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# Investigation into Secondary Phases in Steels Microalloyed with Vanadium and Nitrogen

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**Abstract**

In this work were compared two nitrogen and vanadium microalloyed steels in terms of the nitride or carbonitride phases present. The Thermal Evolved Gas Analysis (TEA) clearly showed that the one steel contains a higher volume fraction of nitrogen bound as vanadium carbonitride compared to the other steel in the natural relation to the total nitrogen content in steels. For promotion of this statement, the content of free nitrogen with using of the Hot Hydrogen Extraction (HHE) method was analysed and the thermodynamic prediction of the equilibrium composition of precipitating phases in microalloyed steels by the CALPHAD method with use of the Thermo-Calc software was carried out.

**KEY WORDS:** microalloyed steel; carbonitride; thermal evolved gas analysis (TEA); hot hydrogen extraction (HHE); Thermo-Calc.

## 1 Introduction

Structural steel microalloyed with nitrogen and nitride forming elements (such as V, Nb and Ti) results in Me(C,N) type phase precipitation. The precipitated phases have a substantial effect upon the mechanical properties of these steels. The most dramatic increase in the values of yield point and overall strength is achieved with these steels if the Me(C,N) phases are finely dispersed in the metallic matrix.<sup>1</sup> A negative effect of these phases may be demonstrated in the course of forming since, due to their hardness, they are not liable to plastic deformation. The given precipitates mostly display a sharp-edged shape and may become stress risers, contributing to the rise of internal stress, which may lead up to the initiation of cracks during the rolling of the steels.<sup>2</sup>

Considering the pronounced effects of Me(C,N) type phases upon the properties of steels, it is of great importance in the technical practice, to know their composition, morphology, and their quantity. The phases are mostly identified and their morphology determined in-situ using microscopic and X-rays techniques. Determining the quantity of these phases requires their isolation from the matrix with the subsequent chemical and structural analyses of the resultant isolated portion.

The main analysis for the determination and quantification of various forms of nitrogen in steels will be described in the following section.

### 1.1 Determination of Composition and Morphology of Precipitates

In practice, the precipitates are mostly investigated and analysed using the Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Both of these methods involve the interaction of the emitted primary beam of electrons and the sample, or the atoms of the elements in the sample, with the subsequent evolution of a range of signals, which may be detected. SEM may generally be used to investigate the precipitates with the size over 1  $\mu\text{m}$ , i.e. the coarser precipitates.

Nitride and carbonitride phases in steels may be identified in-situ using TEM as demonstrated.<sup>3</sup> The disadvantage is the difficulty of sample preparation for this analysis, which renders the analysis quite time-consuming. See Dillen et al.<sup>4</sup> for an overview of the most frequent techniques of electron microscopy used for metallurgical applications.

## 1.2 Quantification of Contents of Various Forms of Nitrogen in Steels

Dorado et al.<sup>5</sup> provides an overview of the methods available for the quantitative chemical analysis of varying forms of nitrogen in steels. Generally, the individual non-metallic phases present in the given steel need to be isolated before their contents are quantified. The best-known chemical method of isolating nitride phases is the one suggested by Beegly,<sup>6</sup> which uses an ester-halogen agent (most frequently bromine with methyl-ester of the acetic acid) to achieve the dissolution of the metallic matrix. The other group of methods for precipitates isolation is based on the electrochemical separation.<sup>7</sup> The isolated portion is subjected to a structural analysis and determination of the volume fractions of the individual constituent elements (XRD, IR, XRFS, AAS, OES-ICP, TEA).

## 1.3 Determination of Free Nitrogen

The content of free (interstitially dissolved) nitrogen is possible to determine by Hot Hydrogen Extraction (HHE) method.

