

## Characterization of Precipitates in the 18-1-1 and 18-1-1-5 High-Speed Steels During Tempering After Previous Quenching

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In this paper the precipitates formed during the tempering after quenching (in salt bath) at temperature 1240 °C for 18-1-1 and 18-1-1-5 high-speed steels are investigated using an analytical transmission electron microscope (A-TEM). The study of this tempering is carried out in isothermal and anisothermal conditions, by comparing the results given by dilatometry and hardness. Tempering is performed in the range of 350-750 °C. Coarse primary carbides retained after heat treatment are of the V-rich MC and W-V-rich M<sub>6</sub>C types. In turn, it gives a significant influence on the precipitation of dispersive secondary carbides (M<sub>4</sub>C<sub>3</sub> type), that is secondary hardening during tempering. The hardness peak is observed in the tempering range of 500-550 °C (66.8 HRC after a double tempering at 550 °C). It was found out that the cobalt in the concentration limited to about 5 % results in increasing the effect of the secondary hardening by 2 HRC. Between 700 and 750 °C, the impoverished phase (retained austenite) transforms on heating. In the end, in this temperature range of tempering, other more stable carbides of the M<sub>6</sub>C and M<sub>23</sub>C<sub>6</sub> types are formed developing at the expense of the carbides M<sub>4</sub>C<sub>3</sub> and M<sub>7</sub>C<sub>3</sub> formed before, which then disappear.

**Keywords:** Carbides, Retained austenite, Tempering, Secondary hardening, High speed steels.

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### 1. INTRODUCTION

High-speed steels are still an important group of engineering materials. Their satisfactory hardness, ductility, good machinability in the annealing state and their common industrial application justify the research on the development of the new grades with higher working properties. The purpose of the present work is to study a new alloy of W-Mo-V-(Co) high speed steels containing about 18 % W, 1 % Mo, 1 % V (wt.%) elements and 0.0-5 % Co, likely to be used to manufacture cutting tools working mainly under the impact and the wear effects. The addition of vanadium has to modify the nature as well as the morphology of primary carbides. This addition allows to confer a secondary hardening by precipitation of dispersive carbides of the M<sub>4</sub>C<sub>3</sub> type in the matrix of the tempered martensite and martensite transformation of the retained austenite, which occurs during cooling at tempering temperature [1-3]. But the addition of cobalt in high speed steels leads to hardness extension during tempering between 540 and 600 °C. So, the effect of the secondary hardening is in direct relationship with the improvement of the work properties of the cutting tools of steels (containing cobalt). On the other hand, the reduction of the volume fraction of the retained austenite is caused by an increase in the cobalt concentration in high-speed steels [4]. Noting also, that the increase of the cobalt concentration (from 5 to 8 %) effect of steel has the direct connection with decreasing impact resistance. So, the investigated high-speed steels have a limit addition of cobalt to approximately 5 %.

The aim of the current work is to confirm (by TEM observation) the presence of the M<sub>4</sub>C<sub>3</sub> carbides, which precipitate during tempering at temperature adequate to the maximum secondary hardness effect. One also has confirmed the possibility of reducing the volume fraction of the retained austenite by carrying out multi-

ple tempering between 540 and 600 °C (after previous quenching at up to 1240 °C). Then, this fact involves an increase in the secondary hardening effect and thus an improvement of the mechanical characteristics of the investigated high-speed steels.

### 2. EXPERIMENTAL PROCEDURE

#### 2.1 Material Studied

The experimental investigations were carried out using samples of the high speed steels: W-Mo-V and W-Mo-V-Co of the types 18-1-1 and 18-1-1-5. The specified chemical composition of these steels is represented in (see Table 1). The samples were heated up to the austenitizing temperatures 1240 and 1260 °C, during 15 min. These samples were quenched with a 5min cooling in a salt bath (BaCl<sub>2</sub>) at 560 °C and then in the air, down to ambient temperature. The samples allocated to the measurement of volume fraction of retained austenite ( $\gamma_r$ ) were investigated in both quenching and tempering states. The samples for A-TEM and hardness investigations were tempered for 2 h at 350-740 °C.

