

Heat and Thermochemical Treatment of Structural and Tool Steels

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1. Introduction

Degradation processes are apparent on the working surfaces of stressed parts, which gradually impair the parameters of machine parts and equipment. These degradation processes include abrasive wear caused by the interaction of hard, usually mineral particles with the working surface of the part. In marginal cases intensive abrasive wear leads to great losses due to output stoppages caused by machine or equipment outages and further due to costs necessary for production of spare parts and/or their renovation and maintenance costs. It is often stated that approximately 50% cases of wear are due to abrasive processes (Krushchov & Babichev,1970; Eyre,1979; Uetz,1986).

Abrasive wear is characterized by separation and displacement of material particles during scratching and cutting caused by hard particles. These particles can either be free or in a certain sense bonded.

Another case of abrasive wear is known from experience in which hard particles are present between two working surfaces moving relatively one to another. This case is typical for crushing and grinding matter. However it can also be found in sliding pairs where hard impurities penetrate into insufficiently sealed working surfaces. Hard particles can also be formed in the process of adhesive wear which can affect one or both surfaces abrasively. Such a classification of types of abrasive wear was generally accepted although it appears that the processes of interaction of abrasive particles and the material subject to wear are much more complicated. What must be taken into account is the character and time response of forces acting between the abrasive particles and the surface subject to wear.

Ideally, the materials for resistance to abrasion should have the hardness that is in excess of that of the mating surface or the abrasive particles. But in the most cases the hardness of abrasive particles is higher than the hardness of abraded materials.

2. Effect of structural factors on abrasion resistance

2.1 Effect of hard structural components on failure of metallic materials by abrasion

The basic concept of the effect of structural factors on abrasion resistance was worked out by (Krushchov & Babichev, 1960). He raised an assumption that the mechanism of wear is

identical for all structural components. The abrasion resistance of heterogeneous materials is given by the sum of products of the volume shares of individual structural phases and their relative abrasion resistance (additivity law). The thermal affection of the process by wear and by structural modifications is not considered. According to (Zum Gahr, 1985) the behaviour of heterogeneous materials is not controlled by a single phase but that the contribution of each phase is linearly proportional to its volume share. Abrasive wear decreases linearly with the growing volume of the hard phase. Both models assume that all components of the composite are subject to wear in the same way and that the contribution of each component depends only on its volume share and proportional wear. The effect of further important factors such as the properties of interphase boundaries, relative size and fracture toughness of the phases are not considered by these models although it is obvious that they have a significant effect on the abrasive wear of a heterogeneous material (Simm & Freti, 1989).

Abrasion resistance of metallic materials depends on the hardness, shape, size and amount of hard structural components and their distribution in the basic metallic matrix. The growing hardness of these phases and their amount in the microstructure increase the abrasion resistance of the material (Roberts et al., 1962; Schabuyev et al., 1972; Suchánek et al., 2007). The share of carbides, however, cannot be considered separately from the basic material. E.g. in pearlite-carbide microstructures the hardness and abrasion resistance grow with the growth of the carbide volume up to 35% (Popov & Nagorny, 1970).

However in ferrite-carbide microstructures abrasion resistance grows with the share of carbides up to 5-6% and further growth does not affect abrasion resistance any more (Popov & Nagorny, 1969). Besides the share of carbides important factors are the type of the carbide phase and its size. According to (Grinberg et al., 1971), who studied abrasion resistance in steels with a constant content of Cr, W and V with a ferritic matrix and uniformly distributed carbides, the abrasion resistance of steels grows with the change of a type of carbide to a type richer in the alloy element. E.g. when changing from a carbide of the M_3C type to a more complex carbide type M_7C_3 , abrasion resistance grows. Special carbides of alloy elements increased abrasion resistance compared with steels containing complex carbides (Popov et al., 1969). A typical example is the addition of vanadium in ledeburitic chromium steels which results in an increase of abrasion resistance due to formation of a very hard VC carbide (2100 – 2800 HV). The effect of the type of carbides on the relative abrasion resistance Ψ_a of quenched steels with a hardness in the range 850 – 900 HV is given in the diagram in Fig. 1 (Suchánek & Bakula, 1987). For this range of hardnesses the share of retained austenite in high-alloy materials is low and affects overall abrasion resistance only slightly. The values of Ψ_a obtained from an apparatus with an abrasive cloth showed that lowest abrasion resistance was found in steels with Fe_3C and/or M_3C carbides. Higher abrasion resistance was found in steels with M_7C_3 carbides and maximum abrasion resistance in steels containing special MC carbides.

High dispersity of carbides is most favourable for the achievement of high wear resistance (Tsy-pin, 1983). This is why abrasion resistance grows in tempered steels with the growing dispersity of cementite particles (Larsen-Badse & Mathew, 1966).

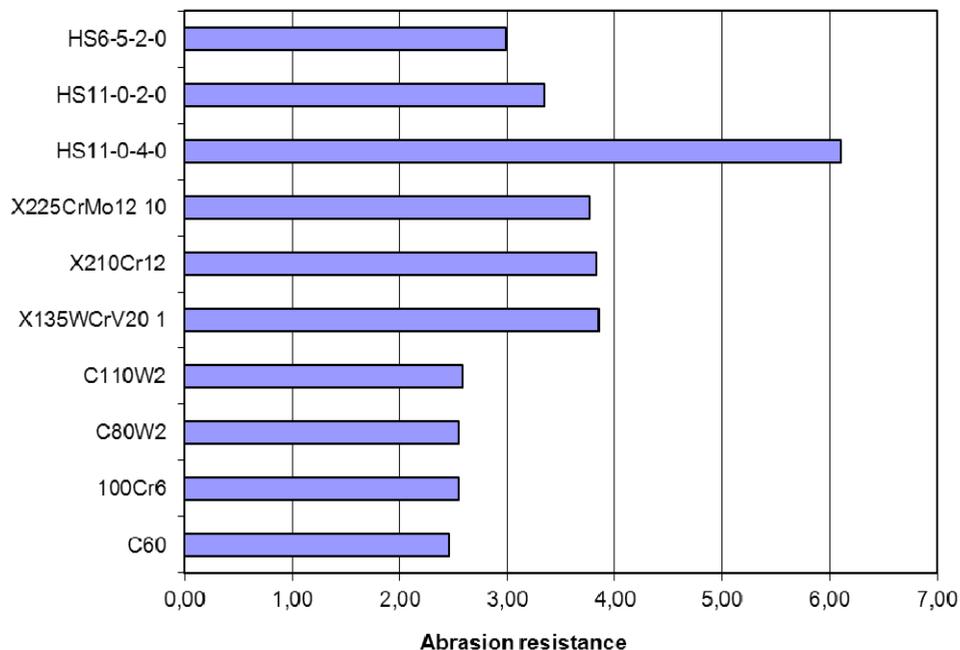


Fig. 1. Influence of the carbide types on abrasion resistance of quenched steels (100Cr6, C80W2, C110W2 – carbide M_3C ; X135CrWV20 1, X210Cr12, X225CrMo12 10 – carbide M_7C_3 ; HS6-5-2-0, HS11-0-2-0, HS11-0-4-0 – carbides $M_6C + M_{23}C_6 + MC$) (Suchánek & Bakula, 1987).

