

Effect of high-temperature heating on chemical changes in M_7C_3 carbides of AISI D2 tool steel

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ABSTRACT

The paper presents the study results obtained on 16H12MF/NC11LV/D2 tool steel. The main purpose of the study was to establish the chemical composition of the coarse primary M_7C_3 carbides occurring in that steel after a standard soft annealing. The effect of high-temperature annealing in the air atmosphere was investigated. The study was limited to the decarburized layer, on the distance of about 0.4 mm from the surface, of hardened steel after annealing and austenitizing at 1150 °C in the air atmosphere for the periods of 30 and 90 minutes. It was found that the coarse primary M_7C_3 carbides of the annealed D2 tool steel differ significantly as to the contents of Cr, Mo, and V, and in the most degree to the contents of chromium and molybdenum. The average concentration of chromium rises successively with the growth of austenitizing time. On the other hand, the concentrations of molybdenum and vanadium are lower after 30 minutes of austenitizing than their concentrations in the similar carbides of the annealed steel. Prolongation of the austenitizing time up to 90 minutes results in the increase of molybdenum and vanadium contents in the coarse carbides. It was found that austenitizing of AISI D2 tool steel at the temperature of 1150 °C in the air atmosphere leads to precipitation of the second phase, brighter in the BSE_Z pictures, in relation to the matrix of carbides, with the amount and magnitude being higher with the annealing time.

Keywords: D2 tool steel; High-temperature heating; Austenitizing; Coarse primary M_7C_3 carbides; Chemical composition

1. INTRODUCTION

The studies concerning the effect of the heat treatment on the chemical composition of M_7C_3 carbides in the tool steels of type about 2 % C and 12 % Cr [1,2] have been carried out for decades by many investigators [3-7], e.g. Sato et al. [3,4], Głowacki [5,6], Kowalski [7], and with the additives of tungsten, molybdenum and vanadium by Gulajev and Sanczyk [8], Kałuża [9], Nykiel [10], Hryniewicz and Nykiel [11,12], Nykiel and Hryniewicz [13-30], Haberling and Schruff [31], Grman et al. [32]. It results from the works that the chromium contents in M_7C_3 carbides occurring in the mentioned steels under annealed state are in the range of about 43 % [3,4] up to 52 % [5,6]. The study results concerned with the effect of austenitizing conditions on the chromium behavior in M_7C_3 carbides are not in agreement [4-22]. According to Gulaev and Sanczyk [8] the weight fraction of chromium in M_7C_3 carbides

of steel of composition: 1.5 % C, 11.3 % Cr, and 0.77 % V hardened after austenitizing in temperatures 950-1150 °C does not undergo changes. Very similar conclusion was formulated by Sato et al. [3,4] in their studies of steel containing 2.25 % C and 12 % Cr hardened after austenitizing in temperatures 800-1050 °C in time 60 minutes. According to Głowacki [5,6] the chromium content in M_7C_3 carbides of NC11 steel decreases with the austenitizing temperature growth 950-1150 °C and time up to 30 min. In the softening annealed steel these carbides contain 45 % chromium.

Decrease of chromium content in M_7C_3 carbides as the function of temperature 950-1150 °C and austenitizing time up to 30 min occurs also in tool steels of type 2 % C and 12 % Cr with the additives of such elements like tungsten and vanadium [9-35]. Apart from this in these works it was also revealed that with the growth of temperature and time up to 30 min, the content of tungsten in carbides also decreases with some slight increase of vanadium. It results from Haberling and Schruff [31] also that with the increase of austenitizing temperature of EN-X155CrVMo121 steel from 1030-1080 °C the chromium content in the M_7C_3 carbides decreases along with the rise of vanadium concentration, with practically no change in molybdenum content observed.

The phenomenon of fluctuation of chemical composition in carbides during austenitizing occurs also in M_6C carbides of high speed steel [32], in $M_{23}C_6$ carbides of corrosion resistant steels [33], as well as cementite $(Fe,Cr)_3C$ carbides of bead steels [34,35].

Many investigators were dealing with the study of structure and chemical composition of chromium-iron carbides [36-49]. The main aim of this work, with the results presented herewith, was to establish the behavior of chromium, molybdenum and vanadium in M_7C_3 carbides occurring in NC11LV (160H12MF) steel austenitized at 1150 °C. The chemical composition of the carbides in these steels after softening annealing was also performed. It was also determined the austenitizing time of this steel in the air atmosphere on the chemical composition and displacement of C, Cr, Mo, and V in the big primary M_7C_3 carbides occurring in the de-carburized layer. Review of the subject literature done shows there is no elaborations concerning presented subject.

2. MATERIAL AND STUDY METHOD

The studies were performed on the NC11LV/D2 steel of chemical composition given in Table 1. These data were obtained by the method presented below.

Table 1. Chemical composition of AISI D2 tool steel (averaged of 6 samples).

Element	Composition, wt %
C	1.500
Cr	11.690
Mo	0.833
V	0.625
Mn	0.399
Si	0.325
Ni	0.238
Cu	0.080
Al	0.045
Co	0.031
S_{max}	0.030

W	0.016
P	0.016
Ti	0.06

Chemical composition with the contents of elements was determined based on the analysis of 6 samples of the softening annealed steel of different rods of diameter 14.5 mm. The rods were coming from the same heat. Chemical composition of the D2 steel was determined on the emission optical spectrometer SPECTROLAB TYPE 05 S/N 45/263. Samples for the studies were heat treated by austenitizing at 1150 °C and hardening in oil. Austenitizing annealing was performed in times 10, 30, and 90 minutes in the air atmosphere. The temperature regulation accuracy was ±5 °C.

