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FLUCTUATIONS IN CHEMICAL COMPOSITION OF M_7C_3 CARBIDES IN THE SOFT ANNEALED NC11LV/D2 STEEL

ABSTRACT

The paper presents the study results on chemical composition of the coarse primary M_7C_3 carbides occurring in the soft annealed NC11LV/D2 tool steel consisting of: 1.53% C; 11.65% Cr; 0.01% W; 0.81% Mo; 0.068% V; (balance iron plus admixtures), used for cold operation. The microanalyzer of type SEMPROBE Su-30, French made by CAMECA Co., equipped with two WDS X-ray spectrometers and an EDS VOYAGER 3 100, NORAN Instruments Co., made in USA.
It was found that out of the three alloying elements occurring in the big carbides of the annealed NC11LV/D2 steel, i.e. Cr, Mo, and V, the chromium appears to be the most uniformly distributed. The big carbides vary concerning C, Cr, Mo, V; the greatest differentiation degree of the contents of Mo and Cr, and the least – of vanadium. The average chemical composition of the big/coarse carbides is as follows: C = 9.42±1.28%; Cr = 44.17±2.95%; Mo = 4.48±3.52%; V = 4.53±0.31%; balance Fe.

Key words: *D2 tool steel, primary carbides M_7C_3, carbides distribution, chemical composition, chromium distribution*

INTRODUCTION

The studies concerning the effect of the heat treatment on the chemical composition of carbides in the tool steels of type about 2% C and 12% Cr were carried out by Sato et al. [1], Głowacki [2], Kowalski [3], and with the additives of tungsten, molybdenum and vanadium - Kałuża [4], Nykiel and Hryniewicz [5,6], Haberling and Schruff [7], Grman et al. [8]. 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% [1] up to 52% [3]. According to Staub et al. [9] the molybdenum and vanadium dissolve in M_7C_3 carbides to 0.055% and 0.16%, respectively. There is lack of the data concerning the dissolution of tungsten; it is usually stated as very little. That finding has not been confirmed by the determination results of tungsten concentration in M_7C_3 carbides for two D3 tool steels coming from different heats/melts [4,5]. In the M_7C_3 carbides occurring in these steels under annealed state the tungsten concentration equals about 4.3% and the vanadium – about 1.1%. It should be noticed that the trace amounts of $M_{23}C_7$ carbides occur in these steels under annealed state; that may appear the real tungsten content in the M_7C_3 carbides to be a little different, i.e. less than that.
There are many sources available concerning behaviour of M_7C_3 carbides in steels [10-16]. Prolonged low-temperature gas-phase carburization of AISI 316L-type austenitic stainless steel can cause intragranular precipitation of the carbide M_7C_3 (M: randomly dispersed Fe, Cr,

Ni); the effect was observed by Ernst et al. [16] . Effect of chromium content on the oxidation behaviour of high-speed steels under dry and moist air environments was studied by Monteiro and Rizzo [17]. Compositional changes in carbide M_7C_3 upon annealing and the effect of Cr content on microstructure and properties of medium-alloy high carbon tool and die steel were studied by Palcut et al. [18], and Zhang et al. [19], respectively. Kinetics of phase transformations during tempering of tool steels with different carbon content was studied by Bała [20]. An interesting study on primary carbides behaviour was delivered by Molinari et al. [21]. They found that whilst the ferrous matrix of spincast HSS used in hot rolling oxidizes homogeneously, carbides have a different oxidation behaviour, whereas M_7C_3 carbides do not oxidize at all.

In the annealed X155CrMoV121 steel the M_7C_3 carbides contain about 52.5% Cr; 5.5% V; 1.9% Mo, and about 0.4% Mn (they are the values acquired from the diagram) [7]. According to Grman et al. [8], in the steel containing 1.95% C; 0.16% Mo; and 0.19% W, the M_7C_3 carbides contain 8.7% C; 50.2% Cr; 40.7% Fe, and 0.4% Mo. Basics of quantitative analysis are given in [22,23], whereas recent experimental study with D2 tool steel are concerned mainly on residual stress evolution in the surface layer [24], chip formation, its morphology and the quality improvement of specific cutting processes [25, 26].