2.2 Effect of matrix on processes of abrasion

If available references in literature are summarized, the following conclusion can be arrived at steels with a ferritic matrix exhibit the lowest abrasion resistance. Substitutional hardening of ferrite by carbide-forming elements (Cr, W, V) does not result in an enhancement of abrasion resistance. The growing share of pearlite in ferritic-pearlitic steels results in enhancement of resistance to wear. Steels and cast irons with a martensitic matrix have a higher abrasion resistance than pearlitic steels and cast irons with a similar chemical composition. The higher content of carbon and alloy elements leads to a marked enhancement of abrasion resistance (Moore, 1974; Filippova & Goldshtein, 1979).

The presence of carbides in the martensitic matrix results in a further increase of resistance to abrasive wear by particles. The hardness and quantity of these carbides makes a significant contribution to the abrasive resistance of a metal. The matrix and carbides resist penetration of abrasive particles that start a cutting action.

During heat treatment of steels and cast irons with a higher content of carbon and alloy elements, which shift M_s and namely M_f temperatures towards lower values, retained

austenite is formed in the structure. A number of papers were devoted to its influence on abrasion resistance (Petrov & Grinberg, 1968; Popov & Nagorny, 1970; Fremunt et al., 1971). The authors of these papers experimentally proved in various grades of steels and cast irons that the function of retained austenite during sliding abrasion is positive. An explanation for this behaviour is that the strain-induced martensitic transformation can contribute to the enhancement of wear resistance at low impact energies.

Steel grade	Heat treatment	Microstructure	Hardness [HV]	ψ_a
RFe100	annealed	ferrite	100	1.0
C45	normalized	ferrite + pearlite	195	1.32
C80W2	soft annealed	spheroidal pearlite	167	1.19
85MnCrV8	soft annealed	spheroidal pearlite	186	1.31
X190Cr12	soft annealed	pearlite + carbides	216	1.56
X195CrVWMo5 4	soft annealed	pearlite + carbides	265	1.66
HS12-0-2-0	soft annealed	pearlite + carbides	223	1.25
C45W	quenched	martensite	789	1.96
C80W2	quenched	martensite	865	2.57
X190CrWV12	quenched	martensite + carbides	801	3.28
X195CrVWMo5 4	quenched	martensite + carbides	772	4.22
HS12-0-2-0	quenched	martensite + retained austenite + carbides	752	3.31

Table 1. Heat treatment, microstructure, hardness and abrasion resistance of selected steels ψ_a

The frequency of failures and the life of machines and equipment in operation depend on a number of factors - e.g. design, material used for significant parts, quality of production, response of the worked medium and operating conditions. In spite of the fact that basic knowledge on the mechanisms of separation of wear particles from the surface of the material subject to wear has already been obtained, the effect of heat and thermochemical treatment, microstructure of metallic materials on the intensity of wear have not as yet been fully explained. Structural effects in carbon and low alloy steels used in cases of low intensities of abrasive wear were studied in a number of published papers (Soroko-Novickaya, 1959; Krushchov & Babichev, 1960; Richardson, 1967; Khruschov, 1974; Eyre, 1979; Wirojanupatump & Shipway, 1999). Experimental work performed in this area has a considerable practical effect since it enables optimum selection of the steel and its heat and/or thermochemical treatment for parts working in conditions of abrasive wear.

3. Method of abrasive wear testing

Abrasive wear resistance of different steels was tested with the apparatus with an abrasive cloth. On the apparatus SVUM AB-1 the pin-shaped specimen with a 10 mm diameter slides against a corundum abrasive cloth. During the tests the disc with a fixed abrasive cloth (grain size 120) rotates and the specimen moves radially with a 3 mm/1 rotation.

Reference specimens (annealed plain carbon steel with 0.045% C, 95-105 HV) and tested specimens were used following a 1-2-1-2-1 scheme. Test parameters: sliding path – 50 m, specific pressure – 0,32 MPa, max. velocity – 0,53 m/s. The abrasive wear resistance ψ_a of the tested steels was estimated from the ratio of the wear volume of the reference material/the wear volume of the tested steel (Vocel & Dufek, 1976; Suchánek & Bakula, 1987).

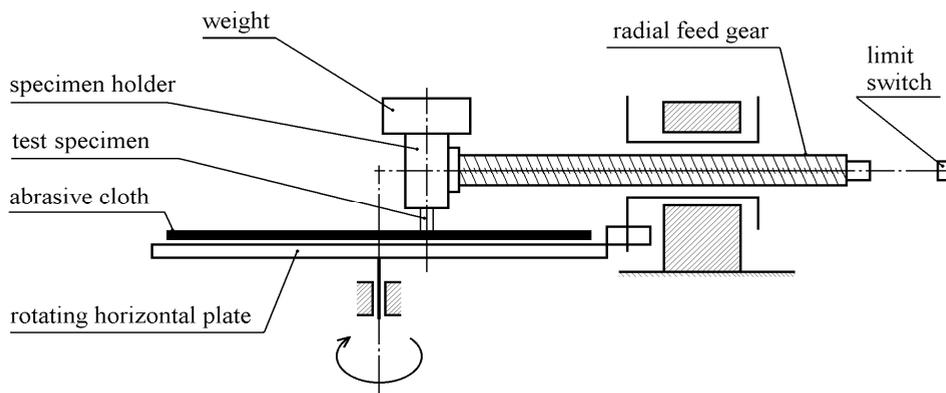


Fig. 2. Apparatus with abrasive cloth for testing abrasive wear

4. Abrasion resistance of heat treated structural steels

The effect of microstructure on abrasion resistance was experimentally tested on a selected group of currently produced structural steels. Besides heat treated carbon and low-alloyed steels, stainless steels and austenitic Mn steel (Hadfield steel) also carburizing and nitriding steels were tested. The chemical compositions of the tested structural steels are given in Table 2.

Heat treatment was applied to modify their microstructure and their physical and mechanical properties. The effect of quenching and tempering temperatures on hardness and abrasion resistance was studied in structural steels. The conditions of heat treatment can modify the microstructure and the physical and mechanical properties of low and high alloyed structural steels within a wide range. Thus consequently also their abrasion resistance changes. A summary of conditions of heat treatment, hardness and abrasion resistance of structural steels is given in Tables 3 and 4.

Grade RFe100 steel with a very low carbon content (0.045%C) used for tests of abrasive wear as a standard material has a ferritic structure after annealing.

The matrix of normalized chromium-manganese carburizing steel grade 20MnCrTi is ferritic-pearlitic. After quenching the microstructure of this steel is martensitic.

The microstructure of Cr-Ni grade 17NiCr6 4 steel after normalizing is ferritic-pearlitic. After oil quenching from 860°C the structure is martensitic. Tempering at 150°C/1h results in a small decrease in the hardness and abrasion resistance.