The complementary tests by dilatometry and differential thermal analysis after anisothermal condition were performed with a heating rate up to 150 °C/h under primary vacuum ( $5 \times 10^{-2}$  Torr, i.e. 6.65 Pa).

**Table 1** – Chemical composition of steels 18-1-1 and 18-1-1-5

Steel type	Designation	Average composition (wt. %)					
		C	Cr	W	Mo	V	Co
18-1-1	HS 18-1-1	0.82	3.76	18.03	0.80	1.05	0.00
18-1-1-5	HS 18-1-1-5	0.82	3.76	18.03	0.80	1.05	5.00

### 3. RESULTS AND DISCUSSION

The micrographic examination (See Fig. 1) shows

that the structure (in quenched state) consists of a martensite, non-dissolved primary carbides of the MC and M<sub>6</sub>C types[1-9], and the primary austenite grain boundaries which are well highlighted. The residual austenite (volume fraction of this phase – determined by the integrated intensities method – is retained at 20 °C: up to 35 % for  $\theta_{\gamma} \geq 1240$  °C). The chemical composition (of the primary carbides MC and M<sub>6</sub>C), estimated according to the results of the microanalysis by X-rays (see Fig. 2a and Fig. 2b). shows that in the case of carbide MC – the “M” represents the metal elements (wt. %): 36 V, 28 Fe, 17 W, 14 Mo and 5 Cr. On the other hand, in the case of the carbide M<sub>6</sub>C the “M” signifies the metal elements (wt. %): 37 W, 33 Fe, 24 Mo, 3 V and 3 Cr.

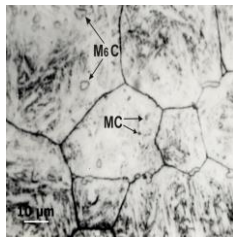


Fig. 1 – Structure of high speed steel 18-1-1 type after quenching at 1240 °C

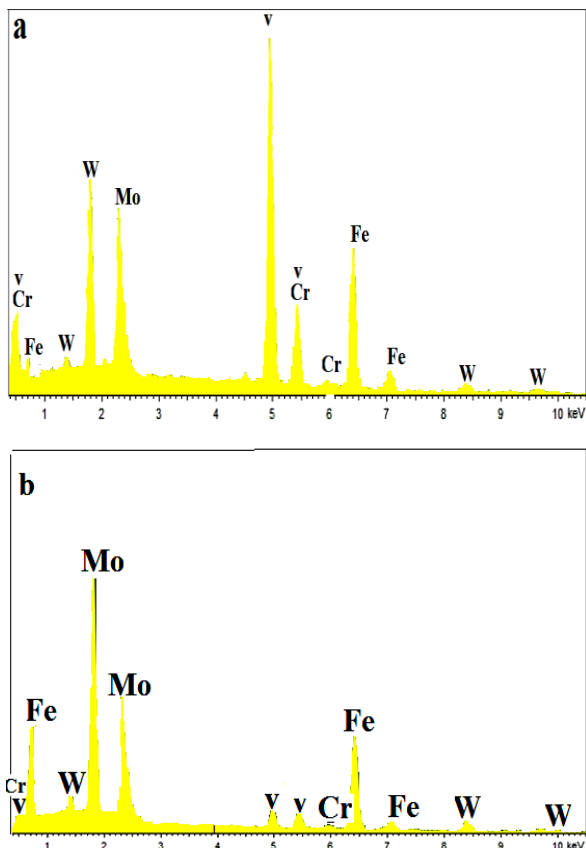


Fig. 2 – Diagrams of the energy dispersive X-ray spectrum of high speed steel of the 18-1-1 type quenched at 1240 °C obtained from (a) MC type carbides

