

## Properties of TiN protective coatings on steel

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**Abstract** The properties of fast cutting steel SW7M, stainless steel 1H18N9T, and tool steel NC11 coated with a TiN protective layer were studied using  $^{57}\text{Fe}$  Conversion Electron Mössbauer Spectroscopy. The adhesion of the coatings is determined by the thickness of Fe-N and Fe-Ti interface. The model of the abrasion of the protected tools, based on fast diffusion of Fe ions to the surface through the TiN layer and further oxidation is proposed.

**Key words** Conversion Electron Mössbauer Spectroscopy • hard coating • oxidation • TiN

### Introduction

The value of steel made products increase significantly after covering their surface by appropriate protecting layers which secure chemical stability and improve hardness and tribological properties. Among such protecting coatings TiN plays since years a leading role.

The main technological limitation is the insufficient adhesion of such covers, arising from structural and chemical misfit between the substrate and the cover; the misfit which must be compensated in an interface region.

Another quite intriguing problem is the microscopic description of the abrasion of tools with refined surfaced. There is a widely spread out, but a rarely published opinion among technologists that the upgraded properties of the specially treated surface survive even when the thickness of the removed by abrasion layer of a tool is many times bigger than the thickness of its protective layer [1].

The aim of this work was to gain a microscopic insight in the local electronic states of iron at the interface and their evolution after thermal treatment of the sample. Such data, related with macroscopic mechanical properties may help in finding optimal conditions for technological processes of surface upgrading.

### Experimental

The samples of high speed steel SW7M, stainless steel 1H18N9T, and tool steel NC11 with the compositions given in Table 1 and prepared accordingly to the technological regimes were covered with a TiN layer. The TiN layers were formed by the Physical Vapour Deposition (PVD) method in an industrial set-up (PUSK) in two steps, according to an industrial procedure [1]. At first, the steel surface was bombarded by 1 keV  $\text{N}^+$  ions for 15 min and next by 1 keV  $\text{Ti}^+$  ions for 90 s. In the second step, the TiN layer was

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**Table 1.** Chemical composition of the investigated steels.

Fast cutting steel SW7M	Stainless steel 1H18N9T	Tool steel NC11
C – 0.8%	C – max. 0.1%	C – 1.95%
Mn – 0.4%	Mn – max. 2%	Mn – 0.35%
Cr – 4.1%	Cr – 18%	Cr – 12%
W – 6.5%	Ni – 9%	Si – 0.35%
Mo – 5.0%	Ti – 0.65%	Fe – 85.35%
V – 1.9%	Fe – 70.25%	
Fe – 81.3%		

formed by a PVD technique for 3 min. The thickness of the TiN layer on the studied samples was about 100 nm, much less than for commercial application, 3  $\mu\text{m}$ . Such a layer transmits still part of the conversion electrons from the iron bearing interface. However, the spectra obtained by Conversion Electron Mössbauer Spectroscopy (CEMS) are usually weak.

To increase the sensitivity of CEMS, the surface layer of SW7M steel was, before covering, enriched in the  $^{57}\text{Fe}$  isotope by implantation of 30 keV  $^{57}\text{Fe}$  ions with a dose of  $10^{16}$  ions/cm $^2$ . In this way, a resonant layer at the interface was formed.

The CEMS spectra of the virgin samples (not refined), samples after each step of upgrading and finally after annealing in air at different temperatures were recorded at room temperature using a specially designed counter for low energy conversion electrons [3].

The surface morphology of the samples after annealing was monitored by measurements of the specular and diffuse reflectance with the use of Integrating Sphere measurements [5]. In general, it is difficult to provide a full interpretation from such spectral data, but qualitative information about surface contaminants on metals and/or about surface roughness may be concluded.

## Results

The CEMS spectra of virgin SW7M steel and those covered with TiN layer are presented in Fig. 1. The coating with TiN leads to the increase of the central, apparently single line which we assign to the interface region. Two samples were studied: one with perfectly adhesive cover and the second with loosely bonded TiN layer, which spontaneously has fallen off after preparation. It turned out that in the last case the interface layer was thinner.

Similar result, i.e. the formation of the interface layer was observed in the case of NC11 steel. In this case the effect was weaker because the surface of the covered steel was not enriched with  $^{57}\text{Fe}$  and, consequently, the spectrum comes mainly from the non alternated substrate. In the case of stainless steel no change in Mössbauer spectra was found after covering with TiN.

