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Structure of friction products and the surface of tribological system elements

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Abstract. The goal of the paper is to identify characteristic features of the surfaces of rubbing bodies and friction products, which come into being when friction processes are realized under optimal conditions, regarding wear resistance. Mössbauer investigations carried out both in scattering and transmission arrangement have evidenced, between others, differences in oxides content and their phase composition, depending on the temperature of tribological system in the course of friction test. It has been found that the wear products obtained at the optimal temperature are composed of the much smaller particles than those produced at lower or at higher temperature.

Key words: abrasive wear • Mössbauer spectroscopy • wear resistance

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Introduction

In the course of wear processes caused by friction of tribological system elements some structural changes in superficial layers of co-working bodies arise, modifying their physical properties. The problem of resistance to abrasive wear is of great importance in technique and, therefore, novel methods are searched in order to reduce tribological wear [12]. In the last years it was found [6, 12] that temperature is a very important factor for friction processes in a tribological system and a significant increase of wear resistance can be reached when a constant, well-chosen temperature is provided in the friction zone. The reduction of wear is accompanied by transfer of the material between surfaces of rubbing bodies and stabilization of coefficient of friction [15]. This phenomenon seems to be very important for decrease of friction losses in tribological systems, although it is not well understood up to now. Mössbauer investigations of the surface layer of rubbing elements and friction products can be helpful for identification of processes that occur in the course of friction as well as comparison of the results obtained under optimal, (i.e. reducing the wear) and non-optimal conditions.

Experimental methods

Samples of C45 steel of chemical composition Fe+C/0.5/Mn/0.67/Si/0.21/Ni/0.08/ Cr/0.15/ were chosen for investigations. The specimen were normalized or previously

Table 1. Attributes of investigated steels and t_{opt} – optimal temperature corresponding to maximal wear resistance, derived from friction tests [13]

	Sample	Material	Conditions of heat treatment	Hardness	t_{opt} (°C)
Specimen	A	Steel C45	normalized	18 HRC	–5
	B	Steel C45	hardened and tempered at 200°C	52 HRC	–10
	C	Steel C45	hardened and tempered at 350°C	38 HRC	–20
	D	Steel C45	hardened and tempered at 600°C	19 HRC	+5
Counter-specimen		Steel 145Cr6	hardened	63 HRC	

subjected to various heat treatment – they were hardened and tempered at temperatures: 200°C, 350°C or 600°C (Table 1). In order to determine the optimal temperature values, corresponding to reduced abrasive wear, tribological measurements were performed under conditions of oxidation wear. For friction tests, a special apparatus, enabling stabilization of the temperature in the friction zone, was designed and employed [14]. The investigated specimens, in form of fixed sliders, were co-worked with a counter-sample made of 145Cr6 steel (of chemical composition: Fe+C/1.4/Mn/0.59/Si/0.28/Ni/0.08/Cr/1.6/V/0.17/), being a rotating ring. The temperature was stabilized by a cooling system supplied by a Julabo Cryo-Compact CF-40 circulator. Friction resistances were stabilized by means of cleaning elements to make the friction coefficient constant. It was maintained at 0.4 during the test. In this case, a Polish patent was used: PL 171768 B1 of 1997: Method of friction resistances regulation.

Phase composition of steel surfaces was investigated using conversion electron Mössbauer spectroscopy (CEMS) based on the ^{57}Fe isotope. A ^{57}Co/Rh source of gamma radiation was used. A single-wire flow counter supplied by a He+4%CH_4 mixture was employed in order to detect electrons emitted from a specimen surface owing to de-excitation of ^{57}Fe nuclei previously excited by gamma radiation of energy about 14.4 keV. The energy of gamma photons was modified – owing to the Doppler effect – by velocity of the radiation source moving in constant acceleration mode. Mössbauer spectra were collected both before and after a frictional test. For selected specimen, the tests were carried out under optimal as well as non-optimal conditions. Friction products in the form of powder were examined by the use of a transmission Mössbauer spectrometer working in a vertical arrangement. In this case, a proportional counter was applied as a detector.

Numerical analysis of Mössbauer spectra was carried out by means of specialized NORMOS program, utilizing conventional least square procedure with additional smoothing terms. It enables identification of iron compounds, particularly secondary iron-oxygen phases.

Results

Optimal temperature values, corresponding to maximal resistance to abrasive wear, deriving from friction tests [13], are shown in the last column in Table 1.

