U.P.B. Sci. Bull., Series B, Vol. 69, No. 1, 2007 ISSN 1454-2331

THE QUATERNARY CARBIDES IN LEDEBURITIC STEELS

V. I. POPESCU [1]

S-au realizat cercetări experimentale, în condiții de uzină şi laborator, în vederea stabilirii mecanismului de omogenizare a structurii oțelurilor ledeburitice şi de formare a carburilor quaternare.

S-a stabilit că omogenizarea structurii oțelurilor ledeburitice, printre care şi a oțelurilor rapide, se produce prin difuzia elementelor de aliere din carburile primare în masa metalică de bază a oțelurilor şi nu prin sfărâmarea acestor carburi în timpul deformării plastice. De asemenea, s-a mai stabilit că o parte din elementele de aliere care prin difuzie trec din carburile primare în austenită contribuie la mărirea concentrației acesteia, iar restul formează o nouă generație de carburi, numite ***carburi quaternare****.*

Experimental researches have been performed in laboratory and factory conditions, for establishing the homogenization mechanism of ledeburitic steels structure and the formation mechanism of quaternary carbides.

It was established that the homogenization of ledeburitic steels structure, including the high speed steels, is produced by the diffusion of the alloying elements from the primary carbides in the metallic matrix of the steels and not by crushing these carbides during the plastic deformation. It was also established that part of the alloying elements, which pass by diffusion from the primary carbides in austenite, contribute to increasing its concentration, and the rest of the elements forms a new generation of carbides, called ***quaternary carbides****.*

Keywords: hot plastic deformation, diffusion, quaternary carbides, structure homogenisation.

1. Introduction

The elucidation of the mechanism by which the homogenization of the structure of ledeburitic steels is produced, among which the high speed steels, has been the subject of numerous researches. Despite the efforts which have been done, this mechanism is still unsufficiently known for the ledeburitic steels and particulary for the high speed steels.

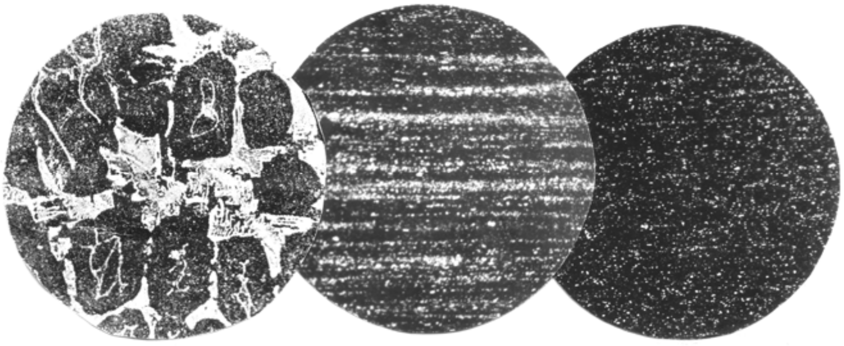
To make clear how dramatic is the structural homogenisation in ledeburitic steels the microstructure of the high speed steel Rp3 (which is equivalent with W1’3355 after DIN standard or T1 after AISI standard) is compared in Fig. 1 for the as cast condition and after partial or complete homogenisation by hot forging

---

[1] Prof., Dept.of Materials Processing and Ecometallurgy, University “Politehnica” of Bucharest

with different reduction ratios. In this case, as well as in the following, the reduction ratio was calculated with the relation $C = A_0 / A_1$, where A_0 represents the ingot cross section area, and A_1 is the cross section area after forging.

Fig. 1 shows that after the forging with C=8.0 the homogenisation processes of the Rp3 steel structure are in incipient state, and at C= 20.0 they are in the final state [1].



(a) (b) (c)