The following studies were carried out:

- (1) the metallographic microscopic studies were performed on the microscope Neophot 2 and Epityp 2. The microsections were prepared mechanically on the abrasive papers of graininess 150-2500, using polishing by means of aqueous Al₂O₃ suspension afterwards. To reveal microstructure of the steel in the softening annealed state the microsections were etched in 4 % HNO₃ diluted with C₂H₅OH, whereas that hardened after austenitizing at 1150 °C and time of 30 min by means of a reagent of composition: 1 g picric acid, 5 ml HCl, and 100 ml C₂H₅OH;
- (2) investigation of microhardness of coarse primary carbides was done by means of Hanemann microhardness tester mph100 and the microscope Epityp 2 using load of 10 G;
- (3) the thin foils studies of samples of other steel of type type 2% C and 12% Cr with the additives of tungsten and vanadium, hardened after austenitizing at 1150 °C and time of 90 min were performed by means of a transmission electron microscope BS613 and BS540 of TESLA Co. Thin foils were prepared by using initial thinning on the abrasive papers of graininess 300-800, with electrolytic thinning performed afterwards by means of TUNEPOL apparatus of STUERS Co. 10 % HClO₄ solution in C₂H₅OH of temperature -5 °C using 40 V voltage was used for the electrolytic thinning. The structure photographs of thin foils were done at 100 kV voltage;
- (4) the volume fraction of carbides was determined by quantitative metallography, i.e. by a point/pointwise method using a network of 169 notches of symmetric distribution. Counting of a number of the network notch hits in the carbide was carried out on the microphotographs. The required/needed number of network applications/taking naps was determined from the relationship:

$$k = t_{\alpha}^2(1-P_w) \cdot \gamma^2 \cdot z \cdot P_w$$

by assuming as follows [50]:

- $\gamma = 0.1$ as an absolute error and the probability $(1-\alpha) = 0.9$, with
- $t_{\alpha}=1.645$ as the value taken from the tables of a standard distribution
- z -number of network applications
- P_w -volume fraction of carbides (determined based on the observations).

It was established that the necessary number of network applications equals 5 for the annealed D2 tool steel and 14 for the hardened steel after austenitizing at 1150 °C and time 30 min. In fact 10 and 15 network applications were used, respectively; therefore more applications were used;

- (5) the steel hardness under annealed state was determined by Brinell method, whereas the hardened steel by a Rockwell method using C scale;
- (6) the studies of surface distribution of Cr, Mo, V and C, and linear distribution of Cr, Mo, and V in the annealed steel and in decarburized layer (on the distance about 0.4 mm from the surface plane) after annealing in time of 30 and 90 minutes, respectively, were performed. They were carried out by means of French made X-ray microanalyzer SEMPROBE Su30 of CAMECA Co. equipped with two X-ray spectrometers WDS and a spectrometer EDS VOYAGER 3 of NORMAN Instruments (USA made). Investigation of surface distribution of elements were performed by means of WDS spectrometer. The accelerating voltage for electron excitation beam was $V = 15$ kV, and the beam current was $I = 15$ nA. The studies of linear displacement of elements were performed using EDS spectrometer at the voltage $V = 15$ kV, and the beam current was $I = 580$ pA;
- (7) the chemical composition studies of coarse primary carbides were performed by X-ray microanalysis method. They were carried out by means of microanalyser CAMECA S 30 equipped with 2 X-ray spectrometers with a dispersion of length wave (WDS). The 20-second measurements of intensity of characteristic X-radiation of carbon, chromium, molybdenum, and iron were performed on each selected carbide at the accelerating voltage $V = 15$ kV and the beam current $I = 20$ nA. Diamond and spectrally pure metals (chromium, molybdenum, vanadium) served for the pattern of analyzed elements. A standard/commercial correction programme, served by CAMECA Co., based on Pouchou and Pichoir model [20], was used to determine element concentrations in the studied samples. The effect of contamination of a specimen surface by carbon during the analysis was corrected by the method described in the work [31].

3. RESULTS

3. 1. Microstructure and hardness of D2 tool steel softening annealed and hardened after austenitizing at 1150 °C

The studied D2 tool steel in the annealed state has the hardness of 201 HB and the structure composed of primary M_7C_3 carbides, and the secondary ones distributed in the ferritic chromium-molybdenum-vanadium matrix (**Fig. 1**). The carbide contribution determined by the point/pointwise method equals 24.7 ± 2 % .

The shape of coarse primary carbides is usually non-regular and on the longitudinal rod cross-section some of them possess the shape close-to-rectangular placed in the direction corresponding with the direction of force action during plastic treatment. The primary carbides of smaller dimensions and the secondary carbides have the shape close-to-spheroidal. The average microhardness of the coarse carbides, determined based on the measurements of 12 carbides, equals 1384 ± 103 HV0.01.

The hardness of steel hardened after austenitizing at 1150 °C for 30 min period equals 37.9 HRC. With the increasing time up to 90 minutes it slightly rises up to 38.6 HRC. The growth of hardness after high-temperature austenitizing and longer times was noted also in other hardened this type of steels [3,5,7,8].

The matrix of the studied steel hardened after austenitizing for 10 to 90 minutes is composed of austenite with the primary carbides appearing on its background and numerous secondary carbides which did not dissolve during the austenitizing.

The steel hardened after austenitizing for 30 min contains 10.4 ± 1.2 vol % of carbides. Microhardness of coarse primary carbides in the hardened steel is higher than the microhardness of similar ones occurring in the annealed steel, e.g. the microhardness in the hardened steel after austenitizing for 30 min equals 1522 ± 39 HV0.01.