In essence, the method involves heating the steel sample to the temperature of mostly below to 500°C in a furnace, whereby diffusion of the free nitrogen to the surface occurs, where the nitrogen reacts with the flowing hydrogen. The resultant ammonia is carried away by the stream of hydrogen from the furnace and is determined by titration, photometrically or using other techniques.<sup>8</sup>

## 1.4 Thermal Evolved Gas Analysis

The Thermal Evolved Gas Analysis (TEA) of the total nitrogen content in steels belongs to the common analytical procedures undertaken at metallurgical laboratories. A steel sample placed in a graphite crucible is heated to high temperatures in a resistance furnace, which is being passed through by a stream of inert carrier gas, most commonly helium. The flowing carrier gas rinses the reaction products from the furnace and carries it to a detection unit. The entire apparatus is equipped with a control process computer, which makes it possible to continuously regulate the temperature according to a predefined temperature schedule. In the course of the heating, the oxides and nitrides decompose depending on their thermodynamic stability.

Subject to the condition of a continual growth of the furnace temperature, the result of TEA is information about the total oxygen and nitrogen contents and a recorded thermo-evolution curve (hereinafter TEK) for oxygen or nitrogen. It was shown that the shape and trend of TEKs for oxygen and nitrogen depend on the chemical composition of the steels and

therefore, these may be assumed to contain encoded information on types of oxides and nitrides presented in the analysed sample. Use of TEA in the study of oxide phases in steels was discussed by Gasik and Grigorovich.<sup>9</sup> Utilization of TEA for study of oxide and nitride phases in steels describe Hocquaux and Meilland<sup>10</sup> and Matějka et al.<sup>11</sup> Determining oxygen and nitrogen content as well as recording their TEKs is a matter of several minutes. Interpreting the recorded TEKs may, however, be difficult and the results should be juxtaposed to those obtained from analyses carried out using different methods.

## 1.5 Thermodynamic Calculations

Among the software used for thermodynamic calculations belongs the Thermo-Calc software, which is based on the CALPHAD (CALculation of PHase Diagram) method, as described.<sup>12</sup>

In practice, the Thermo-Calc software is used to compute the equilibrium composition of phases in the studied materials as a function of temperature close to the thermodynamic equilibrium state. The use of Thermo-Calc in the study of nitride or carbonitride phases is demonstrated by Sopoušek et al.<sup>13, 14</sup> and André.<sup>15</sup>

The Thermo Calc calculations are based upon a model of precipitating phases ( $M_1; \dots; M_n$ ) (C,N,Va), where  $M_1$  to  $M_n$  stands for the metallic atoms deposited in the substitution subgrid of the transition carbonitride, and C, N elements are localised in the interstitial subgrid. The existence of vacancies (Va) is also considered in the thermodynamic description. There is also discussed<sup>14</sup> that the existence of vacancies could induce the deviation from the stoichiometric composition, which however tends to decrease with decreasing temperature and the share of vacancies could be already negligible.

The present paper compares two steels microalloyed with Nitrogen and Vanadium in terms of the nitride or carbonitride precipitates present. The TEA was used to assess the content of nitride or carbonitride precipitates, while the content of free (interstitially dissolved) nitrogen was determined by HHE method. The thermodynamic prediction of the equilibrium composition of the precipitating phases was carried out by Thermo-Calc software.

## 2 Experimental procedures

### 2.1 Materials

In the present paper we compare with 2 steels (hereinafter referred to as A, B) microalloyed with vanadium and nitrogen and produced at Třinecké železářny, a.s. The steels

produced were cast into 300x350 mm blooms at a continuous caster. The resultant bloom was further heated in a walking beam furnace to 1230 °C, rolled and finish-rolled into the final shape of the rails at 960-1060 °C. The chemical composition of the material under investigation is given in Table 1.

**Table 1** Chemical composition of the steels (wt.%).

Steel	C	Mn	Si	P	S	Al	V	Ti	N	O
A	0.33	1.21	0.39	0.015	0.006	0.020	0.095	0.0038	0.0210	0.0009
B	0.32	1.28	0.37	0.013	0.008	0.022	0.125	0.0035	0.0127	0.0012

The samples for the recording of TEKs for nitrogen were taken from the head of the as-rolled rails according to EN 13674. The samples were conditioned into the shape of 5 mm diameter cylinders, while the height of the cylinder was chosen in such a way as reduce the final weight of the samples to below 0.15 g. In order to determine the free nitrogen using the HHE method, the samples were prepared in the shape of thin chips with the thickness of less than 0.1 mm.