Steel grade	Content of elements (%)							
	C	Mn	Si	Cr	Ni	Mo	V	Others
RFe100*	0.045	0.24	0.05	--	--	--	--	--
20MnCrTi	0.20	1.08	0.34	1.10	--	--	--	0.11 Ti
17NiCr6 4	0.16	0.91	0.31	0.94	1.51	--	--	--
33CrAl6	0.36	0.82	0.21	1.58	--	--	--	1.32 Al
30CrMoV9	0.27	0.56	0.30	2.56	0.3	--	0.23	0.35 Al
37MnSi5	0.35	1.32	1.29	-	-	-	-	--
58CrV4	0.61	0.96	0.39	1.06	-	-	0.11	--
100CrMn6	0.96	1.02	0.50	1.45	-	-	-	--
X10Cr13	0.11	0.28	0.30	13.18	0.06	-	-	-
X45Cr13	0.42	0.56	0.49	14.40				
X4CrNi18-10	0.074	0.87	0.27	17.95	9.00			
X5CrNiMoTi17-12-2	0.104	0.47	0.22	16.30	10.70	1.58	-	0.57 Ti
X120Mn12	1.05	11.05	0.21	< 0.10	0.17	-	-	-

Table 2. Chemical composition of tested steels

Steel grade	Heat treatment	Hardness (HV)	Abrasion resistance ψ_a
RFe100	A 700°C/4h/furnace	95-105	1.00
20MnCrTi	A 870°C/air	214	1.28
	Q 850°C/oil	446	1.45
17NiCr6 4	A 900°C/air	261	1.31
	Q 860°C/oil	417	1.44
	Q 860°C/oil + T 150°C/1h/air	413	1.40
30CrMoV9	A 840°C/air	390	1.46
	Q 880°C/oil	495	1.53
	Q 880°C/oil + T 630°C/1h/water	341	1.36
33CrAl6	A 900°C/air	290	1.49
	Q 880°C/oil	520	1.78
	Q 880°C/oil + T 630°C/1h/oil	280	1.38
37MnSi5	A 700°C/4h/furnace	179	1.21
	A 870°C/air	225	1.29
	Q 960°C/oil	485	1.66
58CrV4	Q 960°C/oil + T550°C/1h	276	1.33
	A 720°C/4h/furnace	189	1.40
	A 870°C/air	480	1.89
	Q 820°C/water	825	2.22
	Q 860°C/oil	757	2.17
	Q 860°C/oil + T420°C/1h	527	1.55
100CrMn6	Q 860°C/oil + T670°C/1h	301	1.54
	A 750°C/4h/furnace	181	1.32
	Q 820°C/oil	847	2.59
	Q 820°C/oil + T160°C/3h	724	2.37

Table 3. Heat treatment of tested structural steels (A - annealing; Q - quenching; T - tempering)

Steel grade	Heat treatment	Hardness (HV)	Abrasion resistance ψ_a
X10Cr13	Q 940°C/oil	420	1.62
	Q 940°C/oil + T200°C/2h	420	1.65
	Q 940°C/oil + T450°C/2h	403	1.54
	Q 940°C/oil + T700°C/2h	203	1.27
X45Cr13	Q 1030°C/oil	673	2.17
	Q 1030°C/oil + T150°C/30min	624	2.30
X4CrNi18-10	Austenitizing 800°C/30min/water	166	1.55
X5CrNiMoTi17-12-2	Austenitizing 1060°C/30min/water	195	1.65
X120Mn12	Austenitizing 1070°C/water	220	1.59

Table 4. Heat treatment, hardness and abrasion resistance of stainless steels and Hadfield steel (Q - quenching; T - tempering)

The microstructure of Cr-Mo nitriding grade 30CrMoV9 steel after normalizing comprises ferrite and fine lamellar pearlite. After quenching and tempering to 630°C the microstructure is formed by highly tempered martensite. The decrease of the hardness (about 154 HV) is accompanied by the decrease of abrasion resistance from 1.53 to 1.36.

The microstructure of Cr-Mn-Al nitriding grade 33CrAl6 steel after normalizing contains ferrite and fine lamellar pearlite. After oil quenching from 880°C and tempering to 630°C the microstructure of the steel is formed by highly tempered martensite. During tempering the hardness decreases from 520 HV to 280 HV and abrasion resistance reduces from 1.78 to 1.38.

The microstructure of soft annealed steels grade 37MnSi5 and 58CrV4 is formed by a mixture of ferrite and spheroidal pearlite. These steels after normalizing have microstructures containing ferrite and lamellar pearlite. Quenching and tempering of these steels produces a microstructure of tempered martensite. The net result of tempering of these steels is a reduction of hardness and abrasion resistance (see Table 4).

Ball bearing steel grade 100CrMn6 after spheroidizing has a microstructure of spheroidized pearlite. Oil quenching produces a microstructure containing martensite and carbides. Tempering to 160°C decrease the hardness and abrasion resistance ψ_a (from 2.59 to 2.37). This steel can be used in different applications with intensive abrasive action of mineral particles.

Chromium stainless steel grade X10Cr13 after oil quenching has a martensitic-ferritic microstructure with the hardness 420 HV. Tempering of this steel (up to 450°C) changes the hardness and abrasion resistance in a narrow range.

Chromium stainless steel grade X40Cr13 has a martensitic microstructure after oil quenching owing to a higher content of carbon. It has a higher hardness and abrasion resistance than steel grade X10Cr13. This steel is usually tempered to a low temperature 150°C. During tempering the hardness of the steel decreases, but its abrasion resistance slightly increases.

The microstructure of stainless Cr-Ni or Cr-Ni-Mo steels after austenitizing and water cooling is austenitic with a hardness 166-195 HV. Their abrasion resistance is the same as in quenched and tempered low-alloyed steels ($\psi_a = 1.55-1.65$).

Austenitic manganese steel grade X120Mn12 (well known Hadfield steel) after austenitizing and water cooling has an austenitic microstructure with an original hardness of 220 HV. With continued impact and /or compression it will surface harden to over 500 HV. It should be noted that only the outer skin surface hardens. The underlayer remains highly ductile and tough. As the surface wears, it continually renews itself becoming harder. During sliding abrasion the work-hardening and the transformation of metastable austenite into strain-induced martensite does not begin. Annealed carbon or low-alloyed steels have the same or higher abrasion resistance (see Table 3 and 4).

5. Abrasion resistance of thermochemical treated structural steels

Using surface treatment on steels can increase abrasion resistance. Chemical composition and microstructure of a surface layer can be altered by surface treatment such as carburizing, nitriding and boronizing, while the bulk microstructure is modified only by transformation hardening. Case-hardening and nitriding were applied to standard mild carbon and low-alloy steels. The chemical composition of the tested steels is presented in Table 2.

The case-hardening of carbon and low-alloy steels comprises the case carburizing to the depth about 1 mm with quenching and tempering at low temperature (150 – 180°C). Usually the surface layer is saturated with carbon to a eutectoid or moderately hypereutectoid content. After quenching the microstructure of surface layer comprises high-carbon martensite and eventually a small amount of cementite. The relative abrasion resistance should therefore be comparable with that of structural or tool steels with a high carbon content.

After carburizing (the thickness of the carburized layer is 0.65 mm), quenching and tempering to a low temperature the microstructure of the carburized layer of chromium-manganese steel grade 20MnCrTi and Cr-Ni grade 17NiCr6 4 steel comprises high-carbon martensite and dispersion cementite particles.

The hardness of case-hardened steels changed in the range of HV 741-754. Relative abrasion resistance ψ_a of tested steels changed from 2.38 to 2.48. The achieved values of ψ_a corresponds to relative abrasion resistance of hardened high carbon steels. During abrasion by an abrasive cloth linear wear was very small. In the case of greater linear wear abrasion resistance drops because the hardness falls due to a carbon content reduction in the subsurface layers. The hardness and physical-mechanical properties deteriorate. The chemical composition of case-hardened steels has a very small influence on their abrasion resistance.