The process of the corrosion of SW7M is illustrated in Fig. 2, where the resonant absorption lines characteristic for  $\text{Fe}_2\text{O}_3$  (sextet) and  $\text{Fe}_3\text{O}_4$  (two partly resolved sextets) are marked. In untreated samples, the first sign of oxidation was found at 400°C in the form of hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) fractions. The samples after first step of treatment oxidise directly to  $\text{Fe}_2\text{O}_3$ . In this case the line

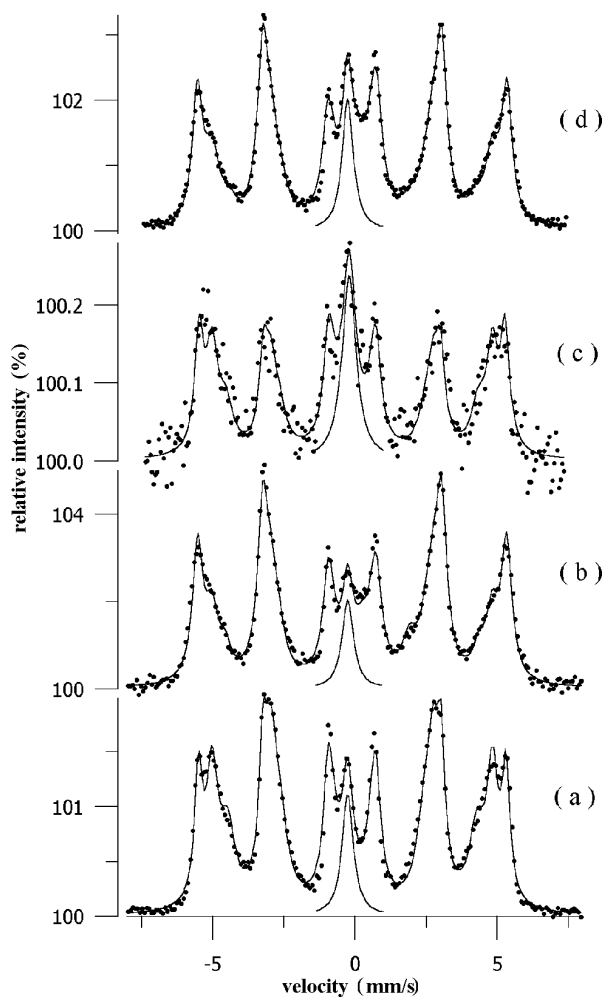
intensity ratio of the hematite sextet deviates strongly from 3:2:1:1:2:3 ratio which is expected for the case of random orientation of magnetic moments. This points out same magnetic texture with preferred orientation of magnetic moments in the sample plane.

The covering with TiN layer reduces the process of corrosion, see Fig. 3. Again, the oxidation leads to the formation of  $\text{Fe}_2\text{O}_3$  for all samples. It is worth of notice an increase in the total resonant scattering effect after heating. In this case  $\text{Fe}_2\text{O}_3$  particles are not magnetically oriented.

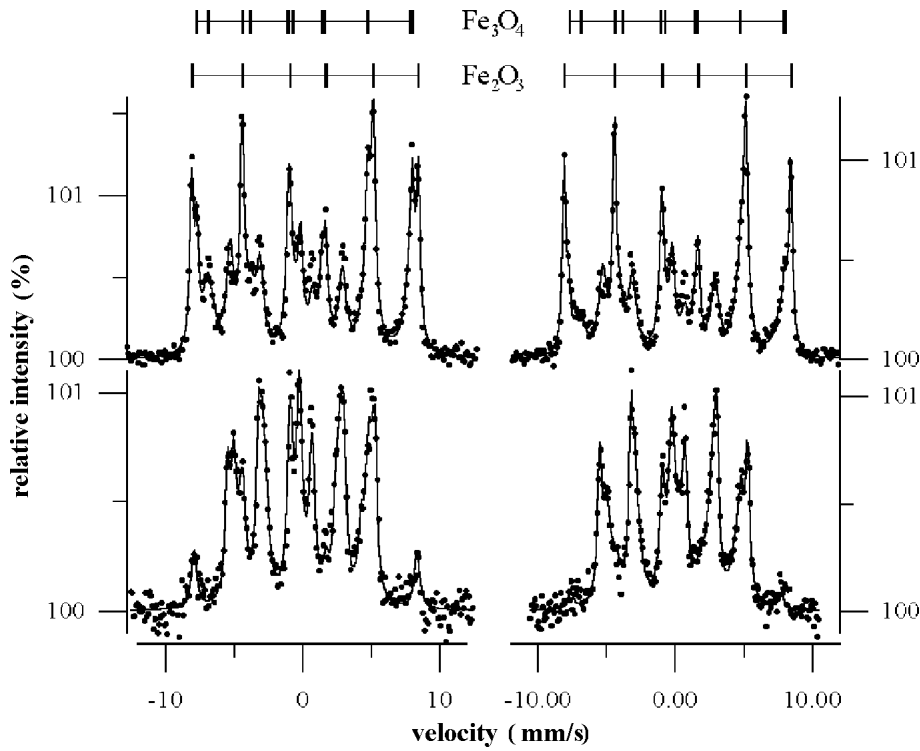
The change of the property of the upper layer is well visible in the specular reflectance spectra, which show intriguing structure for samples annealed at 600°C, see Fig. 4.