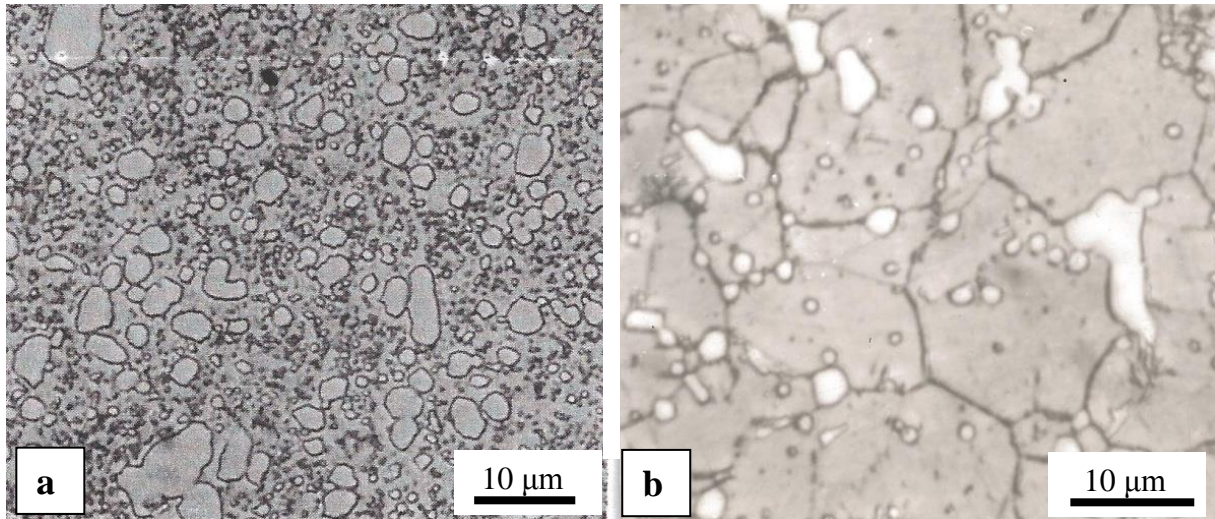


Fig. 1. Microstructure of D2 tool steel: (a) in the softening annealed state, (b) hardened after austenitizing at 1150 °C for 30 min.

The reasons of higher microhardness of carbides are the changes in chemical composition and arising in them, during cooling the steel after austenitizing annealing, different kinds of defects. The occurrence of that phenomenon was found/noticed in the studies of M_7C_3 carbides in other steel of type 2 % C and 12% Cr with the additives of tungsten (1.32 %) and vanadium (0.31 %). The studies were performed on the transmission electron microscopes TESLA BS613 and BS40 using a thin foil technique. Some examples of the occurrence of defects in M_7C_3 carbides in the higher mentioned steel hardened after austenitizing at 1150 °C for 90 minutes, are presented in **Fig. 2** (a-d).

The structure of non-carburized steel on the distance of 0.4 mm from the sample surface of steel hardened after austenitizing for 30 min in the air atmosphere is presented in **Fig. 3** a, b. The magnification of the pictures given in Fig. 3 are comparable to that one of Fig. 1b.

During annealing of the studied steel at 1150 °C for the period of 30 and 90 minutes, the decarburizing occurs on the depth of about 1 and 1.6 mm, respectively. The chemical composition of the decarburized layer on the distance of about 0.4 mm from the surface of hardened steel after austenitizing for 30 min, determined by means of emission optical spectroscope SPECTROLAB, is presented in **Table 2**.

The decarburized layer at the analyzed distance has the structure consisting of coarse primary carbides and some small amounts of secondary ones on the background of austenite and, occurring in some places, the small amounts of martensite. Coarse carbides are placed mostly on the borders of austenite grains. High dispersion of the austenite grain magnitude was found with the smallest grains occurring in the areas of increased density/frequency of primary carbides.