## 2.2 Methods

Total nitrogen content and recording of TEKs for nitrogen were carried out using LECO TC 436 instrument. The measurement was performed in automatic mode, the power of the furnace was linearly increased with a step  $18 \text{ W}\cdot\text{s}^{-1}$  during the analysis. The recalculation of the furnace real power to temperature is implemented in control software supplied by LECO Company.

Determination of the free nitrogen was performed by the HHE method where the sample in form of thin cuts was heated to the 420°C in a tube furnace. Loosed nitrogen reacts with the flowing hydrogen to form ammonia. The resultant ammonia was carried away by the stream of hydrogen from the furnace and determined photometrically.

## 2.3 Thermodynamic equilibrium calculations

The Thermo-Calc, Version 3 for Windows and the TCFE3 thermodynamic database with all its phases it contains were used for the thermodynamic calculation at Montan Universität Leoben in Austria.

### 3 Results and Discussion

#### 3.1 The results of TEA and HHE Method

Considering the chemical composition of steels (Table 1), it may be assumed that with both steels, the nitrogen is bound in the form of stoichiometric aluminium nitride (AlN), vanadium carbonitride (V(C, N)), and may further be present in the form of interstitial solid solution. The presence of these forms of nitrogen should then translate into the TEK for nitrogen by three peaks. Fig. 1 and Fig. 2 shows the recorded TEKs for nitrogen.

TEKs for nitrogen in steels A and B have similar patterns (Fig. 1 and Fig. 2), which imply the present of the same type of nitride and carbonitride phases in these two samples. The similarity of the curves is also apparent when comparing the temperatures at which the maximums of peaks appear. The given curves may also be divided into three regions. An apparent peak is present in each of these regions.

**Region I.** The peaks in this region belong to the nitrogen present in the steel in the form of interstitial solid solution ( $N_f$ ). Moreover, the peak belongs to the nitrogen released from non-stable vanadium carbonitrides rich in carbon could also appear in this region.

**Region II.** The maximum peaks pertaining to this region for A and B samples occur at similar temperatures (1618°C and 1620°C, respectively). The peak presented in this region corresponds to the nitrogen released from the vanadium carbonitride with a high volume fraction of nitrogen ( $N_{V(C,N)}$ ). For steel B, a superimposed peak is moreover present in this region at the temperature of 1768 °C. This peak is probably a result of the mutual overlapping of peaks corresponding to the nitrogen releases from vanadium carbonitrides at various stoichiometric C/N ratios and the associated various thermodynamic stability.

**Region III.** The maximum peaks present in this region again for both samples occur at almost the same temperatures (1850°C and 1855°C, respectively). The peaks in this region correspond to the nitrogen releases from AlN ( $N_{AlN}$ ).

The integral area under the entire TEK for nitrogen ( $S_c$ ) is proportional to the total nitrogen content in the analysed sample ( $w(N_c)$ ) and the area under the TEK for nitrogen in the selected region ( $S_i$ ) is proportional to the content of that form of nitrogen, which is present in the given region ( $w(N_i)$ ). The relative concentration of nitrogen bound to the supposed nitride phase, which is present in the  $i$ -region may then be derived from the following equation (1):

$$w(N_i) = \frac{S_i}{S_c} w(N_c) \quad (1)$$

Where:

$w(N_i)$  content of nitrogen bound to the supposed nitride phase of the  $i$ -region, wt. %,

$w(N_c)$  total nitrogen content in the analysed sample (indicated in Table 1), wt. %,

$S_i$  integral area under the TEK for nitrogen in the  $i$ -region, a.u.,

$S_c$  area under the entire TEK for nitrogen, a.u..

Table 2 gives the computed nitrogen contents that are coupled with the specific nitride phases present in the given area. The calculation was performed for the total nitrogen contents in studied steels (Table 1).

**Table 2 Contents of nitride phases ( $w(N_i)$  wt. %) for individual regions of TEK calculated from equation (1).**

Region	I	Steel A $w(N_i)$ (wt.%)	Steel B $w(N_i)$ (wt.%)
I	$N_f$	0.0015	0.0009
II	V(C,N)	0.0168	0.0092
III	AlN	0.0027	0.0026
Suma	$w(N_c)$	0.0210	0.0127

The given results (Table 2) imply that the steel sample A contains a larger volume fraction of free nitrogen and a higher volume fraction of nitrogen bound as V(C,N) compared to the contents of these elements for steel B. The volume fraction of nitrogen bound as AlN is comparable for both samples.