## Discussion

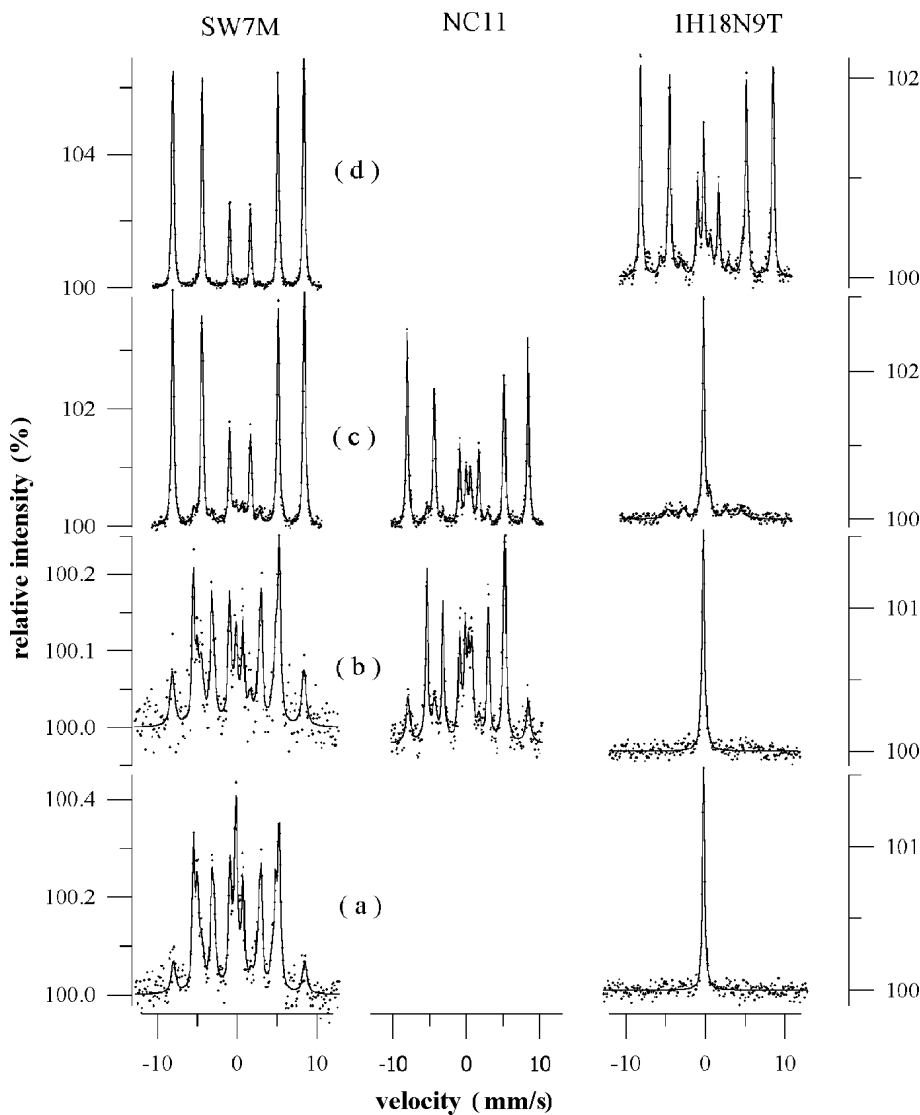
The local states of iron interacting with TiN was studied previously in TiN samples implanted with  $^{57}\text{Fe}$  ions [2] and assigned mainly to  $\text{Fe}_2\text{N}$  and to nonstoichiometric Fe-N complexes. Part of the Fe ions may replace N atoms exhibiting  $\alpha$  and  $\beta$ -Ti(Fe) states. The poorly resolved Mössbauer absorption lines of these fractions are located