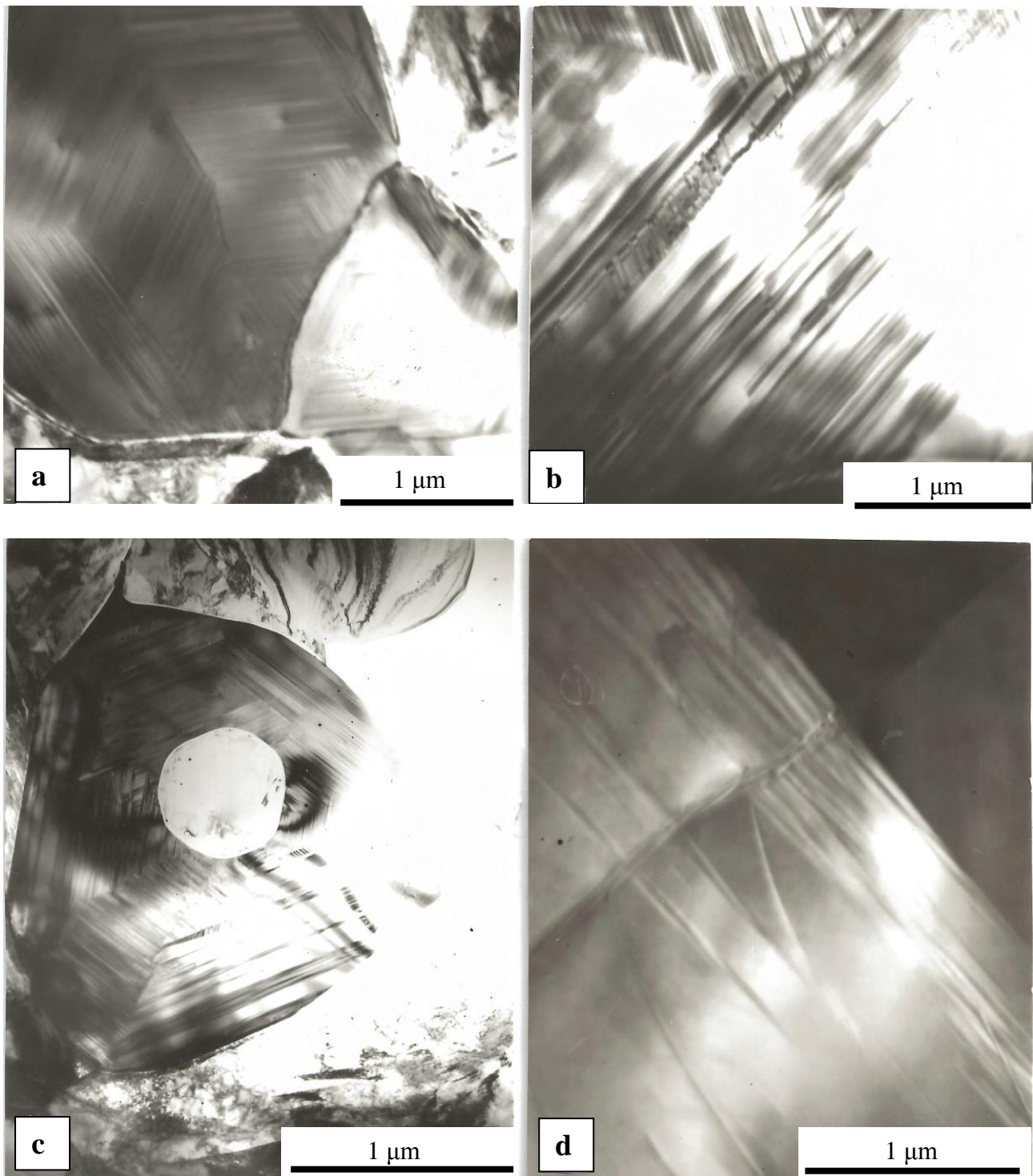


Fig. 2. Defects in M_7C_3 carbides of the D2 steel containing 1.95 % C, 1.56 % Cr, 1.32 % W, 0.31 % V hardened after austenitizing at 1150 °C for 90 minutes: a,b,c – clearly visible signs of occurrence of deformation through twinning and slide. Thin foil (a,b) magn. 20000 \times , (c) magn. 30000 \times , (d) concretion of coarse carbides with clearly marked border of concretion (stick). Deformation of carbides of strip character. Thin foil, magn. 30000 \times .

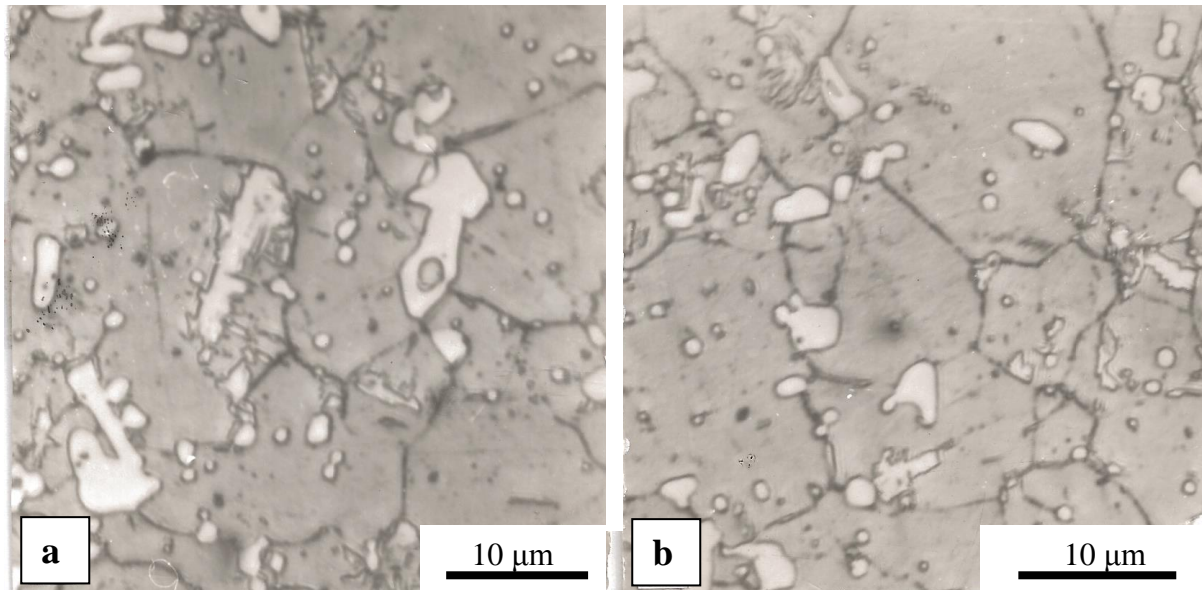


Fig. 3. Microstructure of decarburized layer of D2 steel on the distance of 0.4 mm from the sample surface of the steel hardened after austenitizing at 1150 °C for 30 min in the air atmosphere.

Table 2. Chemical composition of decarburized layer on the distance of about 0.4 mm from the surface of hardened steel after austenitizing for 30 min.

D2/ NC11LV tool steel with de- carburized layer from the surface	Concentration of elements, wt %					
	C 1.01	Cr 11.56	Mo 0.82	V 0.606	W 0.021	Mn 0.404
Si 0.322	Ni 0.251	Cu 0.090	Co 0.036	P 0.020	S _{max} 0.03	

3. 2. Surface and linear distributions of chromium, molybdenum, and vanadium in the softening annealed D2 tool steel

It results from **Figures 4** and **5** that the contents of carbon, chromium, molybdenum, and vanadium in the primary coarse M_7C_3 carbides of the annealed steel are considerably higher than those in the matrix. The results of analyses of chemical composition of coarse primary carbides in the annealed D2 tool steel obtained by the method of X-ray microanalysis are given in **Table 3**.

The results presented in Table 3 indicate that the coarse primary carbides in the annealed D2 tool steel, apart from the earlier/previous high-temperature annealing of the steel in the process of plastic treatment and several hours' annealing in the operation of soft annealing (spheroidizing), differ both as to chromium and molybdenum contents. That means the D2 tool steel heating during the higher mentioned technological operations does not cancel differences in chemical composition of coarse primary carbides, resulting from different chemical composition of dendrite branches arisen during the process of steel crystallization.