The HHE method was employed to determine the following contents of free nitrogen  $N_{f(HHE)}$ :

Steel A -  $N_{f(HHE)} = 0.0017$  wt.%,

Steel B -  $N_{f(HHE)} = 0.0005$  wt.%.

Using the HHE method, the content of free nitrogen in steel A was shown to be higher than that in steel B. If these values are compared with the contents obtained from the TEKs for nitrogen, it becomes clear that even this method proved the higher content of free nitrogen for steel A. The difference between the values of free nitrogen obtained from TEKs by the integration of the area under the peak in region I and by the HHE method may be explained away by the uncertainty imposed when determining the integration limit, which is used to demarcate the given region.

### 3.2 Thermodynamic Equilibrium Calculations

The Thermo-Calc software was used in order to predict, how the different total content of nitrogen in both steels affect the computed equilibrium composition of present phases. Attention was devoted especially to the vanadium carbonitride. Aluminium nitride was considered as stoichiometric composition of AlN.

The composition of the vanadium carbonitride may according to CALPHAD model be deemed to correspond to the stoichiometric compound (Ti,V)(C,N). The Ti content is however very low due to the low Ti content in both steels, though it tends to change as a function of temperature.

The computed temperature dependence of the nitrogen content in the vanadium carbonitride is given in Fig. 3. The figure clearly shows the high volume fraction of nitrogen (around 20 wt. %) at temperatures above the  $\gamma \rightarrow \alpha$  phase transformation down to the liquidus temperature. With decreasing temperature, the nitrogen content in V(C,N) carbonitride drops, while at the same time, the fraction of carbon in the phase increases. At low temperatures, the composition of the carbonitride approaches the vanadium carbide VC, with is especially the case for steel B.

The results of the thermodynamic computations imply that at temperatures around the  $\gamma \rightarrow \alpha$  phase transformation and at lower temperatures (see Fig. 3), the equilibrium content of nitrogen for steel B in the complex (Ti,V)(C,N) is low at approx. 1 wt.%, i.e. the composition approaches the pure VC with 19.05 wt.% of carbon. The nitrogen content in the complex (Ti,V)(C,N) carbonitride for steel A (Fig. 3 - left) is substantially higher compared to steel B (Fig. 3 - right), ranging around 9 wt.% (i.e. the number of carbon and nitrogen atoms is almost equal in the interstitial subgrid of the carbonitride).

## 4 Conclusion

The present paper compared two nitrogen and vanadium microalloyed steels in terms of the nitride/carbonitride phases present. Experimental methods (TEA, HHE) and thermodynamic simulation using the Thermo-Calc software were performed in order to evaluate these phases. The results obtained yield the following conclusions:

- The course of the TEKs for nitrogen, recorded for both steels under investigation, clearly show that steel A contains a higher volume fraction of nitrogen bound as vanadium carbonitride compared to the steel B in the natural relation to the total nitrogen content in steels.

- The quantity of nitrogen bound as AlN does not differ greatly for the two examined steels and corresponds to the aluminium content in steels which preferably reacts with nitrogen.
- The HHE method shows that the free nitrogen content for steel A is higher than that for steel B. The comparison of the results for free nitrogen content obtained from the application of HHE and TEK methods, shows that the results are in good agreement.
- The results of the thermodynamic calculations imply that the content of nitrogen bound as the complex (Ti,V)(C,N) carbonitride is lower for steel B. That is related to the lower phase share of the carbonitride caused by the lower total content of nitrogen in steel B. The aluminium nitride was considered to be a stoichiometric AlN compound in the thermodynamic calculations.
- The above results point to the significance of the Thermal Evolved Gas Analysis used for the determination of nitrogen forms present in nitrogen- and vanadium-microalloyed steels.

