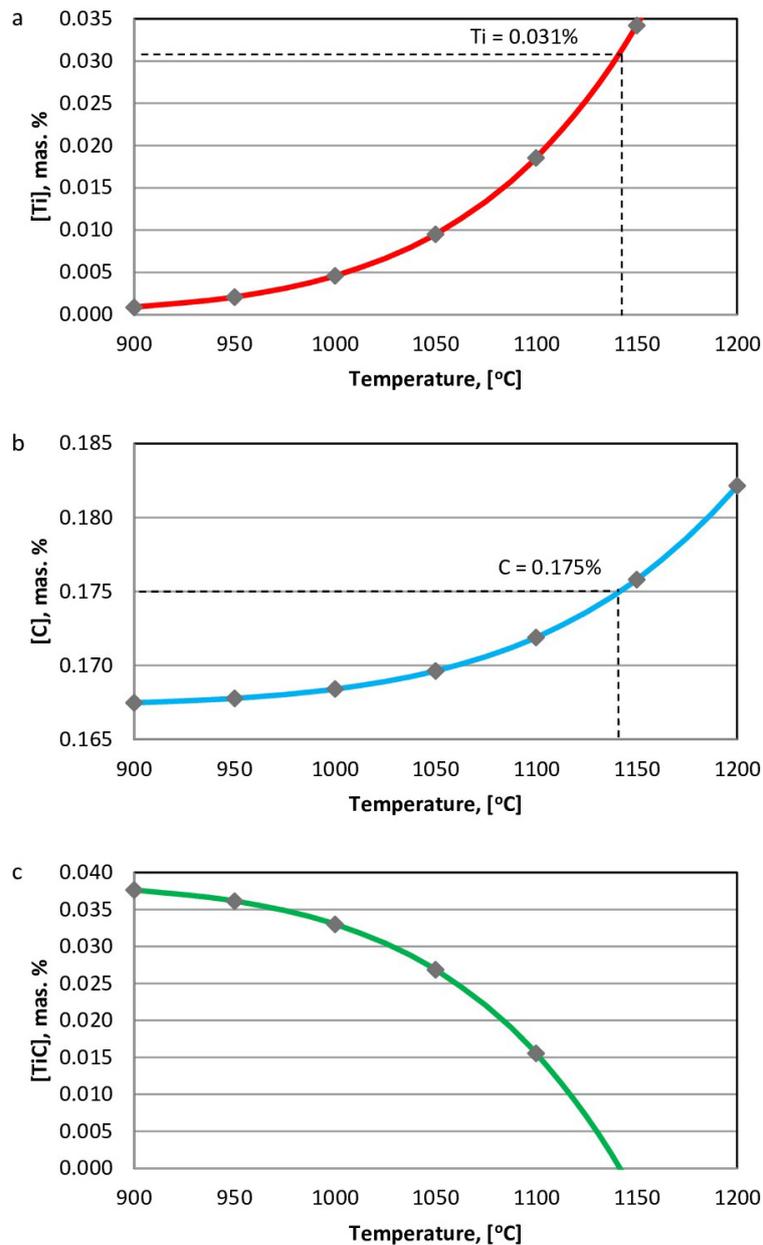


**Fig. 2.** The results of calculations of the precipitation of the TiC interstitial phase in the austenite of the tested steel containing 0.031% Ti and 0.175% C: a) change in the concentration of Ti dissolved in austenite depending on the temperature, b) change in the concentration of C dissolved in austenite depending on the temperature, c) change in the proportion of TiC phase undissolved in austenite depending on the temperature

dissolved in austenite. The calculated stoichiometric compositions of the analyzed carbonitride (Ti,V)(C,N) are presented in Table 1.