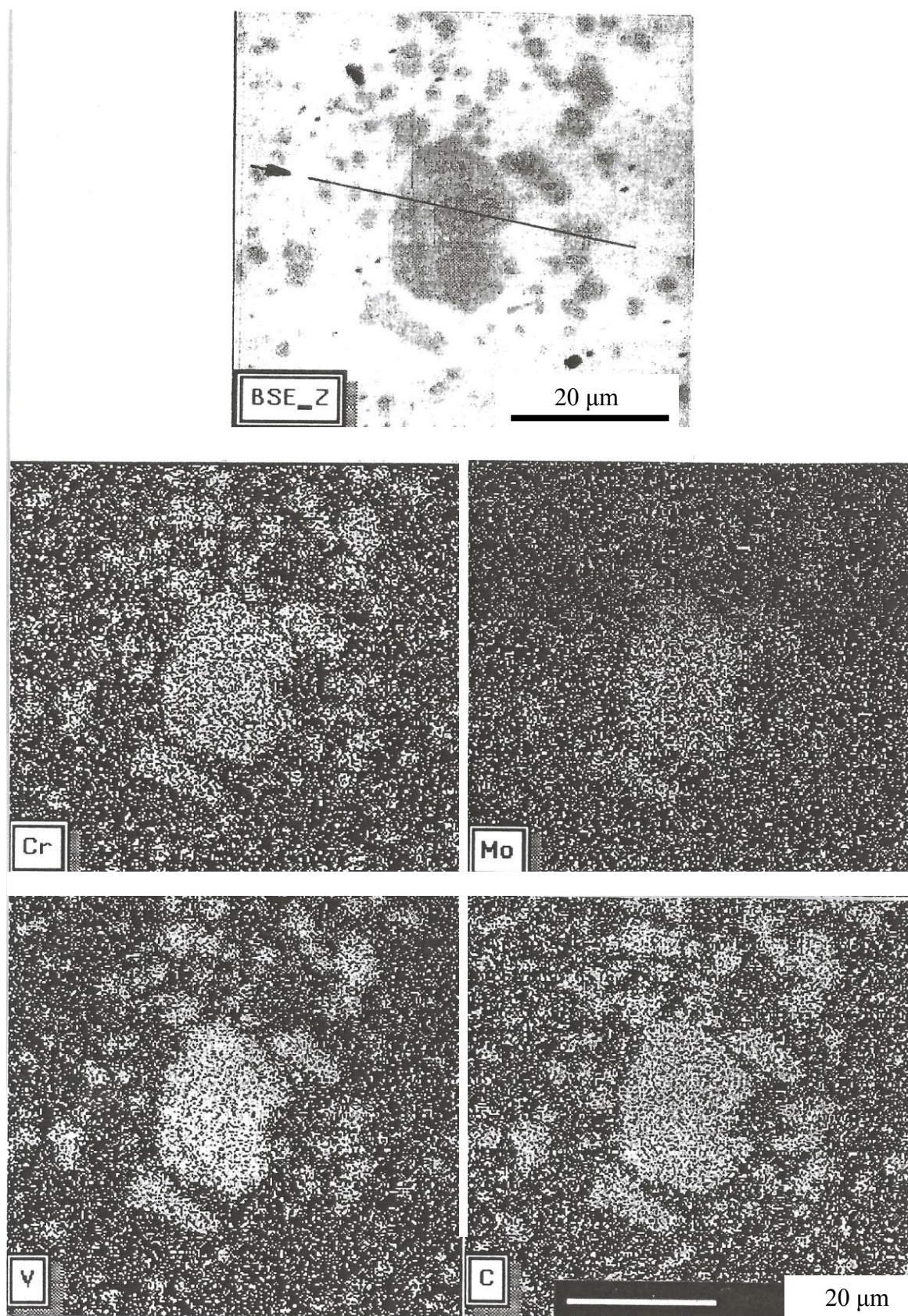


Fig. 4. Surface distribution of C, Cr, Mo, and V in the softening annealed D2 tool steel. BSE_Z – picture of differences of chemical composition of specimen with the marked trace of linear analysis.

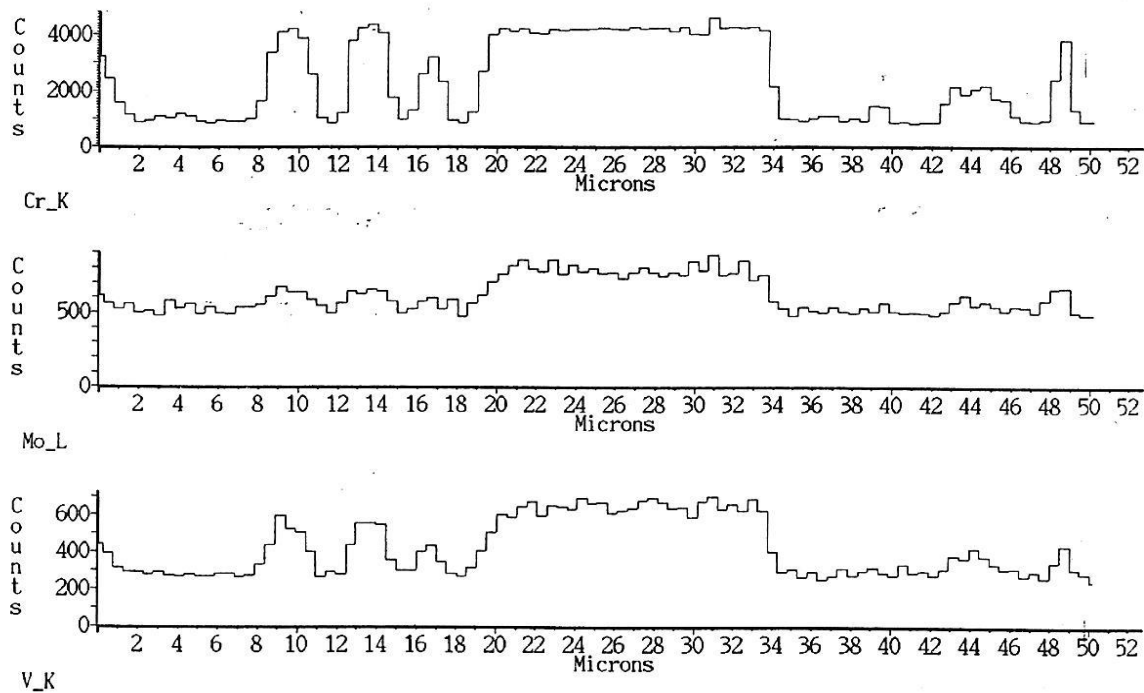


Fig. 5. Displacement of Cr, Mo, and V along the analysis line of Fig. 4.