The microstructure of gas nitrided steels is a combination of that of the nitride surface layer and the subsurface diffusion layer. By nitriding at 500°C in gas a nitride layer was formed on both nitriding steels (Cr-Mo-V grade 30CrMoV9 and Cr-Mn-Al grade 33CrAl6) with a thickness of 0.3 mm. The thin surface nitride layer was removed by grinding.

Steel grade	Heat treatment	Hardness (HV)	Abrasion resistance ψ_a
20MnCrTi	C 940°C + Q 820°C/oil + T 150°C/1h/air	754	2.38
17NiCr6 4	C 940°C + Q 820°C/oil + T 150°C/1h/air	741	2.48
33CrAl6	Q 880°C/oil + T 630°C/1h/oil + N 500°C	953	2.05
30CrMoV9	Q 880°C/oil + T 630°C/1h/water + N 500°C	894	1.99

Table 5. Thermochemical treatment of tested structural steels (Q - quenching; T - tempering; C - carburizing; N - nitriding)

In nitriding steels, after removal of the surface nitride layer, surface hardness was in the range 894 - 953 HV which is about 153 - 212 HV higher than in carburized surfaces. The relative abrasion resistance Ψ_a in nitriding steels was 1.99 - 2.05, which is lower than that in carburized low-alloy steels (see Table 5). Nitrided layers have increased abrasion resistance, but their higher hardness is not expressed in higher abrasion resistance in comparison with the surface layers of case-hardened steels. A relative thin surface layer with high hardness does not facilitate their application in the conditions of intensive abrasion. After removing the nitrided layer erosion resistance decreases very quickly.

Table 6 gives for comparison the values of the abrasion resistance of carburized and nitrided steels and carbon steels tested on an apparatus with an abrasive cloth under identical testing conditions. In quenched carbon steels abrasion resistance and also hardness drop markedly at relatively low tempering temperatures. The slightly higher values of hardness and abrasion resistance of quenched grade C60 and C80W2 steels are therefore in good agreement with the values of hardness and abrasion resistance of carburized steels.

Steel grade	Content of carbon (%)	Heat treatment or thermo-chemical treatment	Hardness (HV)	Abrasion resistance ψ_a
20CrMnTi	0.20	carburizing	754	2.38
17NiCr6	0.16	carburizing	741	2.48
33CrAl6	0.36	nitriding	953	2.05
30CrMoV9	0.27	nitriding	894	1.99
C60	0.68	hardened	851	2.46
C80W2	0.85	hardened	874	2.54
C100W2	0.99	hardened	774	1.87

Table 6. Comparison of hardnesses and relative abrasion resistances of carburized, nitrided and selected carbon steels.

In nitriding steels the surface hardness is higher than that in carburized surfaces, however the abrasion resistance is lower. The hardening of surface layers by dispersion nitrides and interstitial nitrogen atoms only insufficiently prevents penetration of the edges and peaks

of hard abrasive particles and scratching which occur during the relative motion of the abrasive medium and the nitrified surface.

Boronizing is a thermochemical treatment that diffuses boron through the surface of metallic substrates. On the surface of boronized ferrous alloys, a compound layer is generally developed. This compound layer (or boride layer) is normally composed of two sublayers; the outermost and the innermost are rich in FeB and Fe₂B, respectively (Martini et al., 2004). Boronized steels exhibit high wear resistance owing to the high hardness of the boride layer (typically 1500-1800 HV). For abrasion conditions boronizing is superior to carburizing and nitriding (Wang & Hutchings, 1988; Lin et al., 1990; Atik et al., 2003). But the boride layers are thinner than the carburized or nitrified layers (typically 20 – 120 μm).

6. Abrasion resistance carbon and low-alloyed tool steels

Tool steels are basically medium- to high-carbon steels with specific elements included in different amounts to provide special characteristics. Carbon in the tool steel is provided to help to harden the steel to greater hardness for cutting and wear resistance. Other elements are added to provide greater toughness or strength. These steels were developed to resist wear at temperatures of forming and cutting applications. According to their application they can be divided into six categories – cold work, shock resisting, hot work, high speed, mold and special purpose tool steels. Mainly cold work tool steels and high speed steels use in conditions of abrasive wear. Chemical composition of several carbon, low-alloyed, ledeburitic and high speed steels is given in the Table 7. These steels were hardened by processes currently recommended by producers (see Table 8). Cold work tool steels are water quenched (carbon steels) or oil quenched (alloyed steels) and tempered in the range of 150 to 250°C. After quenching their microstructure constitutes martensite with some amount of retained austenite. Tempering to low temperatures decreases the hardness and partly eliminates the high internal stresses of these steels.

Steel grade	Content of elements (%)							
	C	Mn	Si	Cr	Ni	Mo	V	W
C45W	0.48	0.80	0.31	-	-	-	-	-
C80W2	0.85	0.24	0.46	-	-	-	-	-
C110W1	1.16	0.29	0.26	-	-	-	-	-
90MnCrV8	0.86	1.90	0.31	0.28	-	-	0.16	-
X185CrWV12	1.85	0.23	0.22	11.93	--	--	0.31	1.47
X195CrVWMo5 4	1.95	0.42	0.38	5.12	--	0.84	4.19	1.50
HS 12-0-4	1.28	0.32	0.09	4.38	--	0.08	3.91	11.85
HS 12-0-2	0.86	0.26	0.25	4.26	--	0.005	2.15	12.00

Table 7. Chemical composition of carbon, low-alloyed, ledeburitic and high speed tool steels

Steel grade	Heat treatment	Hardness (HV)	Abrasion resistance Ψ_a
C45W	Q 810°C/30min/water	789	1.96
	Q 820°C/30min/water + T200°C/2h/air	645	1.54
C80W2	Q 790°C/30min/water	874	2.54
	Q 800°C/30min/water + T200°C/2h/air	740	1.85
C110W1	Q 780°C/30min/water	889	2.58
	Q 780°C/30min/water + T200°C/2h/air	740	1.82
90MnCrV8	Q 780°C/oil	789	2.27
	Q 780°C/oil + T200°C/2h/air	670	1.77
	Q 780°C/oil + T300°C/2h/air	641	1.54

Table 8. Heat treatment of carbon and low-alloy tool steels (A - annealing; Q - quenching; T - tempering)

7. Abrasion resistance of chromium ledeburitic steels

The microstructure of ledeburitic chromium steel X185CrWV12 after soft annealing is ferritic with a large amount of fine and coarse $M_{23}C_6$ and M_3C_7 complex carbides. After quenching (980°C/1h/oil) the microstructure is formed by fine martensite with a large amount of fine spheroidal and coarse carbides. The share of retained austenite is low - when quenching from high temperatures it gradually grows and the share of martensite and carbides decreases. After quenching from 1150°C the microstructure is austenite-carbide with coarser carbides precipitated at grain boundaries. A further increase of the quenching temperature is accompanied by dissolution of carbides and coarsening of austenitic grains. Due to fluctuations of the chemical composition, melting down of grain boundaries and reverse precipitation of ledeburite during cooling can locally occur.

When tempering to 250°C the decrease of hardness is not accompanied by marked structural modifications. When tempering to 400°C the amount of fine carbides slightly increases. Precipitation of carbides and decomposition of retained austenite occur at higher tempering temperatures.