## CONCLUSIONS

The analysis of the precipitation process of MX-type interstitial phases under thermodynamic equilibrium conditions showed that the first phase to be released in the austenite of the tested steel is TiN-type nitride. The onset temperature of this phase is 1450 °C. Next, carbides of the TiC-type, VN-type nitrides and VC-type carbides will be released. The onset temperature of these phases is 1180 °C, 870 °C and 775 °C, respectively. The analysis of the separation of the MX-type single interstitial phases in a solid solution does not satisfactorily reflect the actual state, because all the described phases show mutual solubility in the solid state and usually separate in the form of complex carbonitrides. Nevertheless, the analysis of the separation of individual MX-type phases is
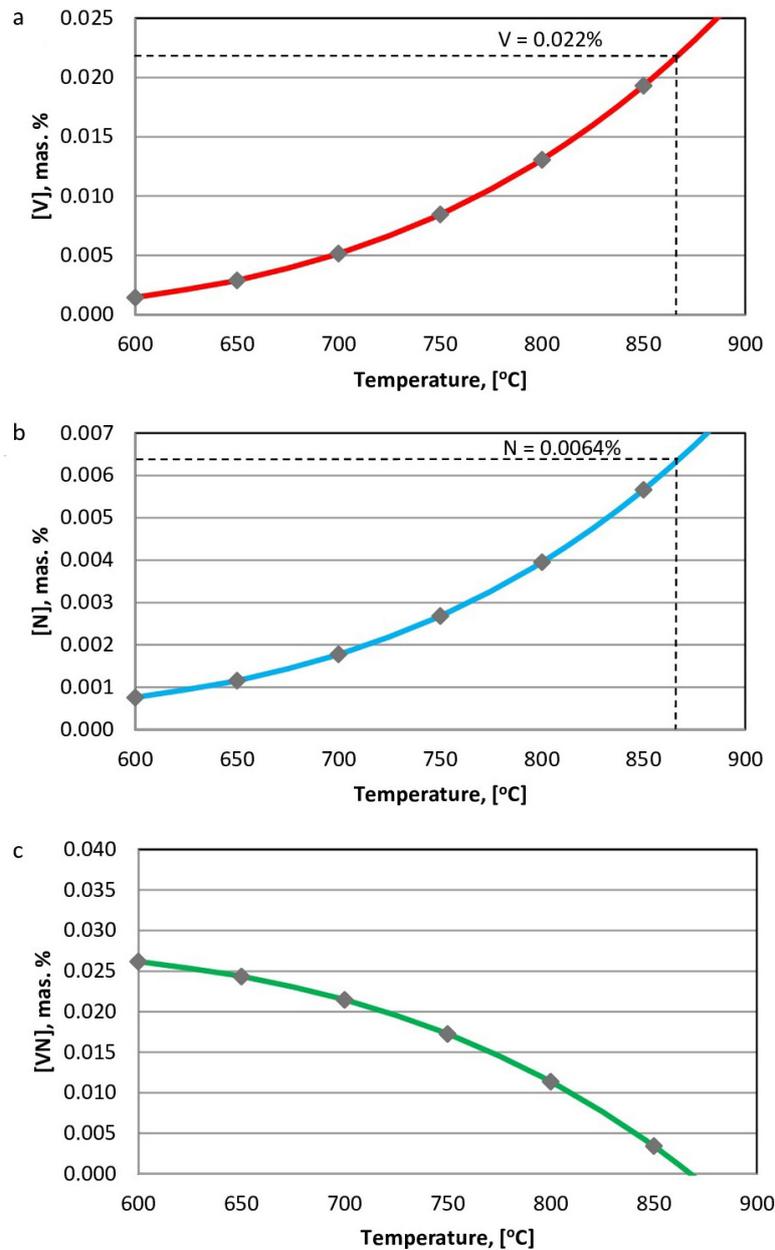