Table 3. Results of analysis of chemical composition of coarse primary carbides in the annealed D2 tool steel.

Number of carbide	Concentration of elements, wt %				
	C	Cr	Mo	V	Fe (balance)
1	9.33	44.84	3.33	4.40	39.08
2	9.98	42.80	6.07	4.58	38.76
3	8.96	44.88	4.05	4.64	38.14
Average value	9.42 ±1.28	44.17 ±2.95	4.48 ±3.52	4.54 ±0.31	38.66 ±1.98

3. 3. Linear distributions of chromium, molybdenum, and vanadium in the decarburized layer of D2 tool steel hardened after austenitizing for 30 minutes in the air atmosphere

It results from the studies carried out using dispersed backscatter electrons that in carbides occurring in the decarburized layer of the hardened D2 tool steel after austenitizing at 1150 °C the second phase arises in the form of bright areas of irregular shape and relatively uniform displacement (**Fig. 6**). The amount of this phase increases with the increase of annealing time from 30 up to 90 minutes.

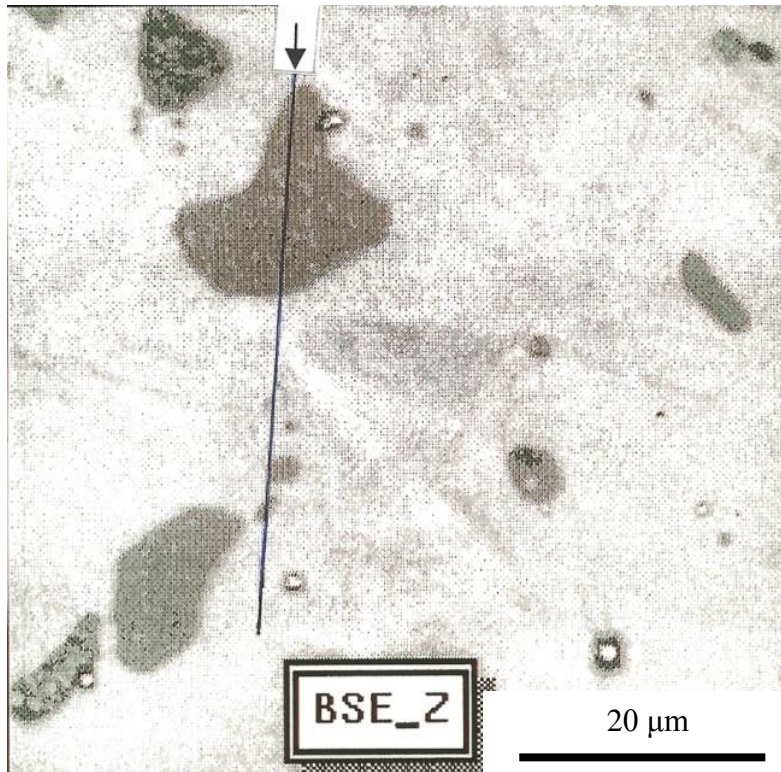


Fig. 6. The picture of differences of chemical composition in the decarburized layer of D2 tool steel hardened after austenitizing at 1150 °C through the period of 30 minutes obtained using backscatter dispersed electrons; visible dark carbides. The direction of linear analysis is marked by arrow.

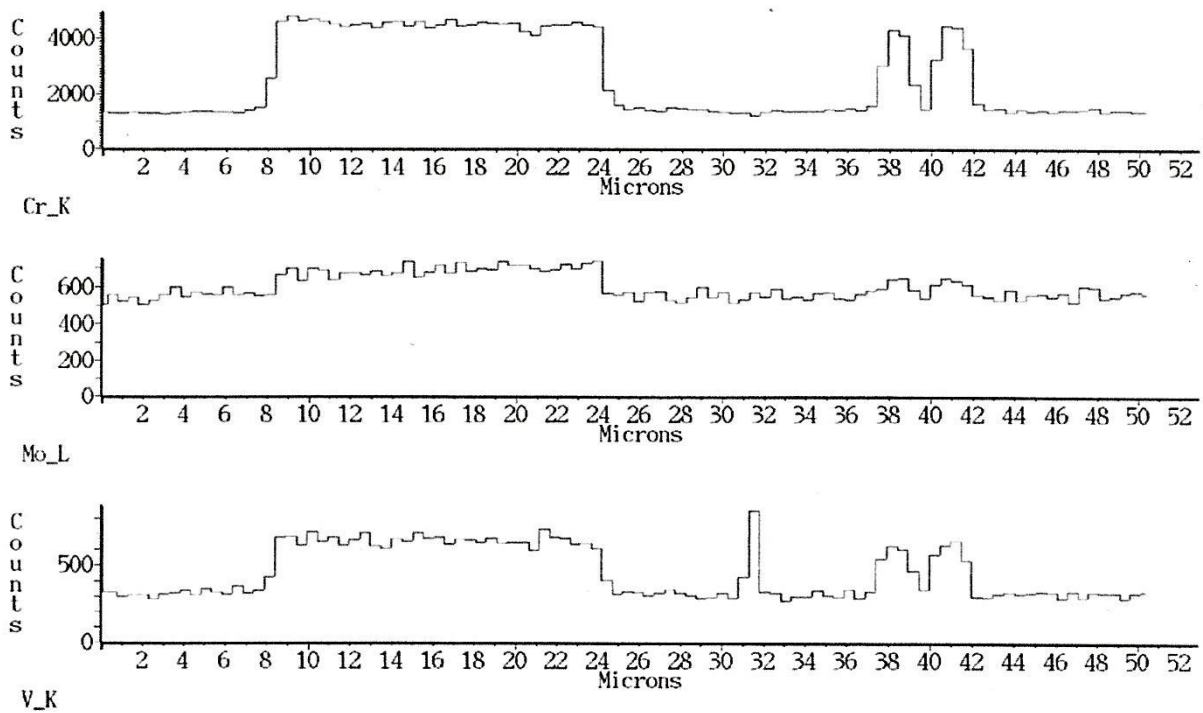


Fig. 7. Linear distribution of Cr, Mo, and V (acc. to the direction marked in Fig. 6) in the decarburized layer of D2 tool steel hardened after austenitizing at 1150 °C through the period of 30 minutes.