Fig. 3 shows the differential dilatometric curves corresponding to the specimens respectively tempered after previous quenching from austenitization tempera-

tures  $\theta_{\gamma} = 1240$  and 1260 °C. Anomalies are observed between the ambient temperature and the austenitic transformation temperature ( $A_{c1} = 800$  °C). For these temperatures  $\theta_{\gamma}$ , we observe two successive contractions (stage I and II) developed between 100 and 400 °C. It must be noted that after quenching from 1260 °C, the slope of the curve is more significant: this is due to the significant quantity of the retained austenite in this state (40 %  $\gamma$ ). The first stage between (100 and 250 °C) corresponds to the precipitation of the carbide  $\epsilon$  ( $Fe_{2.4}C$ ), which is the first to be formed during a tempering, it is not thermodynamically stable. This carbide generates less accommodation stresses with respect to the matrix.

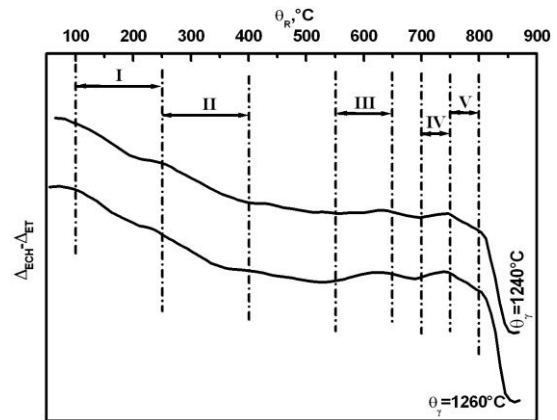


Fig. 3 – Dilatometric curves recorded on heating from quenched states ( $\theta_{\gamma} = 1240$  and 1260 °C)

This process is accompanied by contraction, heat release (see Fig. 4, first peak exothermic) and fall in hardness (see Fig. 5).

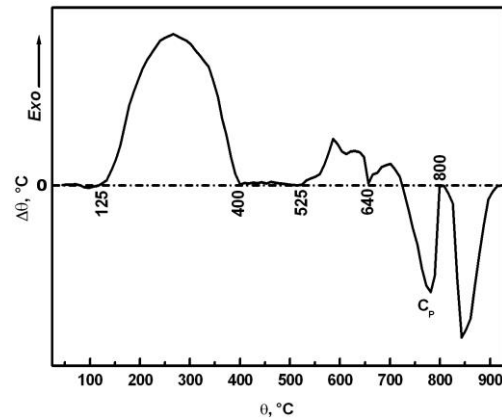


Fig. 4 – Differential thermal analysis curve from a sample quenched from  $\theta_{\gamma} = 1240$  °C

The second stage between (250 and 400 °C) corresponds to the carbide formation of M<sub>3</sub>C type [4, 18] by dissolution of the  $\epsilon$  carbide, previously formed, and the carbon rejected by a martensite structure. We easily distinguish the martensite needles in which fine lengthened particles are distributed (see Fig. 6a). The pattern (Fig. 6b) shows the carbide of the M<sub>3</sub>C type. This evolution results in a second contraction (the martensitic matrix being enriched in iron); and the exothermic reaction is completed.

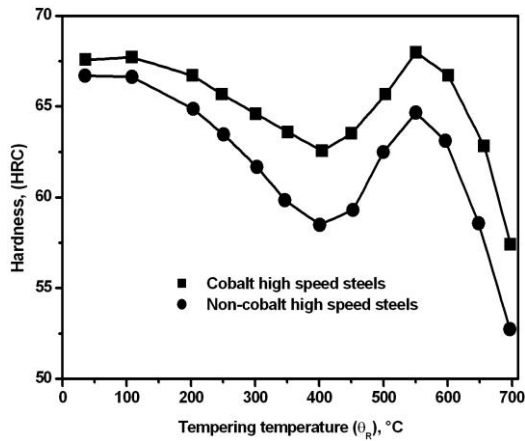


Fig. 5 – Evolution of hardness according to tempering temperature ( $\theta_R$ ) after a previous quenching ( $\theta_\gamma = 1240^\circ\text{C}$ )

These two stages are accompanied by a specific volume reduction, which explains the contractions observed in dilatometry (see Fig. 3). The release of heat observed in D.T.A. (Fig. 4) must be associated with the internal stress relaxation and the precipitations phenomena (phase  $\epsilon$  then  $M_3C$  must be accompanied by negative variations of enthalpy).