Mössbauer spectra collected for individual samples before and after the friction tests are visible in Figs. 1–4. They have a shape typical of crystalline materials, composed of sharp maxima – single lines or lines coupled to doublets (two lines) or sextets (six lines). In all the spectra a slightly asymmetric sextet dominates, attributed to ferrite. Asymmetry of the sextet is caused by alloying elements, which occupy both interstitial and site positions in the vicinity of ^{57}Fe atoms in the crystalline lattice and thus modify the hyperfine interactions parameters of the spectra components, i.e. hyperfine magnetic field (HMF), quadrupole splitting and isomer shift. Therefore, in the numerical analysis of the spectra, the asymmetric sextet characteristic of ferrite was fitted by three or four subspectra, corresponding to several in-equivalent positions of iron in the crystalline lattice of the steel.

Beside ferrite, the following components contributing to the spectra were taken into account in the fitting procedure: martensite (the alloy with tetragonal crystalline lattice), cementite – Fe_3C, austenite – γ-Fe as well as oxide phases: wustite – Fe_xO, ferrihydrite – $Fe_5HO_8{\cdot}4H_2O$, magnetite – Fe_3O_4 and hematite – Fe_2O_3. The literature data of the hyperfine interactions parameters (hyperfine magnetic field – B, quadrupole splitting – Q and isomer shift – δ) of the phases, assumed as initial parameters in the fitting procedure of Mössbauer spectra, are collected in Table 2 [1, 7]. The two last oxides bring contribution

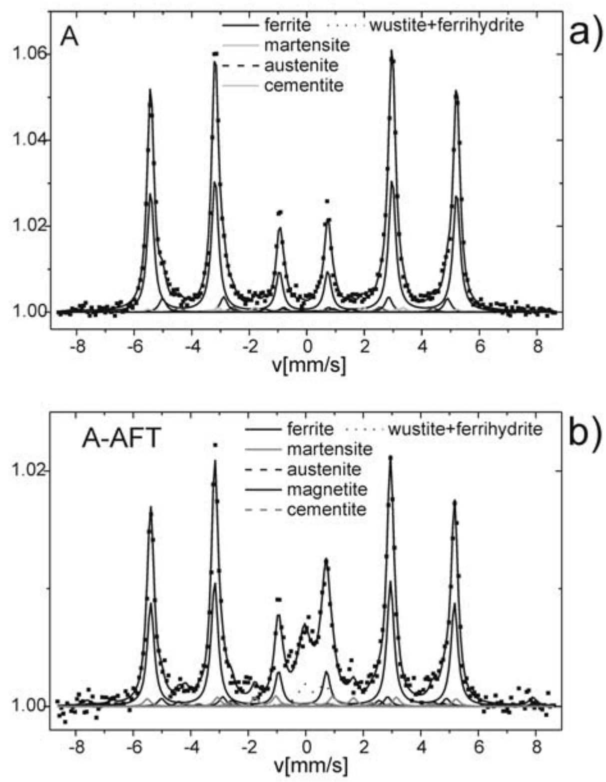

Fig. 1. CEMS spectra collected for sample A: before friction test (a) and after friction test (b).

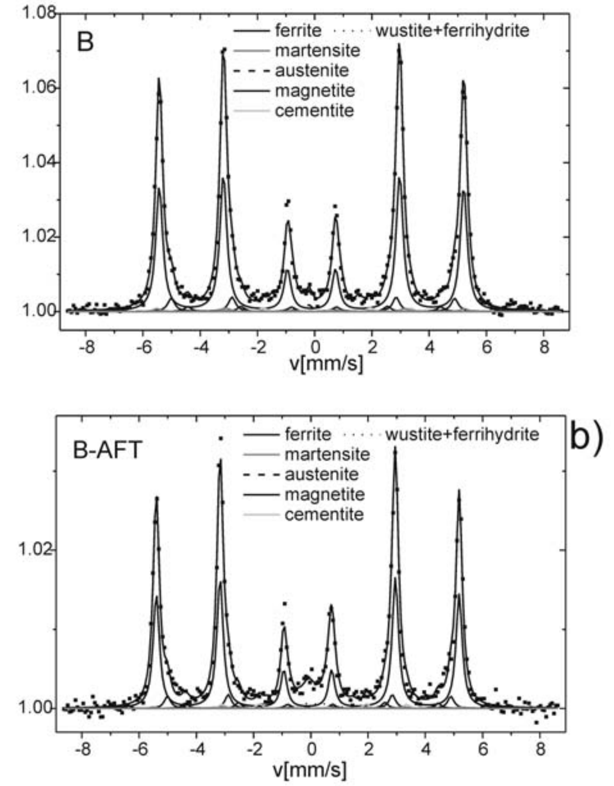

Fig. 2. CEMS spectra collected for sample B: before friction test (a) and after friction test (b).