The aim of the work, with the results presented in the paper, was to:

(a) determine the contents of C, Cr, Fe, Mo, and V in the coarse primary M_7C_3 carbides occurring in the annealed NC11LV/D2 steel,

(b) find out if the big/coarse M_7C_3 carbides differ with the contents of the mentioned elements in an essential degree.

The authors assume the present results may be useful in the studies concerned with the adhesion and durability/stability of the super-hard films deposited on the working surfaces of tools made of NC11LV/D2 steel.

MATERIAL AND STUDY METHOD

The studies were carried out on the NC11LV/D2 steel. Chemical composition of the steel is given in Table 1.

***Table 1**. Chemical composition, wt.% (averaged of 6 samples)*

Material				Composition			
NC11LV steel of type 160H12MF	C 1.500	Cr 11.690	Mo 0.833	V 0.625	W 0.016	Ti 0.006	Mn 0.399
	Si 0.325	Ni 0.238	Cu 0.08	Co 0.031	Al 0.045	P 0.016	S_{max} 0.03

On the steel samples after annealing the following studies were carried out:

(1) chemical composition studies carried out on emission optical specterometer SPECTROLAB TYPE 05 S/N 45/263. The average chemical composition was calculated on the basis of analysis of 6 samples,

(2) investigation of the steel hardness and microhardness of coarse carbides. Hardness of the annealed steel was determined by the Brinell method. Measurements of microhardness of carbides was done by means of Hanemann microhardness tester mph100 and the microscope Epityp 2 using load of 10 G,

(3) The metallographic microscopic studies were performed on the microscope Neophot 2. To reveal the structure of the steel under the soft annealed state the specimens/microsections were etched in 4% HNO_3 diluted with C_2H_5OH,

(4) The surface distribution studies of C, Cr, Mo, and V, and linear distributions of Cr, Mo, V together with the chemical composition of big/coarse primary carbides were done by means of microanalyzer SEMPROBE Su-30, French made by CAMECA Co., equipped with two WDS X-ray spectrometers and an EDS VOYAGER 3 100, NORAN Instruments Co., made in USA.

STUDY RESULTS

Microscopic structure and hardness of the soft annealed steel

The studied NC11LV (160H12MF) steel in the annealed state has the hardness of 201 HB and the structure consisting with M_7C_3 primary and secondary carbides displaced in the chromium-molybdenum-vanadium ferrite matrix (Fig. 1).

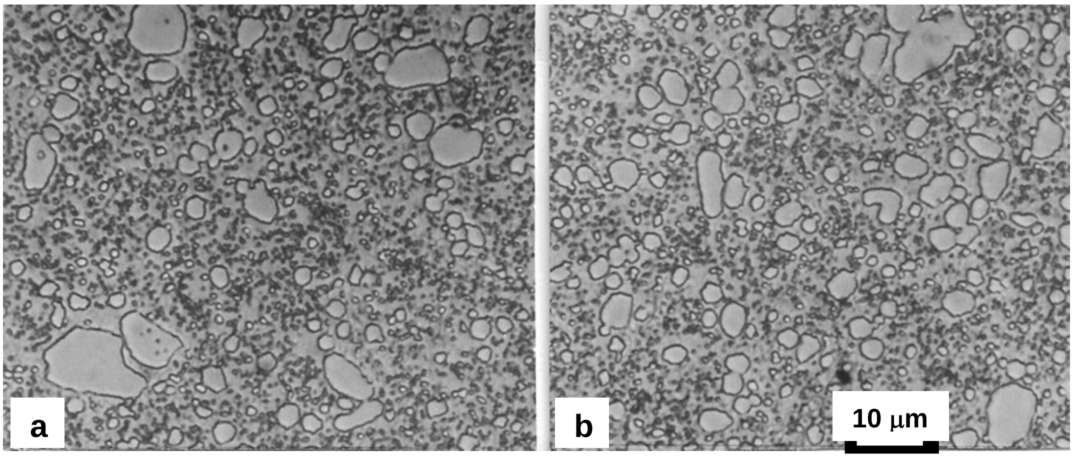

Fig. 1. Microstructure of the soft annealed NC11LV steel: (a) typical structure, (b) segregation area of the primary carbides