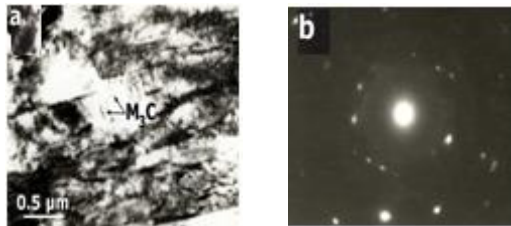


Fig. 6 – Structure of cobalt high speed steel 18-1-1-5 type after quenching at  $1240^\circ\text{C}$  and tempered ( $2h$ ) at  $350^\circ\text{C}$  (a) Bright field (b) Electron diffraction pattern

The structural evolution of the steel between approximately  $550^\circ\text{C}$  and  $650^\circ\text{C}$  is characterized by a first dilatometric expansion (Fig. 3, stage III). This results in the martensitic matrix being subjected to new precipitation phenomena, which are more significant as  $\theta_\gamma$  increases. In addition, in this temperature range, the retained austenite starts to be destabilized by rejecting some of the components which will precipitate in the carbides (to the  $\alpha/\gamma$  interfaces). The carbon reduction in the retained austenite causes the increases of temperature  $M_s$  of the beginning of martensite transformation of this retained austenite and making the possible transformation during the cooling from the tempering temperature between ( $550$  and  $650^\circ\text{C}$ ) (Fig. 7).

On the other hand, the precipitation phenomena are marked in A.T.D. by an exothermic peak which spreads out approximately from  $525$  to  $600-625^\circ\text{C}$  (see Fig. 4). In fact, in this temperature range, the secondary hardening results from the precipitation of new substituted carbides, in extremely divided form, within the matrix. These hardening carbides are, according to several authors [10] of the  $M_4C_3$  type (rich in vanadium). (Fig. 8a) shows the presence of a dispersive and more abundant precipitation within the matrix.

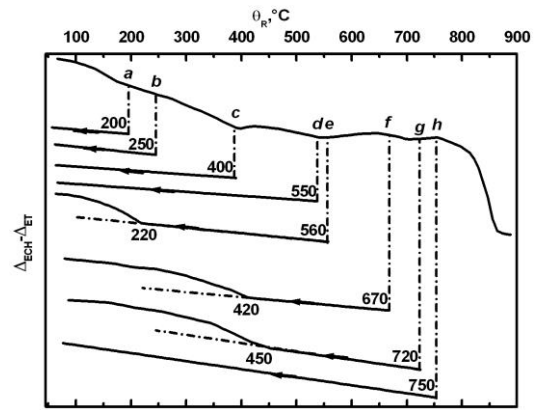


Fig. 7 – Dilatometric curves recorded on cooling after non isothermal tempering up to different  $\theta_R$  temperatures

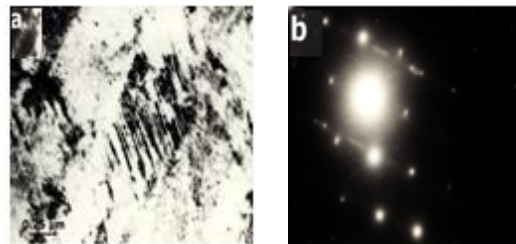


Fig. 8 – Structure of cobalt high speed steel 18-1-1-5 type after quenching at  $1240^\circ\text{C}$  and tempered ( $2h$ ) at  $560^\circ\text{C}$ : (a) Bright field; (b) Electron diffraction pattern