**Fig. 3.** The results of calculations of the precipitation of the VN interstitial phase in the austenite of the tested steel containing 0.022% V and 0.0064% N: a) change in the concentration of V dissolved in austenite depending on the temperature, b) change in the concentration of N dissolved in austenite depending on the temperature, c) change in the proportion of VN phase undissolved in austenite depending on the temperature
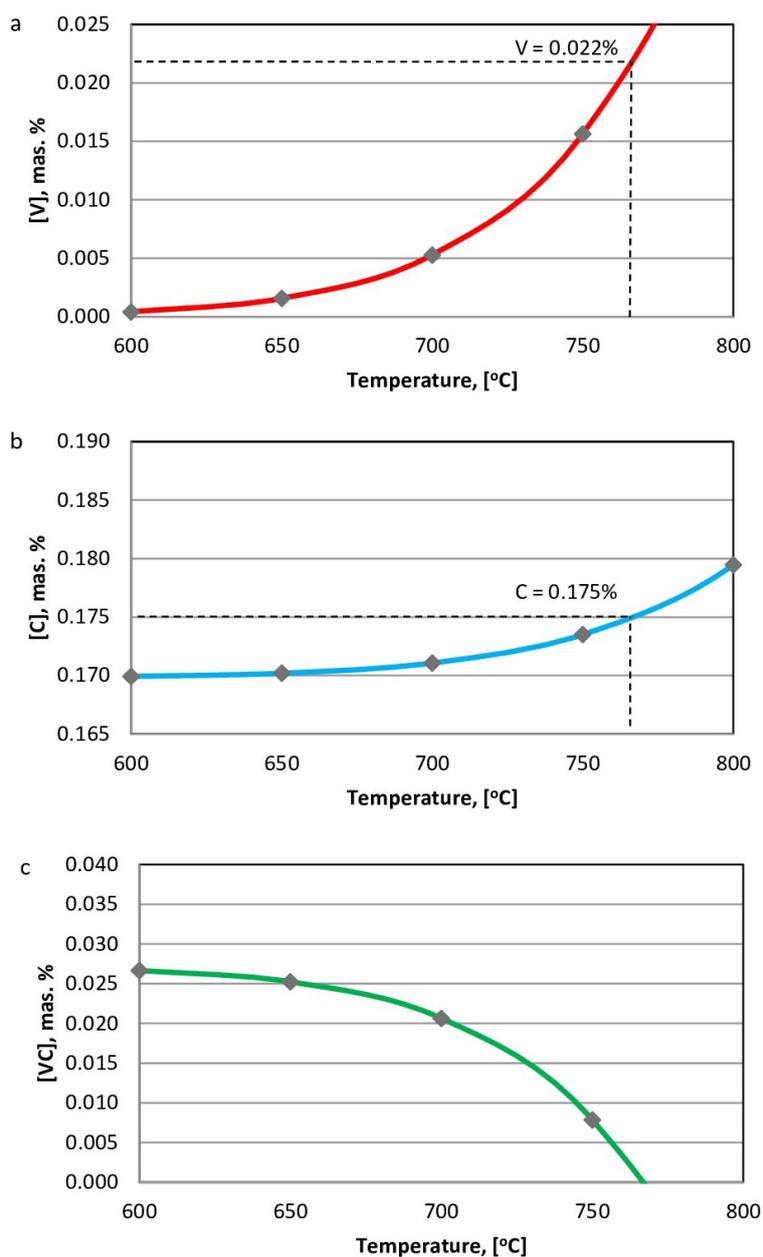
**Fig. 4.** The results of calculations of the precipitation of the VC interstitial phase in the austenite of the tested steel containing 0.022% V and 0.175% C: a) change in the concentration of V dissolved in austenite depending on the temperature, b) change in the concentration of C dissolved in austenite depending on the temperature, c) change in the proportion of VC phase undissolved in austenite depending on the temperature