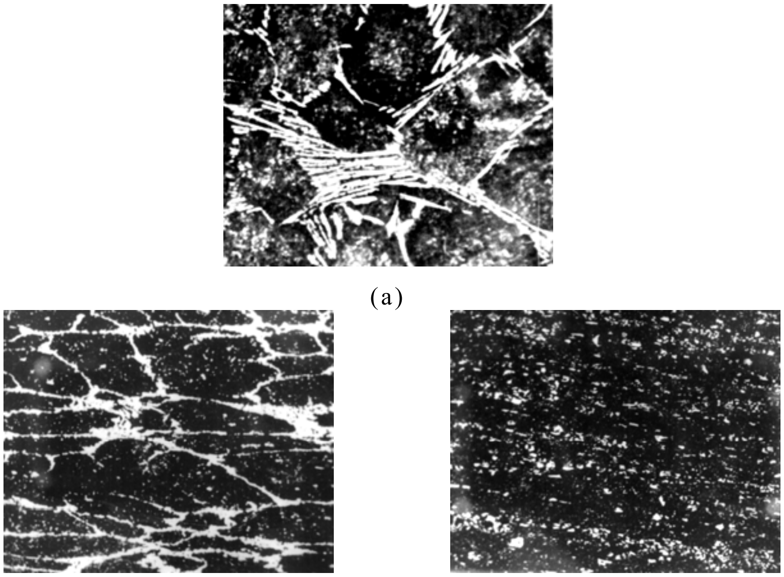
Fig. 1. Optical micrographs of high speed steel Rp3 (Nital etching, x300): (a) as cast; (b) forged with C=8.0 ; (c) forged with C=20.0 .

Starting from the fact that the high speed steels structure homogenization is produced only by hot plastic deformation and not by heat treatments, in the majority of the publications in the speciality literature [2-6] a.o., it is considered that the homogenization of these steels structure is achieved by breaking the primary carbides, during the plastic deformation, and their dispersal in austenite. Such a mechanism that would unavoidably create cracks and microcracks that act as stress raisers is difficult to be associated with the well known improvement in the mechanical and technological properties of high speed steels induced by their structure homogenisation.

2. Experimental

To elucidate the homogenization mechanism of ledeburitic class steels structure, an ingot of one ton mass consisting of high speed steel Rp5 (Romanian standard), having the following chemical composition: 0.87% C, 0.29% Mn, 0.37% Si, 4.24% Cr, 5.0% Mo, 6.73% W and 1.88% V, [7], was forged in steps with reduction ratios from 2.0 to 16.0. The Rp5 steel is equivalent with W1'3343 after DIN standard or M2 after AISI standard, including other steel marks with the same composition.

The microstructure of the investigated steel, before and after forging with different reduction ratios, is presented in Fig. 2.



(a)

(b) (c)

Fig. 2. Optical micrographs of Rp5 steel (Nital etching, x 341):
(a) as cast; (b) forged with C = 4.0; (c) forged with C = 8.0 .

The distribution and concentration of the alloying elements, in the ingot and in the forged bars, were established by means of a SEM scanning microscope provided with an EDS (energy dispersive system) analyser.

Fig. 3 shows the microscopic area and the carbide selected for establishing the alloying elements concentration both in the primary carbides and in the steel matrix, in as cast and in annealed condition.

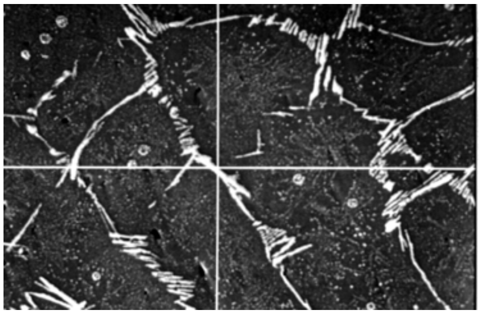
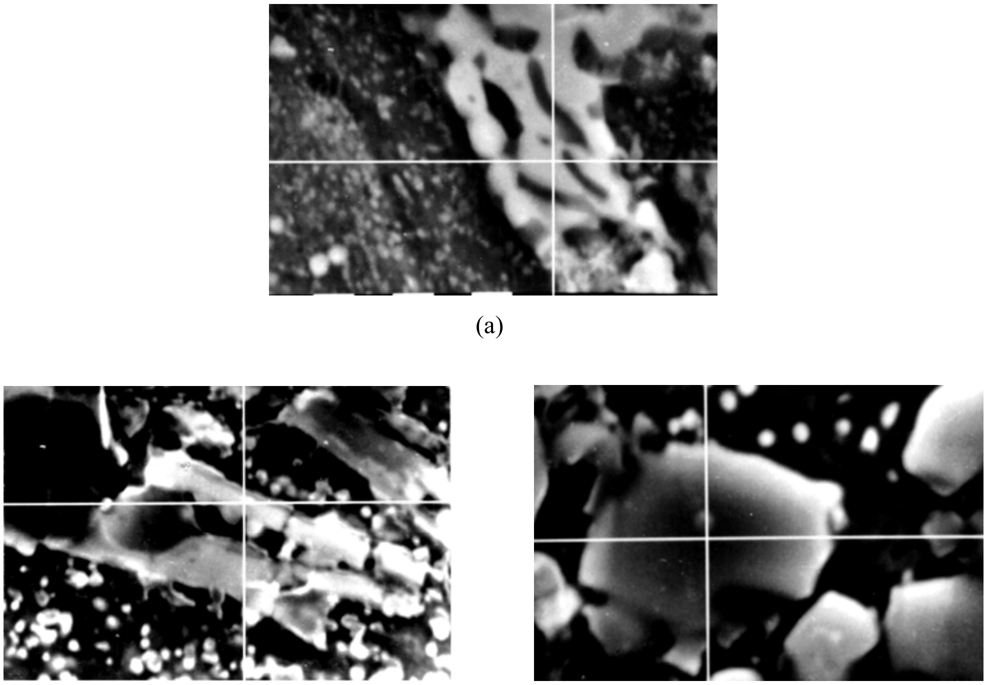