Ledeburitic chromium steel X185CrWV12 is frequently used in conditions of intensive abrasive wear. Abrasion resistance Ψ_a grows with increasing quenching temperatures up to 1100°C, when it reaches its maximum value ($\Psi_a=4.13$). The hardness of quenched specimens decreases from 801 HV to 621 HV. A further increase of the quenching temperature is accompanied by a decrease of the values of Ψ_a . Tempering in the zone of primary hardness exhibits a decrease of both hardness and abrasion resistance, whereas the decrease is only slight, up to a tempering temperature of 250°C (see Table 9).

The microstructure of ledeburitic Cr-V grade X195CrWVMo5 4 steel after soft annealing comprises ferrite, $M_{23}C_6$ and M_3C_7 complex carbides and special MC carbides. The specimens were oil quenched from a temperature within the range 950 - 1200°C. With a growing temperature gradually the share of martensite decreases, complex and special carbides dissolve so that the contents of carbon and carbide-forming alloy elements in austenite grow. The stability of austenite grows and the positions of the M_s and M_f points shift to lower values. Therefore when quenching from high temperatures the share of retained austenite grows whilst the shares of martensite and carbides decrease.

Ledeburitic Cr-V grade X195CrVWMo5 4 steel belongs to materials with high abrasion resistance. The abrasion resistance Ψ_a grows with a growing quenching temperature and reaches a maximum value for quenching from 1150°C ($\Psi_a=6.02$). Hardness with a growing temperature drops from 772 HV for quenching from 950°C to 387 HV for quenching at 1200°C. The hardness of the steel quenched from 950°C during tempering decreases, however the decrease is up to 250°C/2h/air only slight. Tempering in the zone of primary hardness also showed a decrease of abrasion resistance. The decrease of hardness and abrasion resistance was marked when tempering to temperatures above 250°C.

In the tested ledeburitic steels alloyed with Cr and Cr-V a positive effect was found of growing quenching temperature on enhancement of abrasion resistance. The maximum value of the relative abrasion resistance was achieved by oil quenching from 1100°C in steel grade X185CrWV12 and from 1150°C in steel grade X195CrVWMo5 4. The relative growth of Ψ_a in steel grade X185CrWV12 after quenching from 1100°C is 26% compared with the value of Ψ_a after quenching from 980°C. The relative growth of abrasion resistance in steel grade X195CrVWMo5 4 after quenching from 1150°C is 42.7% compared with the value of Ψ_a for quenching from 950°C.

Steel grade	Heat treatment	Hardness (HV)	Abrasion resistance ψ_a
X185CrWV12	A 770°C/4h/furnace	216	1.49
	Q 980°C/oil	801	3.28
	Q 980°C/oil + T 150°C/2h/air	774	3.17
	Q 980°C/oil + T 250°C/2h/air	702	2.99
	Q 980°C/oil + T 400°C/2h/air	656	2.66
	Q 980°C/oil + T 500°C/2h/air	639	2.63
	Q 980°C/oil + T 600°C/2h/air	512	2.09
	Q 980°C/oil + T 700°C/2h/air	345	1.61
	Q 1050°C/oil	765	3.48
	Q 1100°C/oil	621	4.13
	Q 1150°C/oil	385	3.84
	Q 1200°C/oil	374	3.58
X195CrVWMo5 4	A 770°C/4h/furnace	265	1.66
	Q 950°C/oil	772	4.22
	Q 950°C/oil + T 150°C/2h/air	754	3.93
	Q 950°C/oil + T 250°C/2h/air	770	3.84
	Q 950°C/oil + T 400°C/2h/air	685	2.98
	Q 950°C/oil + T 500°C/2h/air	650	2.85
	Q 950°C/oil + T 600°C/2h/air	512	2.40
	Q 950°C/oil + T 700°C/2h/air	332	1.64
	Q 1000°C/oil	730	4.50
	Q 1050°C/oil	723	5.00
	Q 1100°C/oil	523	5.73
	Q 1150°C/oil	454	6.02
Q 1200°C/oil	387	5.59	

Table 9. Heat treatment of ledeburitic chromium steels (A - annealing; Q - quenching; T - tempering)

The decisive role in increasing the abrasion resistance with growing quenching temperatures is assigned to the growing volume share of retained austenite, which, during plastic deformation caused by penetration of abrasive particles and scratching of the surface subject to wear, is hardened and partially transforms to deformation martensite (Berns et al., 1984; Suchánek & Bakula, 1987). The positive effect of the growing volume share of retained austenite in the microstructure of ledeburitic chromium and chromium-vanadium steels is related with the growth of energy required for the separation of the unit volume of particles. The sum of energies for phase transformation, internal stresses and for creation of a critical dislocation density is much higher than the decrease of energy required for penetration of abrasive particles into the surface subject to wear (decrease of hardness) and energy required for the break-up of carbides (decrease of volume share of carbides in the microstructure). Modifications of the microstructure of ledeburitic steels caused by the growth of quenching temperatures are in Table 10.

Steel grade	Heat treatment	Volume share of retained austenite (%)	Surface share of carbides (%)	Type of carbides
X185CrWV12	A 770°C/4h/furnace	0	17.1	M ₇ C ₃
	Q 980°C/1h/oil	18.7	13.7	M ₇ C ₃
	Q 1050°C/1h/oil	36.1	12.65	M ₇ C ₃
	Q 1100°C/1h/oil	45.9	11.56	M ₇ C ₃
	Q 1150°C/1h/oil	89.4	5	M ₇ C ₃
	Q 1200°C/1h/oil	97	2.1	M ₇ C ₃
X195CrWVMo 5 4	A 770°C/4h/furnace	0	13.95	MC (M ₇ C ₃ , M ₂₃ C ₆)
	Q 950°C/1h/oil	15.2	8.29	MC (M ₇ C ₃)
	Q 1000°C/1h/oil	24.2	6.04	MC (M ₇ C ₃)
	Q 1050°C/1h/oil	34.5	3.99	MC
	Q 1100°C/1h/oil	53.3	3.4	MC
	Q 1150°C/1h/oil	72.7	2.37	MC
	Q 1200°C/1h/oil	92.5	1.37	MC

Table 10. Volume share of retained austenite, surface share and type of carbides in ledeburitic steels