important for the development of the temperature sequence of carbonitrides evolution in the tested steel. Due to the mutual solubility of TiN nitrides, TiC-type carbides and V(C,N) carbonitrides, complex carbonitride of the $Ti_xV_{1-x}C_yN_{1-y}$ type will be formed in the analyzed steel. The starting temperature of the formation of complex carbonitride (Ti,V)(C,N) is 1394 °C. At this temperature, the stoichiometric composition of carbonitride is $Ti_{0.985}V_{0.015}C_{0.073}N_{0.927}$. As the lowering the temperature, the atomic fractions of Ti and N decrease, and the atomic fractions of C and V increase. At the same time, the volume fraction of the analyzed carbonitride increases. At 850 °C, the stoichiometric composition of carbonitride is $Ti_{0.883}V_{0.117}C_{0.378}N_{0.622}$, and its volume fraction is 0.132%. At a temperature of 800 °C, more than 80% of the microaddition V is dissolved in the solid solution g, which means that vanadium will have a lesser effect on the formation of the fine-grained structure of austenite, but more strongly on the precipitation hardening of the steel by the dispersion VN and V(C,N) particles.
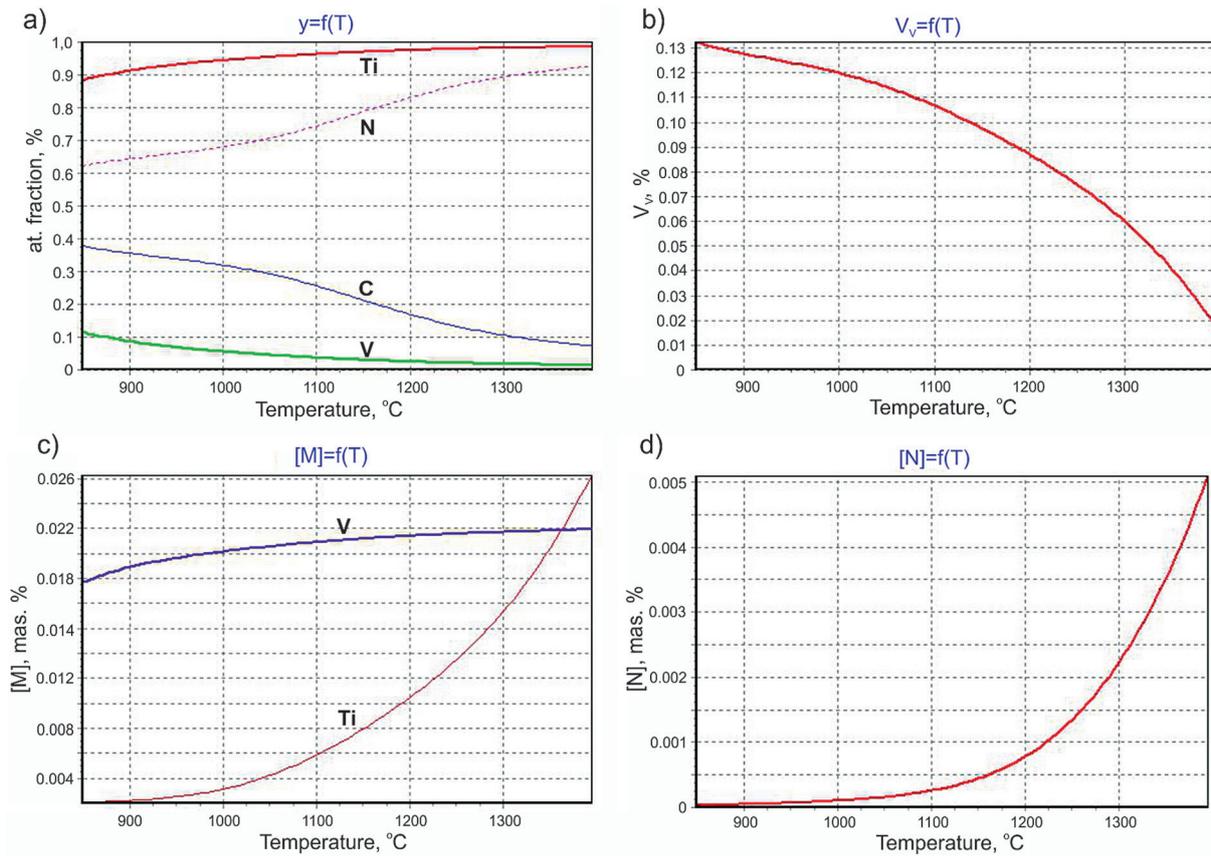
**Fig. 5.** The results of the analysis of thermodynamic equilibrium conditions: a) chemical composition of the complex carbonitride, b) volume fraction, $V_v$ = f(T), c) fractions of titanium and vanadium, [M] = f(T), d) fraction of nitrogen [N] = f(T)

**Table 1.** Stoichiometric compositions of the analyzed complex carbonitrides at the applied austenitizing temperature

| Temperature, °C | Stoichiometric compositions of carbonitride |
|---|---|
| 850 | $Ti_{0.883}V_{0.117}C_{0.378}N_{0.622}$ |
| 900 | $Ti_{0.913}V_{0.087}C_{0.356}N_{0.644}$ |
| 950 | $Ti_{0.932}V_{0.068}C_{0.338}N_{0.662}$ |
| 1000 | $Ti_{0.945}V_{0.055}C_{0.319}N_{0.681}$ |
| 1050 | $Ti_{0.955}V_{0.045}C_{0.293}N_{0.707}$ |
| 1100 | $Ti_{0.963}V_{0.037}C_{0.256}N_{0.744}$ |
| 1150 | $Ti_{0.969}V_{0.031}C_{0.212}N_{0.788}$ |
| 1200 | $Ti_{0.975}V_{0.025}C_{0.169}N_{0.831}$ |
| 1250 | $Ti_{0.979}V_{0.021}C_{0.131}N_{0.869}$ |
| 1300 | $Ti_{0.982}V_{0.018}C_{0.106}N_{0.894}$ |
| 1350 | $Ti_{0.984}V_{0.016}C_{0.086}N_{0.914}$ |

The Adrian's model used in the work to analyze the process of the precipitation of complex carbonitride of the (Ti,V)(C,N) in austenite under thermodynamic equilibrium conditions is a useful tool for optimizing the conditions of thermomechanical treatment of microalloyed HSLA steels.

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