Fig. 3. The microscopic area and the carbide selected in Rp5 steel,
cast and annealed x 341 (SEM micrograph: composition image).

The aspect of the primary carbides in the Rp5 steel, in as cast condition or forged with different reduction ratios, at magnifications of x 10000, is similar to the micrographs presented in Fig. 4.



(a)

(b) (c)

Fig. 4. The aspect of the primary carbides in Rp5 steel, in as cast condition and forged with different reduction ratios x 10000 (SEM micrograph: composition image): (a) as cast; (b) forged with $C = 4.0$; (c) forged with $C = 8.0$.

Fig. 4 clearly shows that the primary carbides are non-homogeneous in the high speed steels both in as cast condition or forged by deformation ratios $C < 8.0$. The non-homogeneity of the primary carbides is due to their different content in alloying elements such as indicated by the formulas Fe_3Mo_3C or Fe_4Mo_2C.

For establishing the concentration of the alloying elements in the carbides as well as in the matrix, the first analizing point, that means step 1, was located inside the primary carbides, at the intersection of the perpendicular lines in Figs. 3 and 4, and the last analizing point, the step 9, was situated in the matrix, at a distance of 3 ÷ 4 steps from the carbide edge. The distance between two analizing points, called step, was 0.7 μm.

3. Results

The concentration values of the alloying elements indicated by the EDS read on the spectrometer, in the investigated steel, are summarized in Table 1.

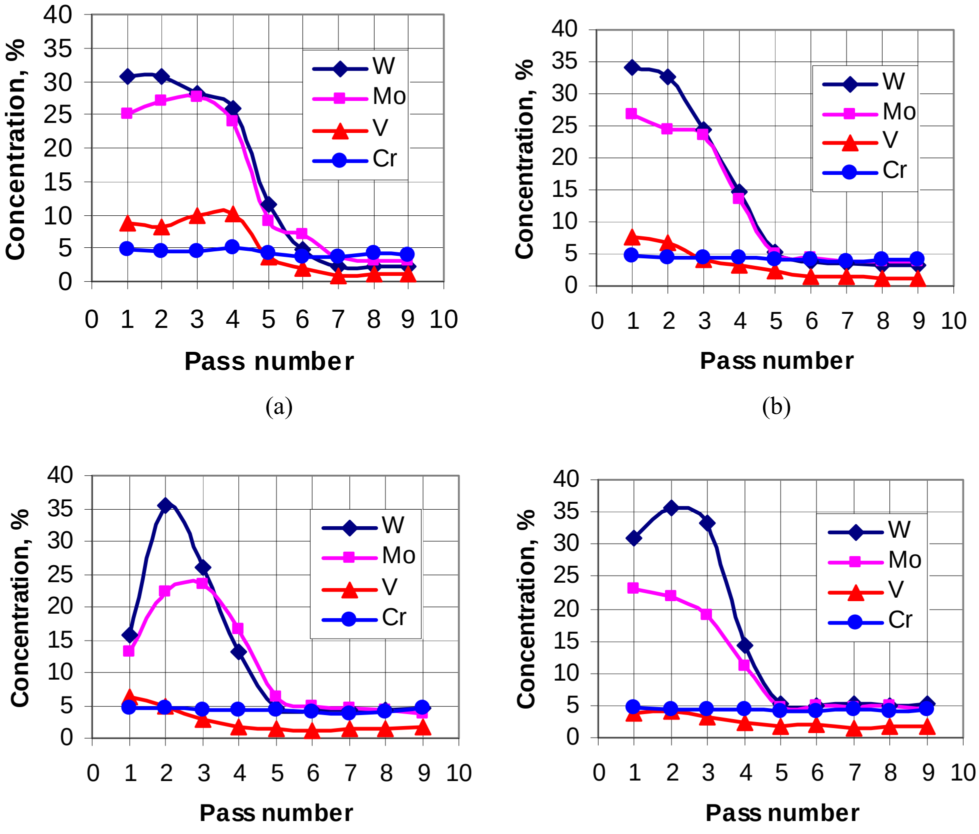
Table 1.