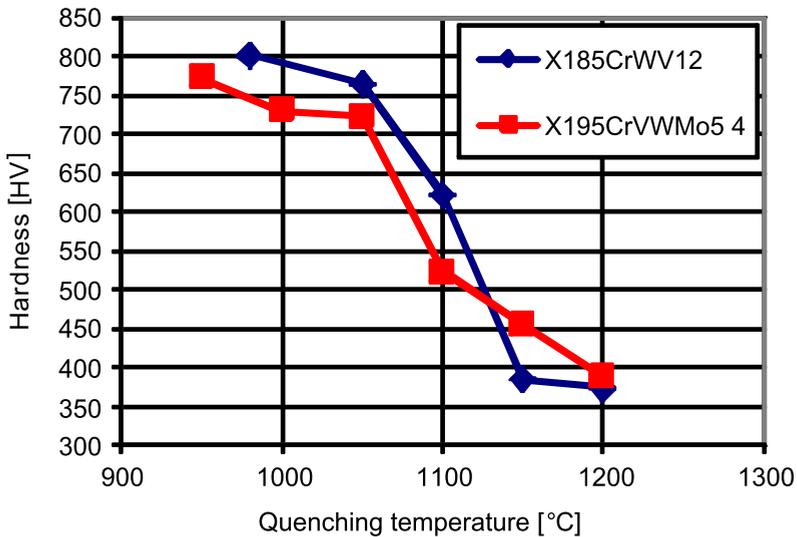


Fig. 3. Effect of quenching temperature on hardness of ledeburitic steels

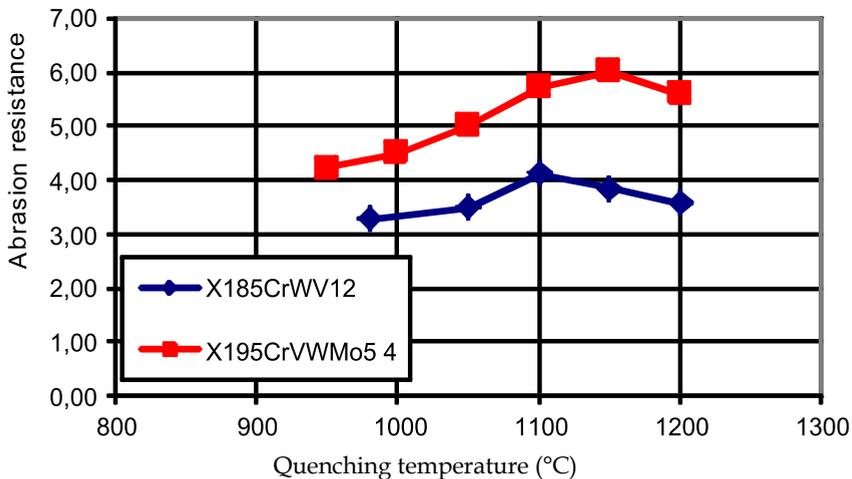


Fig. 4. Abrasion resistance of of ledeburitic steels vs. quenching temperature

The decrease of abrasion resistance with growing tempering temperatures is related with structural and phase modifications which occur both in martensite and retained austenite. Due to the fact that the value of Ψ_a dropped after quenching to 250°C/2h/air only by 9%, it can be assumed that internal stress relief and creation of zones enriched with carbon which gradually take the character of coherent or semicoherent particles do not considerably decrease abrasion resistance.

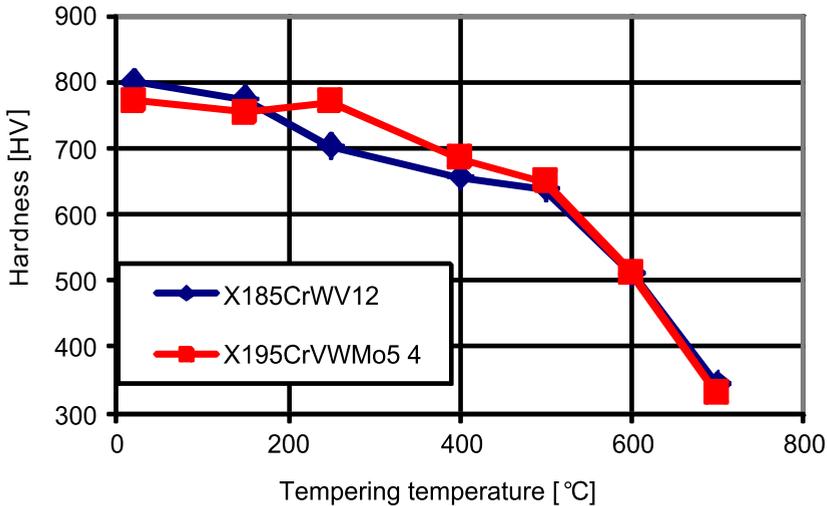


Fig. 5. Hardness of ledeburitic steels vs. tempering temperature

A marked drop of Ψ_a appeared at a tempering temperature of 400°C. This is related with a drop of the concentration of carbon in martensite and in retained austenite and creation of ϵ -carbides. A decrease of the carbon content in martensite impairs its physical and mechanical properties in spite of the fact that formation of ϵ -carbides causes hardening. Another factor which decreases abrasion resistance is the anisotropic decomposition of retained austenite. Tempering to temperatures above 400°C leads to a marked decrease of resistance to wear and also hardness (see Fig. 5 and 6).

Values of abrasion resistance after tempering to temperatures in the zone of primary hardness drop with growing tempering temperatures. Ledeburitic Cr and Cr-V steels should preferably be tempered to a maximum temperature of 250°C/2h/air.

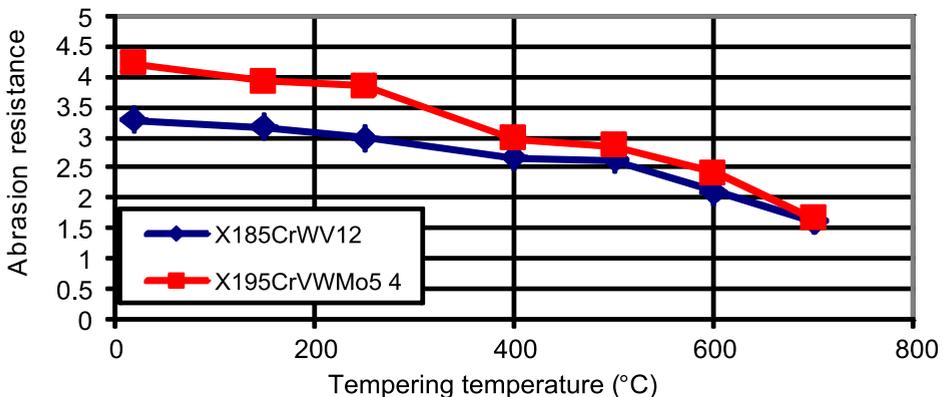


Fig. 6. Abrasion resistance Ψ_a of ledeburitic steels vs. tempering temperature

8. Abrasion resistance of high speed steels

The microstructure of high-speed grade HS 11-0-4 steel after soft annealing is pearlite-carbide. The microstructure after quenching comprises martensite, retained austenite and carbides. With growing temperatures within the range 1000 – 1270°C M_6C and $M_{23}C_6$ complex carbides and MC special carbides (at temperatures >1200°C) dissolve. With an increasing content of carbon and carbide forming elements the hardness of martensite grows and at high quenching temperatures also the content of retained austenite (up to 20 – 25%). By tempering in the zone of primary hardness internal stresses are relieved, carbon diffuses from the martensite lattice, ϵ -carbides are formed and at higher tempering temperatures carbon precipitation and decomposition of retained austenite occurs. In the zone of secondary hardness at repeated tempering, anisotropic decomposition of retained austenite, tempering of martensite and strengthening of the martensitic matrix by precipitated type M_6C , $M_{23}C_6$ and MC carbides occurs.

The microstructure of high-speed grade HS 11-0-2 steel oil quenched from temperatures in the range 1200 – 1270°C comprises martensite, retained austenite, and M_6C , $M_{23}C_6$ complex carbides and special MC carbides. With growing quenching temperatures the share of carbides and martensite decreases and the share of retained austenite grows. In the zone of secondary hardness at repeated tempering the following processes occur: anisotropic decomposition of retained austenite, tempering of martensite and hardening of the martensitic matrix by precipitated secondary carbides. Hardnesses achieved by tempering in the zone of maximum secondary hardness are in many cases higher than those achieved after quenching.