These dispersive precipitates are identified as being of the  $M_4C_3$  type (see Fig. 8b). Noting also that the secondary hardness peak is about 65 HRC (in non-cobalt steel), but for the steels containing 5% Co, it is about 67 HRC (see Fig. 5). So, we can say that the addition of cobalt allows to increase the effect of the secondary hardening by 2 HRC. In the case of a sample having undergone  $2h$  tempering at  $635^\circ\text{C}$ , (see Fig. 9a) shows the presence of precipitates having a lengthened form. These carbides are identified as being of the  $M_7C_3$  type (see Fig. 9b).

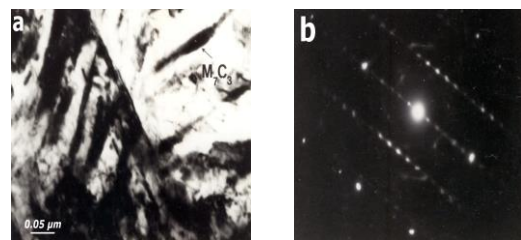
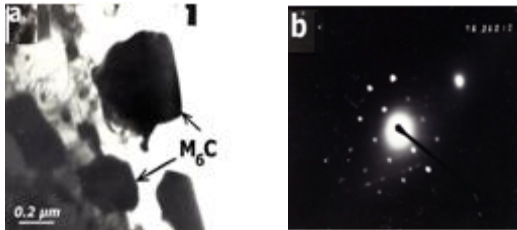


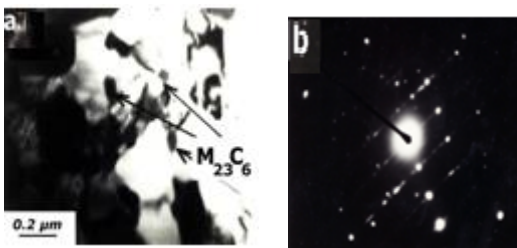
Fig. 9 – Structure of cobalt high speed steel 18-1-1-5 type after quenching at  $1240^\circ\text{C}$  and tempered ( $2h$ ) at  $635^\circ\text{C}$ : (a) Bright field (b) Electron diffraction pattern

Moreover, we observe another dilatometric expansion (between  $700$  and  $750^\circ\text{C}$ ) especially visible if the austenitization has been carried out at  $1260^\circ\text{C}$  (see Fig. 3), stage IV. Hardness continues to decrease gradually (see Fig. 5). These various behaviors correspond to the heat transformation of the retained austenite previously destabilized. In fact, the samples having undergone a tempering at  $\theta_R > 730^\circ\text{C}$  do not present any further transformation during the final cooling (see Fig. 7). Noting also, that the significant fall in hardness must be

associated with the dissolution of the carbides  $M_7C_3$  and  $M_4C_3$ . This phenomenon is followed by a formation of new carbides of the types  $M_6C$  and  $M_{23}C_6$  (see Fig. 10a and see Fig. 10b) and (see Fig. 11a and see Fig. 11b), which develop at the expense of the carbides  $M_4C_3$  and  $M_7C_3$  formed before.



**Fig. 10** – Structure of cobalt high speed steel 18-1-1-5 type after quenching at 1240 °C and tempered (2h) at 740 °C: (a) Bright field; b) Electron diffraction pattern



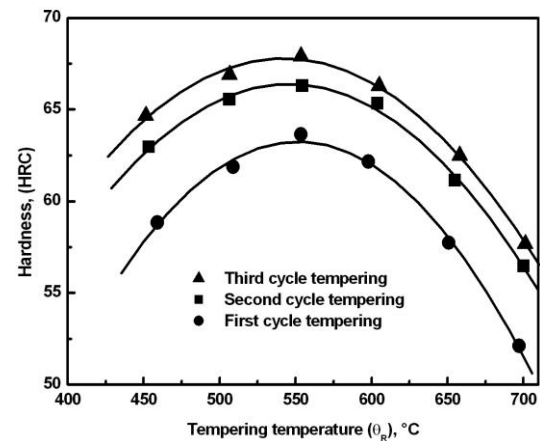
**Fig. 11** – Structure of cobalt high speed steel 18-1-1-5 type after quenching at 1240 °C and tempered (2h) at 740 °C: (a) Bright field; b) Electron diffraction pattern