The concentration of the alloying elements in the primary carbides and in the matrix of Rp5 steel, in as cast condition (C=1) and after forging with different reduction ratios.

Alloying elements	Reduction ratio by forging	Step								
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
		Concentration %								
W	1	30.84	30.65	28.03	25.91	11.42	4.88	2.26	2.17	2.14
	4	34.20	32.60	24.30	14.80	5.23	3.82	3.46	3.34	3.30
	8	15.58	35.49	26.06	13.13	4.44	4.31	4.22	4.25	4.62
	16	30.95	35.73	33.14	14.38	5.20	4.85	5.22	4.95	5.14
Mo	1	25.20	26.97	27.70	23.92	8.93	7.05	3.58	3.11	3.02
	4	26.80	24.40	23.60	13.50	5.14	4.46	3.88	3.74	3.72
	8	13.10	22.30	23.48	16.47	6.21	4.95	4.54	4.22	3.75
	16	22.97	2.84	18.89	11.04	4.61	4.88	4.70	4.82	4.51
V	1	8.85	8.07	9.77	10.07	3.70	1.85	0.95	1.08	1.05
	4	7.66	6.84	4.22	3.26	2.35	1.41	1.34	1.27	1.26
	8	6.23	4.84	2.97	1.80	1.52	1.20	1.29	1.42	1.65
	16	3.77	4.20	3.24	2.45	1.85	2.10	1.48	1.64	1.70
Cr	1	4.68	4.63	4.60	5.01	4.36	3.80	3.70	4.10	3.84
	4	4.66	4.48	4.31	4.36	4.18	4.09	3.96	4.04	4.12
	8	4.64	4.46	4.41	4.35	4.17	4.08	3.82	4.05	4.43
	16	4.60	4.32	4.45	4.25	4.12	4.20	4.24	4.15	4.28

To disclose the homogenisation mechanism induced by plastic deformation in the Rp5 high speed steel we have put the experimental results from Table 1 in graphical form (Fig. 5).

Fig. 5 shows that the general aspect of the concentration variation curves of the alloying elements is approximately the same, irrespective of the steel condition (cast or forged), with the difference that the concentrations values in the matrix are increasing as the deformation ratio grows. Chromium is an exception from this rule; its concentration is almost not modified during hot plastic deformation. This exception can be explained by the very small difference between the atomic radii of Fe and Cr, in comparation with the much bigger differences between atomic radius of Fe on one side and the atomic radii of Mo, V and W on the other side.



(a) (b)

(c) (d)

Fig. 5. The concentration variation of the alloying elements in primary carbides and the matrix of Rp5 steel:
(a) as cast; (b) forged with $C = 4.0$; (c) forged with $C = 8.0$;
(d) forged with $C = 16.0$.

We have payed a special attention to the variation of the alloying elements concentration in the matrix of the high speed steel as indicated by our results in Table 1. The graphical representation in Fig. 6 shows that the concentration of the alloying elements in the matrix of Rp5 steel varies in function of the degree of hot plastic deformation, expressed by the reduction ratio. More specifically Fig. 6 shows that as the reduction ratio increases, the concentration of the alloying elements dissolved in austenite (representing the steel matrix), increases as well.

This increase is more pronounced up to a deformation ratio C = 8.0; at higher deformation ratios, it becomes asymptotical.