3. 4. Thermodynamic calculation

A thermodynamic calculation may be made using the chemical composition given in Table 1 as input (Thermo-Calc Software TCFE7 Steels/Fe-alloys database version 7 [52]). Assuming equilibrium after exposure for 30 minutes at 1150 °C, one may find the following values:

(a) Hardened steel (matrix)

Calculated volume fraction of M_7C_3 -type carbides: 9.52 %

C = 8.71 %
Cr = 48.35 %
Mo = 1.94 %
V = 4.40 %
Fe = 36.28 %

(b) Decarburized layer

Calculated volume fraction of M_7C_3 -type carbides: 4.80 %

C = 8.74 %
Cr = 51.7 %
Mo = 1.80 %
V = 5.69 %
Fe = 31.78 %

These calculated values are close to those obtained from the experiments except by deviations in Mo and Cr contents; the probable reason might be the accuracy of TEM-EDS measurements and/or because equilibrium was not reached for 30 min. Further research are needed to reveal the fluctuations in chemical composition of coarse M_7C_3 carbides.

4. CONCLUSIONS

Based on the studies carried out the following conclusions may be formulated:

1. Present in the soft annealed D2 tool steel the coarse primary M_7C_3 carbides vary as to the contents of chromium, molybdenum, vanadium and iron. The average chemical composition of the coarse carbides is as follows: C = 9.42 ± 1.28 wt %, Cr = 44.17 ± 2.95 wt %, Mo = 4.48 ± 3.52 wt %, V = 4.54 ± 0.31 wt %, Fe(balance) = 37.39 wt %.
2. Austenitizing of D2 tool steel at 1150 °C in the air atmosphere leads to precipitation of the second phase (brighter in the BSE_Z pictures in relation to the carbide matrix) in the carbides of which the amount rises with the annealing time.
3. The concentration of chromium in the coarse primary carbides, occurring in the decarburized layer successively rises with the rise of austenitizing time. After 90 minutes of austenitizing at 1150 °C the content of chromium in the coarse carbides occurring in the analyzed zone of the decarburized layer is of 4.51 % higher than the content of this component in the similar carbides of the annealed steel. Molybdenum and vanadium behave slightly different than chromium in the coarse carbides. With the growth of austenitizing time up to 30 minutes the concentration of molybdenum and vanadium decreases. After 90 minutes of austenitizing the per cent fraction of molybdenum in the coarse primary carbides occurring in the analyzed zone of decarburized layer is

lower of 1.84 %, and vanadium of 0.52 %, than their contents in carbides of the annealed steel.

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References

- [1] Metals Handbook, 10th Edition, Vol. 1, Properties and Selection: Irons, Steels, and High-Performance Alloys, ASM International, Materials Park, OH 44073, 1990.
- [2] M. Blicharski, Wstęp do inżynierii materiałowej. Stal, WNT, Warszawa, 2004.
- [3] T. Sato, Y. Honda, *Journal of the Iron and Steel Institute of Japan = Tetsu to Hagane*, 41 (11) (1955) 1188.
- [4] T. Sato, Y. Honda, *Journal of the Iron and Steel Institute of Japan = Tetsu to Hagane*, 44 (5) (1958) 565.
- [5] Z. Głowacki, PhD Thesis, Politechnika Poznańska, Poznań 1956.
- [6] Z. Głowacki, The studies over carbides in chromium steels (in Polish). 5th PAN Seminar of Metallurgy Committee, Zakopane 25-27 April 1968, pp. 1-17.
- [7] W. Kowalski, *Prace Instytutu Mechaniki Precyzyjnej (Transactions of IMP) (in Polish)*, 14(8) (1966) 1.
- [8] A.P. Gulajev, J.E. SANCZYK, *Zhurn. Techn. Fiz.* 22(11) (1952) 1718.
- [9] K. Kałuża, *PhD Thesis*, Politechnika Poznańska, Poznań, 1979.
- [10] T. Nykiel, *PhD Thesis*, Politechnika Poznańska, Poznań, 1982.
- [11] T. Hryniewicz, T. Nykiel, *Inżynieria Materiałowa* 1 (2000) 32-35.
- [12] T. Hryniewicz, T. Nykiel, Proc. of the METAL 2001 10th International Metallurgical and Materials Conference, 15-17 May, 2001, Hotel ATOM, Ostrava, Czech Republic; Symposium C: Paper no. 190.
- [13] T. Nykiel, T. Hryniewicz, Proc. 6th Intern. Seminar IFHT, Kyongju TEMF Hotel, Kyongju, Korea, October 15-18, 1997, pp. 222-229.
- [14] T. Nykiel, T. Hryniewicz,, Proc. of the 6th Intern. Seminar IFHT, Kyongju TEMF Hotel, 15-18 October, Korea, 1997, pp. 238-245.
- [15] T. Nykiel, T. Hryniewicz,, Proc. of the 11th Congress of the International Federation for Heat Treatment and Surface Engineering, Florence, Italy, 19-21 October, 1998, 116, pp.87-96.
- [16] T. Nykiel, T. Hryniewicz, *Metallurgical and Materials Transactions A*, 31A (2000) 2661-2665.
- [17] T. Nykiel, T. Hryniewicz,, Proc. of the METAL 2001 10th International Metallurgical and Materials Conference, 15-17 May, 2001, Hotel ATOM, Ostrava, Czech Republic; Symposium C: Paper no. 191.