The shape of coarse primary carbides is mostly irregular and on the longitudinal microsection of rods some of them have the shape approaching rectangles positioned in the direction consistent with the direction of maximum forces acting during plastic working. The primary carbides of lower dimensions and the secondary carbides possess spheroidal shape or approaching that shape. The average microhardness of the coarse carbides determined, based on the measurements of 12 carbides, equals 1384±103 $HV_{0.01}$.

Study of surface (C, Cr, Mo, V) and linear (Cr, Mo, V) distributions of elements in the NC11LV annealed steel

The studies were carried out by means of WDS spectrometer. The voltage accelerating exciting electron beam was V = 15 kV and the beam current I = 15 nA. The surface distribution of C, Cr, Mo and V in the annealed NC11LV steel has been presented in **Fig. 2**.

It results from the surface distributions that, apart from carbon and chromium, vanadium reveals the high tendency to concentrate in the coarse primary carbides with molybdenum revealing some lower level.

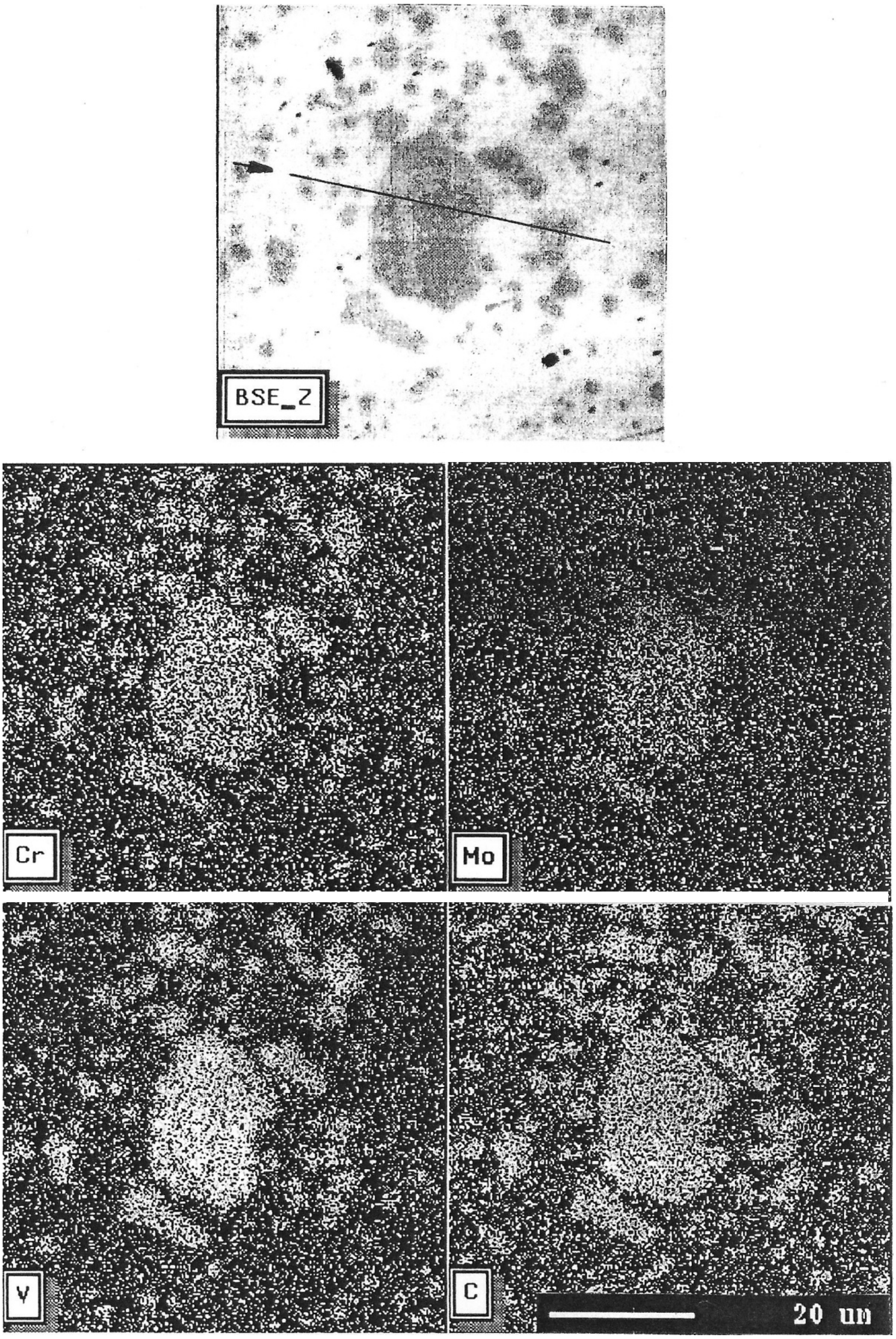

Fig. 2. Surface distributions of C, Cr, Mo and V in the soft annealed NC11LV steel. BSE_Z – image of differences in chemical composition with the marked path/line of linear analysis

The studies of linear distribution of elements were performed by means of EDS spectrometer at the voltage $V = 15$ kV and the beam current $I = 580$ pA. The analysis path/line for the annealed sample of NC11LV steel is presented in Fig. 2, whereas the linear distribution of Cr, Mo, and V is given in Fig. 3.