to the spectra in the form of rather well resolved sextets which are characterized by large values of hyperfine magnetic field. The other phases give subspectra which overlap mutually. Particularly, the sextets characteristic

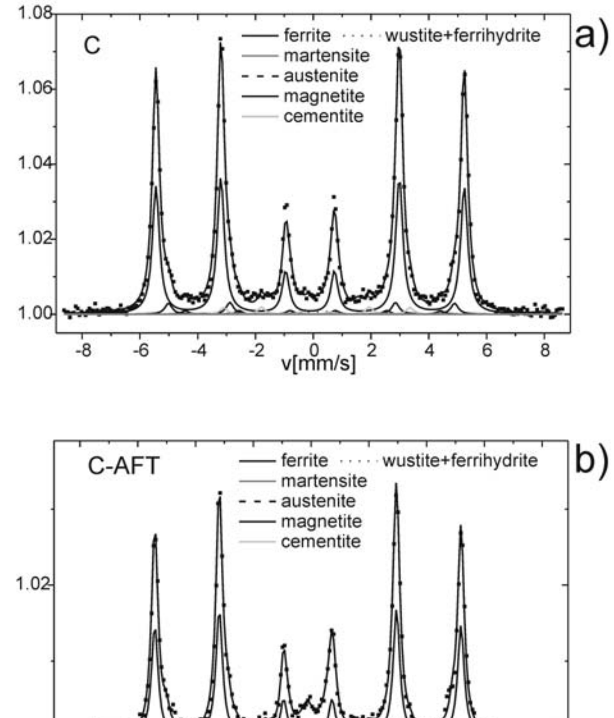

Fig. 3. CEMS spectra collected for sample C: before friction test (a) and after friction test (b).

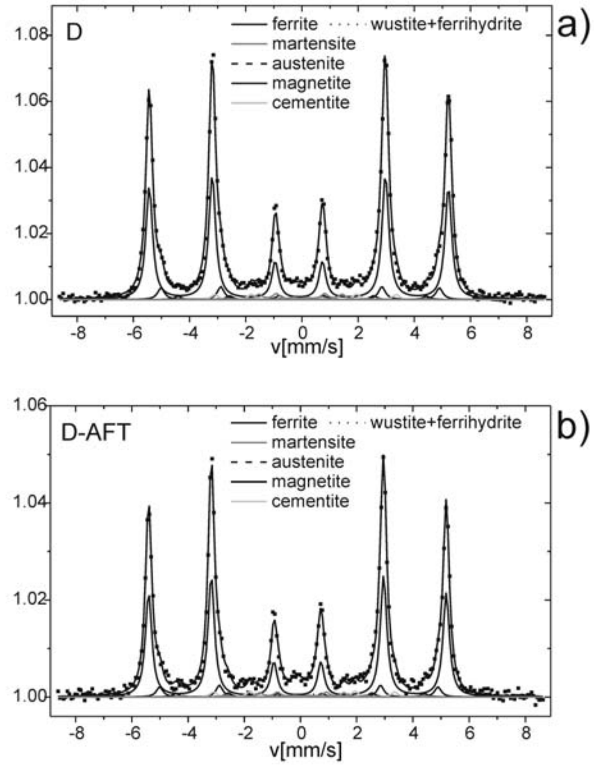

Fig. 4. CEMS spectra collected for sample D: before friction test (a) and after friction test (b).

of ferrite and martensite are poorly separable; the same refers to the subspectra attributed to austenite, wustite and ferrihydrite, especially when the phases bring small contribution. This is why the percentage of individual phases, derived from Mössbauer spectra, has considerable uncertainty.

The values of relative content of subspectra attributed to different phases, derived from CEMS spectra, collected for particular specimens of steel are presented in Table 3. Assuming that the Debye-Waller factor of all the phases has a similar value, we can identify the results with the distribution of iron atoms over the phases. Taking into account different ratio of iron atoms to other ones in oxides compared to ferrite together with martensite we can estimate that real volume relative content of oxides in the investigated materials is about twice larger than the results presented in Table 3.

From Table 3 it may be noted that iron in ferrite and martensite makes in total $84 \div 95\%$ all iron atoms in the surface of steels and the value decreases slightly after friction tests. Moreover, a small rise of iron contribution in martensite and also in oxides (especially wustite) is observed after tests and the latter composes up to 10% all iron atoms; the maximal value corresponds to the normalized C45 steel. In all samples the relative contribution of cementite is less than 4%.

