Effect of Copper on Tribological Characteristics and Subsurface Structure of Cast Fe-Cr-C Alloys in Sliding Friction

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Abstract
The purpose of this work is to research the tribological characteristics and peculiarities of subsurface structure of friction layers formation of the cast Fe-Cr-C (1.2% C, 17–19% Cr) alloys with the copper content lower (0.4%) or higher (14.0%) than its limit of solubility in the matrix of the alloy. The different contents of copper in cast alloys have a significant influence on the characteristics of the alloy structure in the original state and subsurface friction layers and thus influence the tribological characteristics of these alloys. The alloy with 14.0% copper has minimal wear rate under dry and boundary frictions at the pressures of 1 and 5 MPa. This is achieved through optimizing the parameters of the fine structure of the surface friction layers of alloys and through plating effect of copper transferring from specimen to the counterbody and preventing the friction pair from severe wear.

Keywords: Fe-Cr-C alloy, copper, sliding friction, subsurface structure

1. Introduction
Technological progress and economic prosperity demand continuous development of new materials. To this category belong the materials with high operating characteristics under extreme conditions. The materials of many equipment parts (especially parts of friction units) operate in these conditions. The performance of machinery in terms of quality and reliability is strongly associated with the tribological behavior of the materials used. Cast alloys can be used as such materials. Varying their chemical composition, modes of heat treatment, and using special technological methods, it is possible to synthesize the alloys that satisfy the necessary requirements.

One of the methods resulting in increased durability of alloys in sliding friction is optimization of initial structure of alloys which is then able to generate subsurface structures on friction layers. This ensures maximum durability of friction parts in the condition of sliding friction.

Copper is used as an alloying element in this work. The problem of optimal alloying of alloys by copper for a long time attracted the attention of material scientists, metallurgists, and tribologists. Copper can give alloys necessary combinations of physicomechanical characteristics (Mikhaylov, 1926; Gudzov & Mikhaylov-Mikheev, 1928). There are date showing influence of copper on structure, phase transformation, chemical and technological properties of alloys, and their operating characteristics. This allows copper alloying to be used in Fe-Cr-C alloys used by energy industry (Lunev, 1955; May & Schetky, 1982).

Some of the studies (Tikhonovich et al., 1977; Novytsky et al., 2002) show positive effect of copper in Fe-Cr-C alloys. These alloys must satisfy the whole complex of requirements-to be corrosion and erosion resistant, to resist abrasive influence, and to have high wear resistance under sliding friction in different media. High wear resistance of such alloys under boundary friction is reached by formation in friction surface layers of dissipative structures which are capable of dissipation of friction energy by thermal fields, and also by convertible phases and structural transformations. The minimal wear rate of such alloys is achieved by formation of the specific dynamic ratios between phases and the lattice irregularities in subsurface structures of friction layers of alloys (Novytsky et al., 2002; Gorskiy et al., 1981; Novytsky, 2004; Novytsky & Tikhonovich, 2000). Stabilization of these ratios for as long as possible favours localization of wear process to friction layers. It counteracts the transition from fatigue wear to adhesion wear, when the underlying layers of a material are involved in the wear process.
The increase of chromium content in friction surface layers can minimize the wear rate of such alloys by reduction of oxidation rate, thus increasing the time between activation and passivation processes in these layers (Gorskiy et al., 1981). It is also determined that the protective films of high-strength alloys alloyed by oxygen (AAO) are formed on friction surfaces of Fe-Cr-C alloys. These AAOs have liquid-like structure, microvolumes of which at contact points of friction surfaces are capable of transforming into a structurally unstable state, favoring hydrodynamic friction in such points without loss of layer continuity, and preventing the accumulation of lattice defects which can lead to surface fracture of alloys (Gorskiy et al., 1987; Gorskiy, 1989).

The protection of alloy friction surface layers against fracture is also achieved by using various solid lubrications: disulfide molybdenum, graphite, gold, silver, indium, etc., which deposit on friction surfaces. At the same time, the increase of power transmitted through the friction parts necessitates the use of cast alloys with matrix solid lubricant, i.e. lubricant located within the alloy matrix. The combination of several components with different physical-mechanical properties allows creating compositions with a number of unique and very important properties for engineering: high heat conductivity, self-lubrication, high damping capacity, etc. (Beliy, 1982; Bushe et al., 1982).

The most advantageous in terms of loading and self-lubricating are the macroheterogeneous pseudo-alloys (Anziferov & Tcherepanova, 1970; Fedorchenko et al., 1982, 1984) and monotectic alloys (Xie et al., 2004). Depending on external friction conditions on surface of such alloys, a film of soft material on hard component parts is formed due to a difference of thermal expansion of antifriction and hard components under heating of friction pair, or as a result of mechanical smearing.

It is possible to use a solid lubricant which is distributed in alloy structure as soft inclusions. High copper content ε-phase can be used as such inclusions. The ε-phase appears by introducing an amount of copper into an alloy which surpasses the limit of solubility of copper in this specific alloy. During friction copper will emerge on surface contacting parts, protecting them from direct impact.