Abrasion resistance in high-speed grade HS11-0-4 steel grows with a growing quenching temperature and slightly decreases in the zone of primary hardness with tempering temperatures growing up to 250°C (see Table 10). The same behaviour of abrasion resistance was found in high-speed grade HS11-0-2 steel. A high increase of hardness and abrasion resistance with growing quenching temperatures is related with structural modifications in high-speed steels. Carbides dissolve and the carbon content and share of carbide-forming elements in austenite grows. This is manifested by greater stability during quenching. The share of retained austenite grows. The highest values of Ψ_a ($\Psi_a=6.88$) were found in grade HS 11-0-4 steel for quenching from 1270°C, i.e. from the highest point of the range of quenching temperatures recommended by the producer of the steel (see Table 11).

The decrease of abrasion resistance in the zone of primary hardness is more marked in steels quenched from higher temperatures. When tempering in the zone of secondary hardness, both the hardness and the values of Ψ_a grow with rising quenching temperatures. Maximum abrasion resistance and hardness of quenched and tempered specimens were achieved after three-fold repeated tempering to 560°C. Tempering to temperatures above the maximum of secondary hardness leads to a marked decrease of both hardness and abrasion resistance (see Table 9).

High-speed steels can be considered as composite materials where large primary carbides (1 – 10 μm) are dispersed in the martensitic matrix together with a much finer dispersion of small secondary carbides (<100 nm). Secondary carbides are the cause of precipitation hardening of the martensitic matrix. Primary carbides, namely MC and M_6C (1500 – 2800 HV) are harder than the matrix and consequently enhance abrasion resistance (Suchánek & Průcha, 1984; Badisch & Mitterer, 2003; Wei et al., 2006).

Steel grade	Heat treatment	Hardness (HV)	Abrasion resistance ψ_a
HS11-0-4	A 800°C/4h/furnace	223	1.25
	Q 1000°C/oil	578	1.98
	Q 1050°C/oil	636	2.34
	Q 1050°C/oil + T 150°C/1h/air	753	2.39
	Q 1100°C/oil	743	3.22
	Q 1100°C/oil + T 150°C/1h/air	800	2.84
	Q 1100°C/oil + T 250°C/1h/air	698	2.86
	Q 1150°C/oil	826	3.90
	Q 1150°C/oil + T 150°C/1h/air	801	3.70
	Q 1150°C/oil + T 250°C/1h/air	685	3.52
	Q 1150°C/oil + T 400°C/1h/air	654	3.44
	Q 1170°C/oil + 3×T 610°C/45'/air	740	4.27
	Q 1200°C/oil + T 150°C/1h/air	772	4.31
	Q 1200°C/oil + T 250°C/1h/air	675	3.60
	Q 1210°C/oil	853	6.03
	Q 1210°C/oil + 3×T 560°C/45'/air	843	4.60
	Q 1210°C/oil + 3×T 600°C/45'/air	739	3.72
	Q 1210°C/oil + 3×T 640°C/45'/air	653	3.04
	Q 1240°C/oil	848	6.10
	Q 1240°C/oil + 3×T 150°C/45'/air	828	4.56
	Q 1240°C/oil + 3×T 250°C/45'/air	732	3.74
	Q 1240°C/oil + 3×T 400°C/45'/air	728	3.68
	Q 1240°C/oil + 3×T 500°C/45'/air	757	4.56
	Q 1240°C/oil + 3×T 560°C/45'/air	882	5.15
	Q 1240°C/oil + 3×T 600°C/45'/air	761	4.04
	Q 1240°C/oil + 3×T 640°C/45'/air	692	2.94
	Q 1240°C/oil + 3×T 680°C/45'/air	598	2.25
Q 1270°C/oil	802	6.88	
Q 1270°C/oil + 3×T 560°C/45'/air	900	6.33	
HS11-0-2	Q 1200°C/oil	709	2.59
	Q 1200°C/oil + 3×T 560°C/45'/air	791	3.06
	Q 1240°C/oil	758	2.89
	Q 1240°C/oil + 3×T 560°C/45'/air	852	3.34
	Q 1240°C/oil + 3×T 570°C/45'/air	887	2.92
	Q 1240°C/oil + 3×T 600°C/45'/air	766	2.91
	Q 1240°C/oil + 3×T 640°C/45'/air	671	2.57
	Q 1240°C/oil + 3×T 670°C/45'/air	587	2.14
	Q 1270°C/oil	752	3.31
Q 1270°C/oil + 3×T 560°C/45'/air	879	3.63	

Table 11. Heat treatment, hardness and abrasion resistance of high-speed steels (A - annealing; Q - quenching; T - tempering)

Enhancement of hardness and abrasion resistance with growing quenching temperatures is related with structural modifications of high-speed steels. M_6C and $M_{23}C_6$ complex carbides dissolve at quenching temperatures and special MC carbides dissolve at temperatures above 1200°C. The presence of higher carbon and carbide forming additions induces growth of the strength and hardness of martensite and at high temperatures also growth of the volume share of retained austenite (up to 20-25%). The higher strength of the martensitic matrix manifests itself positively by a higher resistance to scratching by abrasive Al_2O_3 particles. Besides the matrix also special MC carbides with hardnesses in the range 2700-2990 HV play a significant role – they blunt the cutting edges of abrasive particles and decrease their scratching effect. The decrease of macrohardness after quenching from 1270°C was not accompanied by a decrease of relative abrasion resistance. It can be assumed that hardening of retained austenite and its partial transformation to martensite initiated by the penetration of edges of abrasive particles and their scratching effect has eliminated the drop of the share of carbides and grain coarsening. During tempering in the zone of primary hardness (150°C/30'/air) the following processes occur : internal stress relief, diffusion of carbon from the martensite lattice and formation of ϵ -carbides. These processes proceed with a higher intensity after quenching from higher temperatures and hence the decrease of Ψ_a values is more pronounced.

A further drop of the values of abrasion resistance during tempering at 250°C and/or 400°C is less pronounced since the matrix is hardened by fine particles.

A marked maximum of hardness and abrasion resistance during tempering in the zone of maximum secondary hardness (560°C/3x45') is closely related with the anisotropic decomposition of retained austenite and hardening of the matrix by precipitated M_6C , $M_{23}C_6$ and MC carbides [25]. High-speed grade HS 11-0-2 steel has a lower content of carbon and vanadium and hence also a lower share of carbides. Compared with high-speed grade HS 11-0-4 steel it has a markedly lower abrasion resistance. The high content of vanadium both in high-speed and ledeburitic steels positively affects abrasion resistance.

9. Conclusions

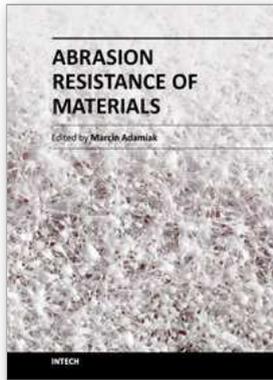
1. Abrasion resistance of carburized low-alloy steels is on the same level as in high-carbon structural and tool steels.
2. Resistance of nitrided steels to abrasion by hard particles is lower than that of carburized low-alloy steels.
3. Relative abrasion resistance of ledeburitic chromium and high-speed steels grows with growing quenching temperatures. In ledeburitic chromium grade X185CrWV12 steel maximum abrasion resistance was achieved by quenching from 1100°C whilst in ledeburitic chromium-vanadium steel the optimum quenching temperature was 1150°C. Maximum abrasion resistance in high speed steels was achieved by quenching from 1270°C.
4. Values of relative abrasion resistance after tempering to temperatures in the zone of primary hardness drop with growing tempering temperatures. Ledeburitic Cr and Cr-V steels should preferably be tempered to a maximum temperature of 250°C/2h/air.
5. The values of abrasion resistance in high-speed steels in the zone of secondary hardness grow with growing quenching temperatures. The values of Ψ_a achieved are lower than those obtained only by quenching.