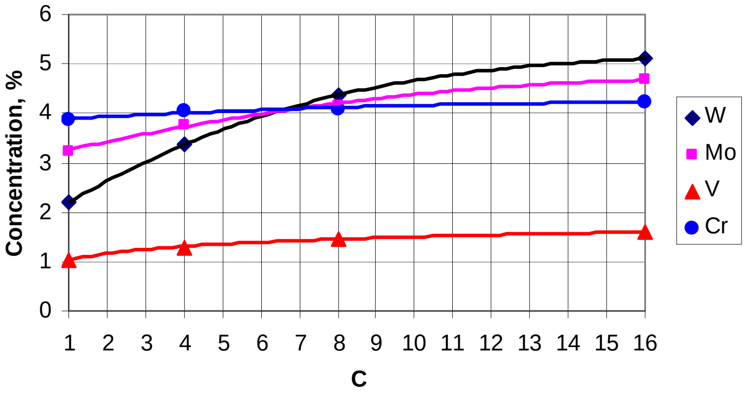
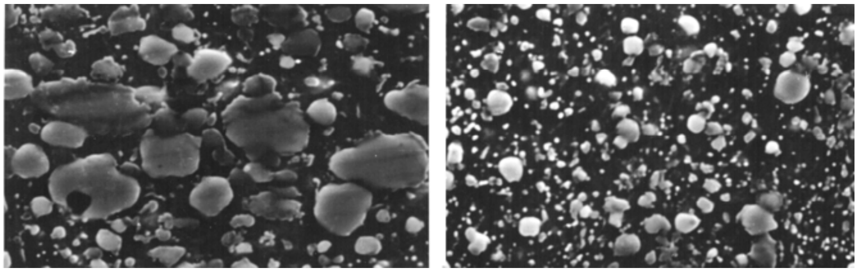


Fig. 6. Influence of the deformation ratio on the concentration of the alloying elements in the Rp5 steel matrix.

The difference between the total concentration of the alloying elements in steel and the concentration dissolved in austenite is found again in the primary carbides that have remained after the hot plastic deformation and the carbides which appeared during plastic deformation and which will be called ***quaternary carbides***.

The microscopic aspect of the primary and quaternary carbides in Rp5 high speed steel forged with $C \geq 8.0$ is shown in Fig. 7.



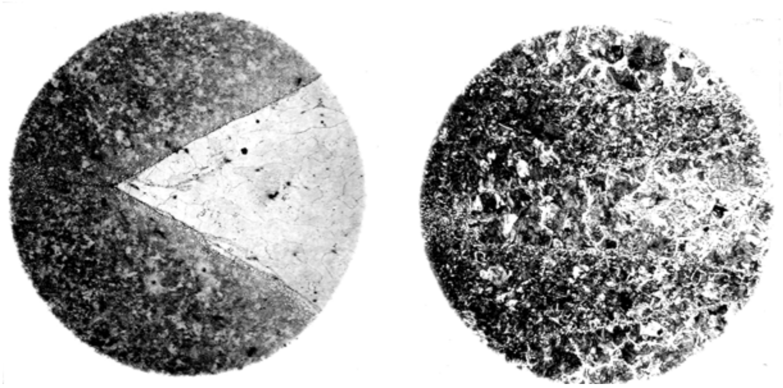
(a) (b)

Fig. 7. Primary and quaternary carbides in Rp5 steel hot plastic deformed x 5000 (SEM micrographs): (a) $C = 8.0$; (b) $C = 16.0$.

Fig. 7 shows that in the case of Rp5 steel forged with reduction ratios equal or higher than 8.0 , there is a homogenisation of the primary carbides that are decreasing in size and are becoming rounded. Simultaneously with the primary carbides decrease in size one also notice the appearance of quaternary carbides, whose dimensions are much smaller; on this account the latter cannot be seen at usual magnification below x 1000. Beside the size, the difference between the quaternary carbides and the primary ones, including the secondary and tertiary ones, also consists in the fact that the quaternary carbides appear during the hot plastic deformation, whilst the primary carbides appear during the solidification and the cooling after solidification.

4. Discussion

Our results show that the homogenization, the decrease in size and the rounding of the primary carbides, and the emergence of quaternary carbides are structural modifications that have to be ascribed to the diffusion processes. These diffusion processes are favoured by the appearance and disappearance of the lattice defects, which are formed and cancelled during hot plastic deformation. It is a well known fact that in the case of hot plastic deformation the diffusion rate is about some hundred times higher than in the case of heating and cooling in the same conditions of time and temperature [8], [9], [10]. An eloquent example in this respect is represented in Fig. 8, which points to a strong influence of hot plastic deformation on diffusion speed.



(a) (b)

Fig. 8. Optical micrographs of the samples with screws eccentrically introduced (Nital etching, x 100): (a) not – deformed; (b) hot plastic deformed.

Indeed Fig. 8 shows two non-alloyed steel samples (0.8 % C) both of them having an Armco iron screw introduced eccentrically in them [10]. After heating in the same conditions, approximately at 1000°C, one of the samples was air cooled, the other one was plastic deformed by one hammer blow and then cooled near the first sample.

Fig. 8 clearly shows that in the case of the non- deformed sample, the diffusion of carbon is negligible, whilst in the case of the hot deformed sample, the diffusion is nearly completed.