Mössbauer transmission spectra of friction products produced in the course of friction tests carried out for sample A at different temperatures are shown in Fig. 5. It may be seen that the shape of Mössbauer spectrum collected for the powders obtained at optimal temperature (regarding wear resistance) $t_a = t_{\mathrm{opt}} = -5^{\circ}\mathrm{C}$ is quite different than those related to the temperature distinctly higher or lower than the optimal one ($t_b = -20^{\circ}\mathrm{C}$, $t_c = 15^{\circ}\mathrm{C}$). The significant part of the spectrum consti-

Table 2. Hyperfine interaction parameters (hyperfine magnetic field – B, quadrupole splitting – Q and isomer shift – δ) of iron phases, assumed as initial parameters in the fitting procedure of Mössbauer spectra

Phase	Component	δ (mm/s)	Q (mm/s)	B (T)	Ref.
bcc Fe (ferrite)	Fe – sextet Fe(1) – sextet Fe(2) – sextet	0.00 0.11 0.07	0.00 0.02 –0.04	33.0 27.4 30.7	[7]
bct Fe (martensite)	Fe – sextet Fe(1) – sextet Fe(2) – sextet	0.06 0.08 –0.05	–0.18 0.28 0.20	33.3 26.5 34.3	[7]
fcc Fe (austenite)	singlet	–0.05	0.0	0.0	[7]
Fe_3C (cementite)	Fe_3C (a) – sextet Fe_3C (b) – sextet	0.21 0.19	–0.06 0.32	19.7 20.5	[1, 7]
$Fe_{1-x}O$ (wustite)	doublet	0.7	0.36	0.0	[1]
$Fe_5HO_8 \cdot 4H_2O$ (ferrihydrite)	doublet	0.3	0.7	0.0	[1]
Fe_3O_4 (magnetite)	Fe_3O_4(a) – sextet Fe_3O_4(b) – sextet	0.33 0.66	–0.15 0.06	48.5 45.4	[1]
Fe_2O_3 (hematite)	sextet	0.36	0.0	51.7	[1]

Table 3. Distribution of iron over different phases, derived from CEMS spectra collected for particular specimens of steel (the last column – non-identified phases)

Sample	Distribution of iron over different phases (%)					
	bcc-Fe + bct-Fe	fcc-Fe	Fe_3C	Fe_3O_4	$Fe_{1-x}O/Fe_5HO_8 \cdot 4H_2O$	Others
A	91.7 + 2.3 = 94.0	0.0	2.9	0.4	0.6	2.1
A-AFT*	76.6 + 7.1 = 83.7	0.1	0.1	2.9	7.8	5.4
B	92.2 + 2.1 = 94.3	0.0	2.1	0.0	0.0	3.6
B-AFT	93.3 + 0.5 = 93.8	0.3	2.9	0.0	2.5	1.5
C	91.2 + 0.6 = 91.8	0.0	4.3	0.5	1.0	2.4
C-AFT	89.2 + 1.7 = 90.9	0.1	2.3	0.0	3.1	3.6
D	90.9 + 0.8 = 91.7	0.1	3.6	0.0	0.9	3.7
D-AFT	89.5 + 1.2 = 90.7	0.2	3.8	0.7	1.5	3.1

*AFT – after friction test.

Table 4. Distribution of iron over different phases, derived from TMS spectra collected for friction products obtained for sample A (normalized C45 steel) as a result of friction test carried out at different temperatures

Temperature (°C)	Distribution of iron over different phases (%)						
	bcc-Fe + bct-Fe	fcc-Fe	Fe_3C	Fe_3O_4	$Fe_{1-x}O/Fe_5HO_8 \cdot 4H_2O$	Others	Smeared compounds
–5 (optimal)	11.9(±5%)	0	0	39.5	21.4(±10%)	0	27.2(±10%)
–20	81.1 + 0.5 = 81.6(±2%)	8.4(±50%)	0	0.2	3.1(±50%)	1.2 Fe_2O_3	5.5
+15	81.5 + 0.2 = 81.7(±2%)	3.3(±50%)	1.0	1.5	3.8(±50%)	1.3 Fe_2O_3	7.4

tutes a smeared component with broad spectral lines that has been fitted by a continuous distribution of hyperfine interactions parameters. We attribute the component to ultra-fine powder particles. They are characterized by large intensity of strain, a large number of defects and a considerable contribution of surface regions in comparison to the volume ones. Possibly, some of them have superferromagnetic (or superparamagnetic) properties and contribute to the smeared component (or the central part) of the spectrum. One cannot also exclude arising of amorphous regions that bring a contribution to the "continuous" subspectrum. As is shown in Table 4, the smeared component (excluding a high-field part attributed to magnetite and hematite) constitutes about 27% of the spectrum in Fig. 5a – for friction products obtained at optimal temperature – and only 5–7% in the cases of powders produced in the course of friction test realized at non-optimal temperature. Moreover, much more oxides arise in friction products obtained under optimal conditions, especially Fe_3O_4 (about 40%), $Fe_{1-x}O$ and $Fe_5HO_8 \cdot 4H_2O$ (about 21%), while only several percent of these phases as well as traces of Fe_2O_3 have been found in the spectra of powders produced at non-optimal temperature. Vestigial amount of austenite has been also stated.