6. Relative abrasion resistance in high-speed steels quenched and tempered in the zone of secondary hardness drops with growing tempering temperatures. The optimum tempering temperature is 560°C/3x45'/air.

10. References

- Atik, E., Yunker, U. & Meric, C. (2003). The effects of conventional heat treatment and boronizing on abrasive wear and corrosion of SAE 1010, SAE 1040, D2 and 304 steels. *Tribology Intern.*, Vol. 36, pp. 155-161, ISSN 0301-679X
- Badisch, E., & Mitterer, C. (2003). Abrasive wear of high speed steels: Influence of abrasive particles and primary carbides on wear resistance. *Tribology Intern.*, Vol. 36, pp. 765-770, ISSN 0301-679X
- Berns, H., Gümpel, P., Trojahn, W. & Weigand, H. H. (1984). Gefüge und abrasiver Verschleiß von Kaltarbeitsstählen mit 12% Cr. *Archiv f. Eisenhüttenwesen*, Vol. 55, No. 6, pp. 267-270
- Eyre, T. S. (1979). *Wear Resistance of Metals*. In: *Treatise on Materials Science and Technology*, vol. 13, Wear, Academic Press, Inc., pp. 363-442
- Filippova, L. T. & Goldshtein, J. J. (1979). Effect of composition and structure on the resistance of steels to abrasive wear. *Metalloved. Term. Obrab. Met.*, No. 2, pp. 10- 15, ISSN 0026-0673 (in Russian)
- Fremunt, P., Musilova, L. & Pacal, B. (1971) Effect of V on the increase in abrasion resistance of ledeburitic Cr steels. *Slévárenství*, Vol. 19, No. 11, pp. 466-471 (in Czech)
- Grinberg, N. A. Livshits, L. S. & Sherbakova, V. S.(1971). Influence of alloying ferrite and carbide phase on wear resistance of steels. *Met Sci Heat Treat.*, Vol. 13, No. 9-10, pp. 768-770 ISSN 0026-0673
- Krushchov, M. M. & Babichev, M. A. (1960). *Research of metal wear*, Publ. House AN SSSR, Moscow, (in Russian)
- Krushchov, M. M. & Babichev, M. A. (1970). *Abrasive wear*. Publ. House Science (Nauka), Moscow, (in Russian)
- Khrushchov, M. M. (1974). Principles of abrasive wear. *Wear*, Vol. 28, pp. 69-88, ISSN 0043-1648
- Larsen-Badse, J. & Mathew, K. G. (1966). Abrasion of Some Hardened and Tempered Carbon Steels. *Trans. Metall. Soc. AIME*, Vol. 236, pp. 1461-1466
- Lin, Z., Wang, Z. & Sun, X. (1990). The influence of internal stress and preferred orientation on the abrasive wear resistance of a boronized medium carbon steel. *Wear*, Vol. 138, pp. 285-294, ISSN 0043-1648
- Martini, C., Palombarini, G., Poli, G. & Prandstraller, D. (2004). Sliding and abrasive wear behaviour of boride coatings. *Wear*, Vol. 256, pp. 608-613 ISSN 0043-1648
- Moore, M.A. (1974). The relationship between the abrasive wear resistance, hardness and microstructure of ferritic materials. *Wear*, Vol. 28, pp. 59-68, ISSN 0043-1648
- Petrov, I.V. & Grinberg, N.A. (1968). Wear resistance of hardfacing under abrasive wear conditions. *Svar. Proizv.*, No. 2, pp. 30-33 (in Russian)
- Popov, V. S., Nagornyj, P.L. & Garbuzov, A. S. (1969). Specific energy of rupture of carbides and the wear resistance of alloys. *Fizika Metallov Metallovedenie*, Vol. 28, No.2, pp. 332-336 (in Russian)
- Popov, V. S. & Nagornyj, P.L. (1969). Influence of carbides on the abrasive wear resistance of alloys. *Liteinoe Proizv.*, No. 8, pp. 27-29 (in Russian)

- Popov, V.S. & Nagorny, P.L. (1970). Abrasive wear of chromium alloys. *Liteinoe Proizv.*, No. 3, pp. 27-28 (in Russian)
- Richardson, R. C. D. (1967). The wear of metal by hard abrasives. *Wear*, Vol. 10, pp. 353-382, ISSN 0043-1648
- Roberts, G. A., Hamaker, J. C. & Johnson, A. R. (1962). *Tool Steels*. ASM, Metal Park, Ohio
- Schabuyev, S. A., Mrkrtychan, Y. S & Pishchanskiy, V. I.(1972). Influence of composition and structure of chromium alloys on their abrasion resistance. *Liteinoe Proizv.*, No. 3, pp. 28-29 (in Russian)
- Simm, W. & Freti, S. (1989) Abrasive wear of multiphase materials. *Wear*, Vol.129, pp.105-121, ISSN 0043-1648
- Soroko-Novickaya, A. A. (1959). Wear resistance of carbon steel with different structure. *Friction and Wear in Machines (Trenie i iznos v mashinach)*, Vol. 13, pp. 5-18, Publ. House AN SSSR, Moscow.
- Suchánek, J. & Průcha, J.(1984) The effect of thermal treatment and structure on the resistance to abrasive wear of the high speed cutting steel 19 810. In: *Proc. 2-nd Symposium „INTERTRIBO 84“*, pp. 678-682, High Tatras, October 3-5,1984 (in Czech)
- Suchánek, J. & Bakula, J. (1987). Influence of structural factors on resistance of metallic materials in abrasive wear. *Strojirenstvi*, Vol. 37, pp. 232-236 (in Czech)
- Suchánek, J., Kuklík, V. & Zdravecká, E. (2007). *Abrazivní opotřebení materiálů (Abrasive wear of materials)*. CTU Prague, ISBN 978-80-01-03659-4 (in Czech)
- Tsy-pin, I.I. (1983). *Wear resistant white cast irons. Structure and properties*. Moscow, Metallurgiya (in Russian)
- Uetz, H. (1986). *Abrasion and Erosion*, Carl Hanser Verlag, München, Wien
- Vocel, M. & Dufek, V. (1976). *Friction and wear of machine parts*. SNTL, Prague, 374 pp. (in Czech)
- Wang, A. G. & Hutchings, I. M. (1988). Mechanisms of abrasive wear in a boronized alloy steel. *Wear*, Vol. 124, pp. 149-163, ISSN 0043-1648
- Wei, S. , Zhu, J. & Xu, L. (2006). Effect of vanadium and carbon on microstructures and abrasive wear resistance of high speed steel. *Tribology Intern.*, Vol. 39, pp. 641-648, ISSN 0301-679X
- Wirojanupatump, S. & Shipway, P. H. (1999). A direct comparison of wet and dry abrasion behaviour of mild steel. *Wear*, Vol. 223-235, pp. 655-665, ISSN 0043-1648
- Zum Gahr, K.H. (1985). Abrasive wear of two-phase metallic materials with a coarse microstructure. In: K.C. Ludema, (Ed.), *International Conference on Wear of Materials*, ASME, Vancouver, p. 793



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