The formation mechanism of the quaternary carbides during the hot plastic deformation process results from the analyze of the processes which are taking place during plastic deformation and the alternation between the deformation recrystallization (dynamic recrystallization) and the coalescence recrystallization, as depicted in Fig. 9.

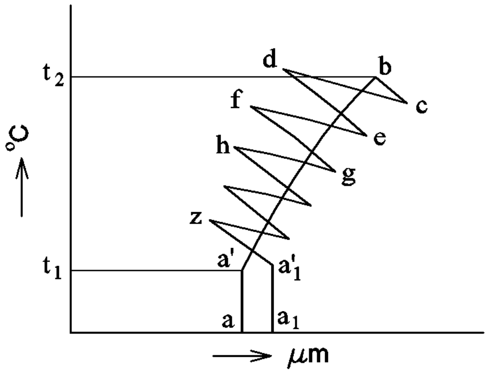


Fig. 9. The alternation between the deformation recrystallization and the coalescence recrystallization processes.

Indeed during the heating for plastic deformation, after the end of the $\alpha \rightarrow \gamma$ transformation, up to the temperature t_1, the grain size remains constant (Fig. 9). Within temperature interval $t_1 - t_2$ the coalescence recrystallization takes place and the grain size grows from a' to b. During the transfer from the furnace to the plastic deformation equipment, the temperature drops and the grain size continues to increase within the interval b – c. During plastic deformation, at either first hammer blow or press stroke, or by other means, the temperature grows and the grain size decreases inside the c – d interval due to the deformation recrystallization. Simultaneously with the grain size and temperature modification, the diffusion of the alloying elements from primary carbides in austenite also develops within the c – d interval. At the end of the plastic deformation, achieved by first hammer blow or press stroke, the atoms which have diffused in austenite remain trapped in the positions they reached, positions out of which only one part are in a steady equilibrium. Within the pause between the first and the second plastic deformation, interval d – e, part of the atoms which have diffused in austenite and which have remained in un-steady equilibrium positions, pass to steady equilibrium positions, because of the coalescence recrystallization, the rest of them re-groups and forms quaternary carbides.

Within the intervals e – f and f –g, as well as in the following intervals until the end of plastic deformation, the above mentioned processes repeat, and the grain size, dependent on the end of plastic deformation temperature in point z, reaches a certain value a_1 , value that can be equal, smaller or higher than the initial value. By reiteration of the diffusion processes and regrouping of the alloying elements atoms, the concentration of the alloying elements in austenite increases, as well as the density of quaternary carbides. On the contrary the volume and share of the primary carbides decreases. Such a mechanism offers an explanation for the structure homogenization that is strongly supported by our experimental results.

5. Conclusions

During hot plastic deformation, the structure homogenisation of ledeburitic steels (including among them the high speed steels) takes place by the diffusion of the alloying elemens from the primary carbides in austenite, and not by mechanical breaking of these carbides and their dissipation in the metallic matrix. Due to the diffusion processes, beside the structure homogenisation, also takes place the enrichment of the steel matrix in alloying elements, that results in the appearance of a new generation of carbides, called quaternary carbides.

REFERENCES

[1]. *V. I. Popescu a.o.*, Oţeluri Rapide, AGIR Press, Bucharest, 2002.
[2]. *T. Dulămiţă*, Oţeluri de scule, Editura Tehnică, Bucharest, 1990.
[3]. *J. Field*, Reduce Carbide Segregation in High Speed Steels, in: Iron Age no. 31/1959.
[4]. *A. Geller,* Instrumentalniie Stalli, Metallurgya, Moscova, 1983.
[5]. *G. A. Roberts a.o.*, Tool Steels, American Society for Metals, Ohio, 1992.
[6]. *H. Schumann*, Metallographie, Deutscher Verlag für Grundstoffindustrie, Leipzig, 1991.
[7]. *V. I. Popescu a.o.*, Cercetări cu privire la omogenizarea structurii oţelurilor rapide, in: Metalurgia no. 12/2001.
[8]. *J. W. Cristian*, The Theory of Transformations in Metals and Alloys, Pergamon Press, New York, 1981.
[9]. *B. B. Khina*, Theory of deformation-enhanced diffusion during mechanical alloying, http://event.ua.pt/dsl2005/Khina.pdf , 2005.
[10]. *V. I. Popescu a.o.*, O nouă metodă pentru determinarea difuziei ca o consecinţă a deformării plastice, in: Metalurgia no. 6/1971.