Summary and discussion

It was found that as a result of friction under optimal conditions the content of martensite slightly increases on the surface of the specimen. Similarly, a small rise of percentage in the oxides Fe_3O_4 and $Fe_{1-x}O$ is observed. According to the recognized mechanism of oxidational

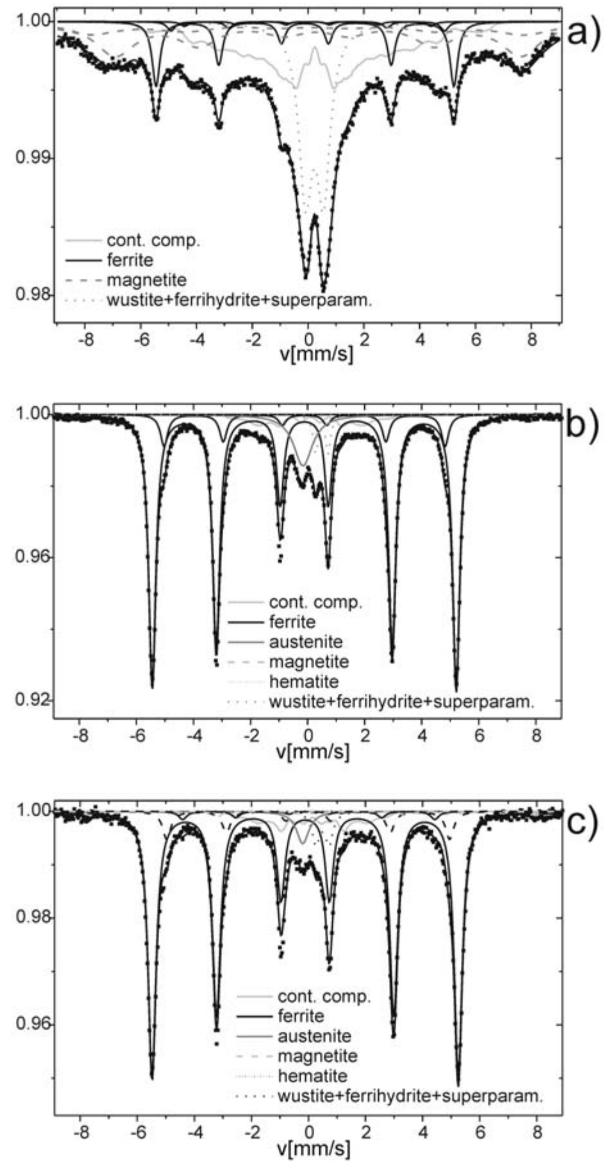

Fig. 5. Mössbauer spectra of friction products obtained at the temperature: $t_a = t_{opt} = -5^{o}C$ (a), $t_b = -20^{o}C$ (b), $t_c = 15^{o}C$ (c).

wear, all three types of iron oxides should occur on the specimen surface. Presented findings show that only slight amount of hematite appears in the regime of friction at the temperature that assures enhanced resistance to wear. Similar mechanisms of oxide generation in various regimes of friction have been described in several papers [2–5, 8–11].

Transmission Mössbauer spectroscopy investigations of pulverous products of friction, arising at optimal temperature, have shown that they are composed of the ultra-fine particles, much smaller than the wear products obtained at other temperatures. The relative content of individual oxides and their global percentage has been also changed in dependence on the friction test temperature. It has been stated that after friction test realized at optimal temperature the oxides percentage is about 60%, while the content of magnetite is about twice larger than the relative fraction of other oxides. In friction products obtained at non-optimal temperature the oxides content is much smaller and is equal to about 5%. Traces of hematite and vestigial amount of austenite have been also found.

Summing up, the outcomes of Mössbauer investigations enabled analysis of friction effects in the studied systems and evidenced that the character of wear processes accompanying the friction under wear minimizing conditions is clearly different from those occurring under non-optimal conditions.

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