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## **List of figure captions**

**1 TEKs of nitrogen for steel A**

**2 TEKs of nitrogen for steel B**

**3 Change in the equilibrium nitrogen content (wt. %) in (Ti,V)(C,N) with temperature for steel A (Fig. 3 - left) and steel B (Fig. 3- right) computed using the Thermo-Calc software**

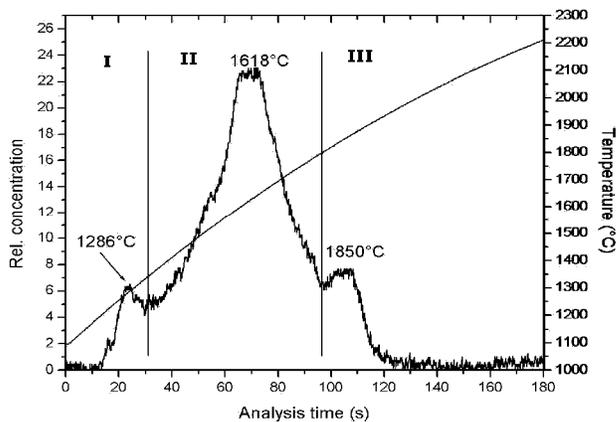


Fig. 1 TEKs of nitrogen for steel A.

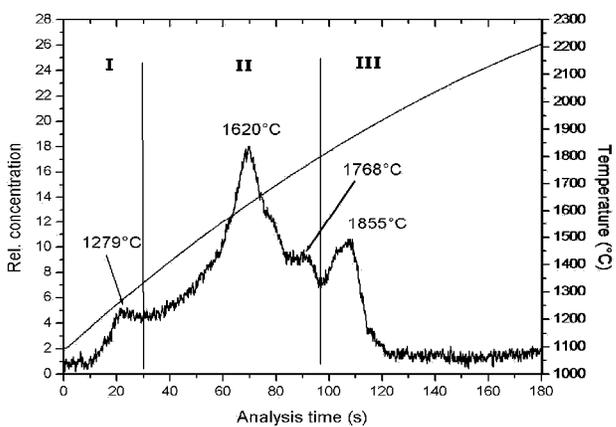


Fig. 2 TEKs of nitrogen for steel B.

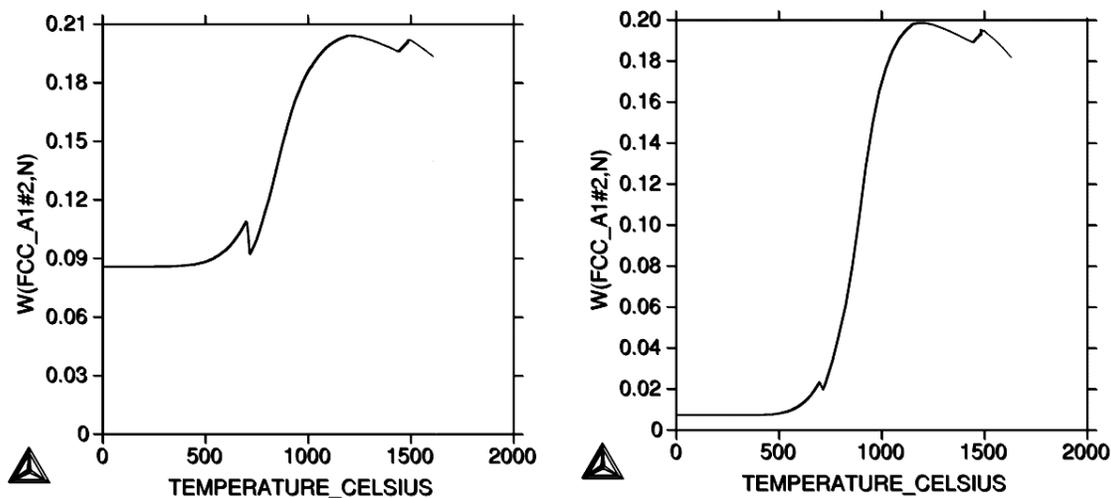


Fig. 3 Change in the equilibrium nitrogen content (wt. %) in (Ti,V)(C,N) with temperature for steel A (fig. 3 - left) and steel B (fig. 3 - right) computed using the Thermo-Calc software.