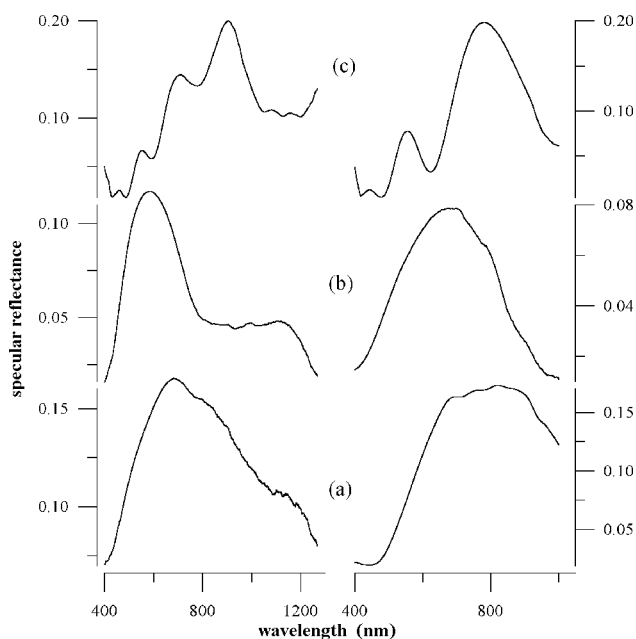
**Fig. 1.**  $^{57}\text{Fe}$  CEMS spectra of high speed steel (SW7M). (a) – Virgin sample; (b) – sample implanted with  $10^{16}$  ions/cm $^2$   $^{57}\text{Fe}$  ions; (c) – sample covered with TiN; (d) – sample after improper covering (TiN layer has fallen off).



**Fig. 2.**  $^{57}\text{Fe}$  CEMS spectra of SW7M steel after annealing in air at 300°C (bottom) and 400°C (top), left – virgin sample, right – sample after first step of covering. The bars show the positions of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  sextets lines.



**Fig. 3.**  $^{57}\text{Fe}$  CEMS spectra of SW7M (high speed steel), left, NC11 (tool steel), middle, 1H18N9T (stainless steel), right, covered with TiN, after annealing in air at: (a) – 500°C, (b) – 600°C, (c) – 700°C, (d) – 800°C.



**Fig. 4.** Specular reflectance spectra of SW7M (left) and 1H18N9T (right) steels covered with TiN, after annealed in air at: (a) – 400°C; (b) – 500°C; (c) – 600°C.

close to zero velocity and it is hard to separate them from austenite fractions in steels.

In the technological process of coating with TiN layer it happens that the obtained covers are weakly bonded to the substrate. These cases are out of control and tools then obtained are of no value. Our experiments clearly show that this is caused by too thin interface region. Certainly, we cannot explain why sometimes such thin interface is formed.

The oxidation of virgin steel samples to  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  is obviously understood as a result of the penetration of oxygen into the steel. The arrangement of the magnetic moments of these corrosion products reflects the magnetic texture of steel surface c.f. the line intensity ratio in Fig. 2. The oxidation of upgraded samples directly to  $\text{Fe}_2\text{O}_3$  is

quite unexpected. Such oxidation means that the iron is fully exposed to oxygen. The  $\text{Fe}_2\text{O}_3$  particles exhibit no preferential magnetic ordering, c.f. the line intensity ratio in Fig. 3, which means that they are well separated from steel surface. When, in addition, the increase in the resonant absorption effect and the variation in specular reflectance after oxidation are considered, one may conclude that the  $\text{Fe}_2\text{O}_3$  appears on the surface(!) of the specimen, above the protecting layer.

## Conclusions

The obtained data allows us to propose the model of oxidation based on the diffusion of iron through the cover to the surface and further oxidation at the surface. This model explains the abrasion of the refined tools in a very simple manner: during the work of the tool iron diffuses to the surface at elevated, at least locally temperature, oxidises and the weakly bounded  $\text{Fe}_2\text{O}_3$  is removed, while the hard covers survive. The diffusion of iron may be enhanced by structural defects. Indeed, the commercial TiN coatings, produced in a quite simple (but effective) industrial equipment are poorly crystallised and show frequently a deviation from stoichiometry [4].

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