Finally, between 750 °C and 800 °C the sample contraction slows down more especially as the temperature  $\theta_R$  tends towards 800 °C (see Fig. 3, stage V). In fact, the preceding observations suggest that the coalescence processes of carbides develop from now on significantly.

We have also proceeded to hardness measurements on various samples subjected to the multiple tempering during 2 h between 500 and 600 °C after previous quenching at up to 1240 °C (see Fig. 12) shows that the curve corresponding to the first cycle of tempering is located below those cycles. At temperature 550 °C (for example), the major part of residual austenite was transformed into secondary martensite during the cooling of the first cycle of tempering: there remains 7.4 %  $\gamma_R$  for non-cobalt HSS and 6.9 %  $\gamma_R$  (for cobalt- HSS). The latter has been evaluated during the second cycle of tempering: therefore the hardness is about 66.8HRC and the retained austenite ( $\gamma_R$ ) is lower than 5 % (in non-cobalt HSS). Besides, the third cycle of tempering has no significant effect (see Fig. 12). On the basis of these results, it can be limited to a double tempering (carried out between 540 and 560 °C).

#### 4. CONCLUSION

The aim of this study is to characterize the structural evolutions likely to be developed in high speed steels (with limited addition of 5 % Co) subjected to tempering after a direct quench from the austenitic



**Fig. 12** – Multiple tempering effects on the secondary hardening of non-cobalt high speed steels

field and to estimate their effect on some of the mechanical properties of the material. From the whole of the obtained results we can elucidate the following points:

(i)-The processes developed successively during the tempering show that:

- Martensite evolves by rejecting carbide  $\varepsilon$  (at  $\theta_R < 250$  °C), and then substituted cementite  $M_3C$  (between 250 and 400 °C). The latter carbide tends to evolve to the carbide  $M_7C_3$  (between 500 and 650 °C). In parallel, between (540 and 560 °C) there intervenes a secondary hardening which due to the precipitation in the matrix of substituted carbides of the  $M_4C_3$  type. A maximum hardening is observed after a double tempering at 550 °C (i.e.66.8 HRC).

Retained austenite does not destabilized-by carbide precipitation on the  $(\alpha/\gamma)$  interfaces- below 550 °C; it can then transform on cooling, to the secondary martensite (between 550 and 650 °C). However, after a single tempering at 550 °C, there remains 7.4 %  $\gamma_R$  (in non-cobalt HSS) and 6.9 %  $\gamma_R$  (in-cobalt high speed steels); while after double tempering at the same temperature, the volume fraction of retained austenite ( $\gamma_R$ ) is lower than 5 %.On the other hand, this destabilized austenite persists up to 700 °C. Between700 and 750 °C, this impoverished phase transforms on heating. Within this temperature range of tempering, there is formation of other more stable carbides of the  $M_6C$  and  $M_{23}C_6$  types which develop at the expense of the carbides  $M_4C_3$  and  $M_7C_3$  formed before, which then disappear.

(ii)-The study of the influence of the cumulated tempering allow us to conclude that it is beneficial to proceed with a double tempering between 540 and 560 °C. Indeed, during the cooling of the single tempering, the major part of destabilized residual austenite is transformed into secondary martensite; this latter evolves then – during the heating of the double tempering – so that the hardness of the high speed steels remains reinforced. This fact suggests an interesting possibility of improvement of the mechanical properties of the alloy and thus a reinforcement of its resistance in service.

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