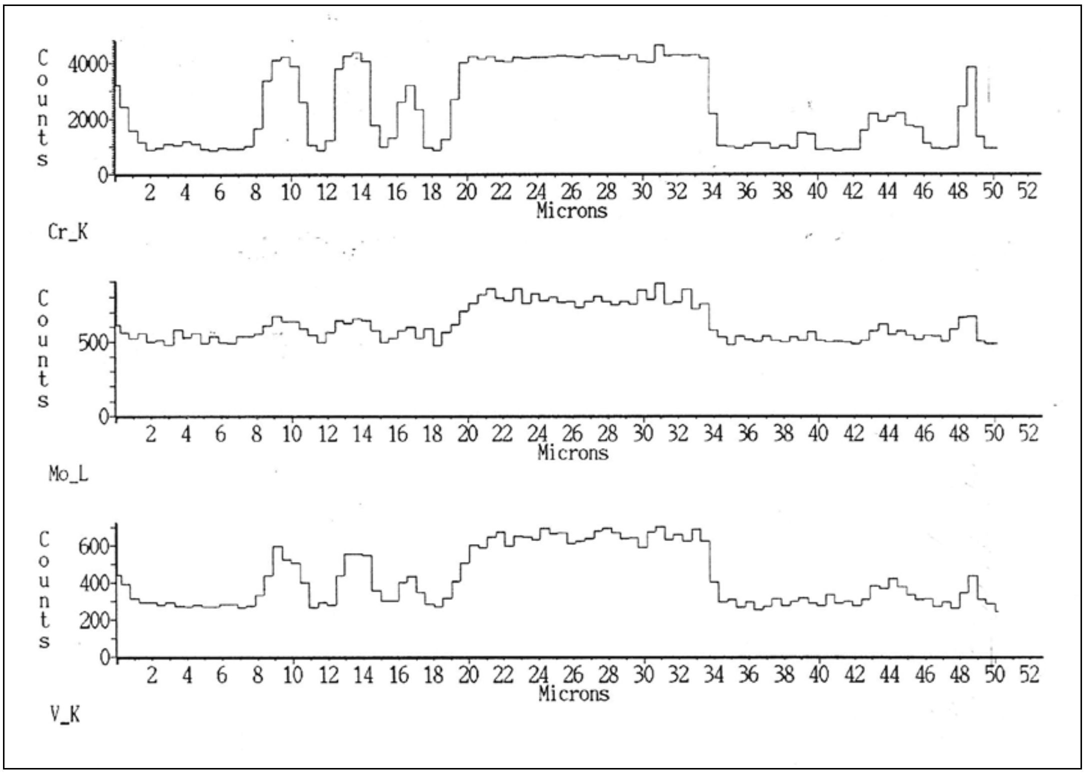

Fig. 3. Distribution of Cr, Mo, and V along the analysis line marked in Fig. 2

The studies of the linear distribution confirm the high concentration of chromium and vanadium in the coarse primary carbides with the chromium contents being comparable both in carbides of bigger and smaller dimensions. However, molybdenum does not segregate in the coarse carbides so clearly as chromium and vanadium do. The obtained linear distributions indicate also that out of the three alloying elements occurring in the primary carbides the most uniform is the chromium distribution with the next lower ones being molybdenum and vanadium.

The studies of chemical composition of the coarse primary carbides were performed by means of WDS spectrometers. In view of reducing the volume of the analyzed material, the voltage accelerating the exciting electron beam was limited down to the value of $V = 12$ kV and the increased beam current up to $I = 20$ nA with the aim to increase the measurement accuracy. Spectrally pure elements of Cr, Mo, and V served for the standards. Diamond was the standard for carbon. Correction to the measurement results was carried out by means of a correction programme of CAMECA Co., having application to the samples containing light elements [12,13,14]. The analyses of three different carbides were performed on the sample. Due to the non-homogeneous carbides composition the sum of concentrations of the elements slightly deviates from 100%. The chemical composition of the coarse primary carbides determined by means of the X-ray SEMPROBE Su-2 microanalyzer using a point method is presented in Table 2.

The obtained results indicate (Table 2) that the coarse primary carbides in the annealed NC11LV steel, in spite of the earlier high-temperature annealing of steel in the process of plastic treatment and several-hour annealing in the process of soft spheroidal annealing, are