- [18] T. Nykiel, T. Hryniewicz, L. Lemiesiewicz, Mater. II Pomorskiej Konferencji Naukowej "Inżynieria Materiałowa 2001", Gdańsk-Sobieszewo, 31.05-1.06.2001, 167-173.
- [19] T. Nykiel, T. Hryniewicz, Proc. of 11th International Metallurgical & Materials Conference METAL 2002, 20-22 May 2003, Hradec nad Moravici, Czech Republic, Symp. C, (Steel Products Properties).
- [20] T. Nykiel, T. Hryniewicz, Proc. of 11th International Metallurgical & Materials Conference METAL 2002, 14-16 May 2002, Hradec nad Moravici, Czech Republic, Symp. C, p. 54.
- [21] T. Nykiel, T. Hryniewicz, Proc. of 11th International Metallurgical & Materials Conference METAL 2002, 14-16 May 2002, Hradec nad Moravici, Czech Republic, Symp. C, p. 56.
- [22] T. Nykiel, T. Hryniewicz, *Materiały i Technologie*, ed. WM Politechniki Gdańskiej, 1(1) (2003) 125-130.
- [23] T. Nykiel, T. Hryniewicz, *Advances in Materials Science* 4(2) (2003) 49-60.
- [24] T. Nykiel, T. Hryniewicz, *Advances in Materials Science* 4(2) (2003) 61-70.
- [25] T. Nykiel, T. Hryniewicz, Proc. of 17th International Metallurgical & Materials Conference METAL 2008, 13-15 May 2008, Hradec nad Moravici, Czech Republic, Symp. C, p. 24.
- [26] T. Nykiel, T. Hryniewicz, Proc. of 18th International Metallurgical & Materials Conference METAL 2009, 19-21 May 2009, Hradec nad Moravici, Czech Republic, Symp. C, p. 10.
- [27] T. Nykiel, T. Hryniewicz, Proc. of 18th International Metallurgical & Materials Conference METAL 2009, 19-21 May 2009, Hradec nad Moravici, Czech Republic, Symp. C, p. 11.
- [28] T. Nykiel, T. Hryniewicz, *Trans. Indian Inst. Met.* 65(1) (2012) 37-48.
- [29] T. Nykiel, T. Hryniewicz, *Trans. Indian Inst. Met.* 65(2) (2012) 219-230.
- [30] T. Nykiel, T. Hryniewicz, *Journal of Materials Engineering and Performance.* 23(6) (2014) 2050-2054.
- [31] E. Haberling, I. Schruoff, *Thyssen Edelst. Techn. Ber.* 13(1) (1987) 64.
- [32] D. Grman, N. Klantschi, C. Solenthaler, *Material und Technik* 4 (1988) 81.
- [33] Z. Bojarski, *Prace Instytutu Hutnictwa* (in Polish), 12 (1960) 262.
- [34] Z. Głowacki, H. Leda, *Zeszyty Naukowe Politechniki Poznańskiej* (Transactions of PP) (in Polish), 5(37) (1966) 181.
- [35] Z. Głowacki, A. Barbacki, *Zeszyty Naukowe Politechniki Poznańskiej* (Transactions of PP) (in Polish), 6(33) (1965) 133.
- [36] J.L. Pouchou, F. Pichoir, *La Recherches Aerospatiale*, 5 (1984) 13.
- [37] T.M. Breunig, F.J. Worzala, Dynamic fracture toughness characteristics of D2 tool steel, Proc. of the 6th Intl. Congress on Heat Treatment and Surface Engineering, Chicago, 28-30 Sept. 1988, pp. 207-211.
- [38] S.D. Carpenter, D. Carpenter, *Materials Letters* 57 (2003) 4456.

- [39] S.D. Carpenter, D. Carpenter, *Materials Letters* 57 (2003) 4460.
- [40] S.D. Carpenter, D. Carpenter, J.T.H. Pearce, *J. Alloys and Compounds* 494 (2010) 245.
- [41] F. Ernst, D. Li, H. Kahn, G.M. Michal, A.H. Heuer, *Acta Materialia* 59 (2011) 2268.
- [42] M.J. Monteiro, F.C. Rizzo, *Mater. Sci. Forum* 522-523 (2005) 171.
- [43] M. Palcut, V. Vach, R. Cicka, J. Janovec, *Archives of Metallurgy and Materials*, 53(4) (2008) 1157.
- [44] Y. Zhang, G. Zong, K. Shui, M. He, *Heat Treatment of Metals* 10 (2010) 44.
- [45] P. Bała, *Archives of Metallurgy and Materials* 54(2) (2009) 491.
- [46] Molinari, M. Pellizzari, A. Biggi, G. Corbo, A. Tremea, Proc. 6th Intern. Tooling Conference, 2002, [Karlstad University, 10-13 September 2002]. Vol. 2, ed. Jens Bergström, 33_437_452_pdf_66272.
- [47] A.K. Sinha, *Physical metallurgy handbook*, The McGraw-Hill Companies, Inc., 2003.
- [48] L. Zhou, D. Sun, C.-S. Liu, Q. Wu, *J. Iron and Steel Research Intern.* 13(6) (2006) 49-52.
- [49] F. Ernst, D. Li, H. Kahn, G.M. Michal, A.H. Heuer, *Acta Materialia* 59 (2011) 2268-2276.
- [50] J. Ryś, *Wstęp do metalografii ilościowej* (Introduction to quantitative metallurgy; in Polish), ed. by Biblioteka Fizyki Metali, Wydawnictwo Śląsk, Katowice 1970.
- [51] K. Sikorski, Przegląd metod korekcyjnych w ilościowej mikroanalizie rentgenowskiej próbek litych (Review of corrections methods in X-ray quantitative analysis of solid samples), in *Podstawy ilościowej mikroanalizy rentgenowskiej* (in Polish), ed. by A. Szummer, WNT, Warszawa, 1994, pp. 140-166.
- [52] Thermo-Calc Software TCFE7 Steels/Fe-alloys database version 7, <http://www.thermocalc.com>, 2012, http://web.access.rwth-aachen.de/THERMOCALC/proceedings/proceedings2012/2012_Henrik_Larsson.pdf

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