Table 2. *Results of the chemical analysis of the coarse primary carbides occurring in the annealed NC11LV steel*

Analysis site	Element concentration, wt.%				
	C	V	Fe	Mo	Cr
1	9.33	4.40	39.08	3.33	44.84
2	9.98	4.58	38.76	6.07	42.80
3	8.96	4.64	38.14	4.05	44.88
Average value	9.42	4.54	38.66	4.48	44.17

not homogeneous concerning the chemical composition. These carbides differ in the highest degree in case of the molybdenum content, then also carbon and chromium, whereas the differences in the vanadium contents are insignificant and in the analyzed carbides this difference equals 0.24%. That means the annealing of the steel during the higher mentioned technological processes does not annihilate the differences in the chemical composition of coarse primary carbides resulting from the different chemical composition of the dendrite branches arisen in the process of crystallization.

CONCLUSIONS

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

(1) Occurring in the annealed NC11LV steel the coarse primary M_7C_3 carbides vary as to the contents of C, Cr, Mo, and V; in the highest degree with Mo and Cr contents, and in the lowest – with vanadium content. The chemical composition of the coarse carbides was found to be as follows: C = 9.42±1.28%; Cr = 44.17±2.95%; Mo = 4.48±3.52%; V = 4.53±0.31%; balance Fe.

(2) In the M_7C_3 carbides of big dimensions out of three alloying elements, i.e. Cr, Mo, and V, occurring in them and constituting the structure, the chromium distribution is the most uniform.

Of particular note are the conditions for the micro beam analysis of the carbide composition. Our findings, indicating that chromium is uniformly distributed whereas molybdenum showed worst uniformity, have been confirmed also concerning the results obtained for other steel alloys, with the supporting data given in [13,17-21].

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