Manufacturing of such alloys with heterogeneous structures has been investigated in works (Kirievskiy & Izyumova, 1992; Tikhonovich et al., 1994). It is established, that due to additional alloying, changes of kinetic and parameters of crystallization it is possible to obtain a novel class of alloys. The structure of these alloys, beside hard inclusions of complex carbides, contains a soft component (the high-copper ε-phase) which can serve as a solid lubricant. The tribotests of such alloys under dry and boundary frictions (Novytskyy et al., 2000) have shown that these alloys can be used for friction units.

The aim of this work is to study the tribological characteristics and peculiarities of subsurface structures in friction layers formation of Fe-Cr-C alloys with copper content lower or higher than the limit of copper solubility in the alloy.

2. Materials and Methods

The following Fe-Cr-C alloys were chosen as object of the study: (1) – (C~1.2%, Cr = 17–19%), the base alloy, (2) – (C~1.2%, Cr = 17–19%) + ~ 0.4% Cu, the alloy developed by us and used in industry (Tikhonovich et al., 1977) and (3) – (C~1.2%, Cr = 17–19%) + ~14.0% Cu. These alloys allowed to obtain two original structures: (1, 2) – a matrix + a hard phase (eutectic carbides) and (3) – a matrix + a hard phase (eutectic carbides) + a soft phase (the high-copper ε-phase). The alloys were investigated after heat treatment, which included quenching in oil at 1080 °C and tempering at 580 °C. This heat treatment is optimal for alloys operating in water (Novytskyy et al., 2002; Gorskiy et al., 1981; Novytskyy, 2004). The original structures of studied alloys were examined with optical microscope, and the chemical composition of structural components was determined using a scanning electron microscope equipped with a microanalyzer. The chemical composition of specimen and counterbody surfaces was determined by scanning the entire work surfaces.

The phase composition and the parameters of the fine structure of the studied alloys were found by X-ray structure analysis in iron Kα-radiation. The tribotests were carried out using the block (specimen)-on-ring (counterbody) arrangement. The ratio of the specimen surface area to the counterface area (the overlapping factor) was k=0.08. The counterbody was made of steel 20Cr13 GOST 5632–72 containing 0.23% C and ~13.0% Cr (similar to steel grade AISI 420) with a hardness of HRC 38–40. The tests were performed under dry friction (in air) and boundary friction (with water supply in the contact zone) conditions. The sliding velocity was 1 m/s and the pressures were 1 and 5 MPa. Specimens were weighed before and after the tests to determine the specimen mass loss. The wear rate of specimens (Iq) was the ratio of the worn material mass (g) to the fiction distance (km).
3. Experimental Results and Discussion

3.1 The Characteristics of Original Structure of Studied Alloys

The studied alloys of the system Fe-Cr-C (C~1.2%, Cr = 17–19%) contained different amount of copper: 0%, ~0.4%, and ~14%. This difference of copper amount in alloys resulted in specific changes their original structure (Figure 1).

The original structure of alloys with 0% and 0.4% copper after heat treatment represents troosto-sorbite matrix with eutectic carbides. In structure of the alloy with 14.0% copper, the high-copper inclusions (ε-phase) are located over the boundaries carbide eutectic as well as are found inside the grains of matrix consisting of α- and γ-phases. The results of hardness and microhardness of the alloys are given in Table 1. The data show that the hardness and the microhardness of alloys are significantly changed depending on amount of copper used for alloying. The maximal microhardness of structural components of alloys is observed in the alloy with 14.0% copper, due to age hardening, caused by exceeding solubility of copper in the alloy (May & Schetky, 1982; Blank & Hornbogen, 1974).

![Figure 1. Micrographs of studied Fe-Cr-C alloys alloyed by 0 (a), 0.4 (b), and 14.0% Cu (c) after quenching at 1080 °C in oil and tempering at 580 °C](image)

1–eutectic carbides, 2–inclusions of high-copper ε-phase

<table>
<thead>
<tr>
<th>No</th>
<th>Cu, wt%</th>
<th>Hardness, HRC</th>
<th>Microhardness, MPa</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>matrix</td>
<td>eutectic carbides</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>37</td>
<td>4730</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>40</td>
<td>4980</td>
</tr>
<tr>
<td>3</td>
<td>14.0</td>
<td>48</td>
<td>6620</td>
</tr>
</tbody>
</table>
3.2 The Results of Wear Tests of Alloys under Dry Friction

The tribotests of the alloys under dry friction at sliding velocity 1 m/s and pressures of 1 and 5 MPa have shown that the original structure of alloys influences the wear rate of the specimens (Figure 2). The fatigue wear at pressure 1 MPa is observed for all studied alloys but the wear rate of the alloy with 14.0% copper is minimal, and, the wear rate of this alloy is 2.1 and 1.3 times less than that of the alloys with 0 and 0.4% copper, respectively. The wear rate of the alloys with 0 and 0.4% copper has increased by more than two orders of magnitude at the pressure of 5 MPa. In this case severe wear is observed. The wear rate of the alloy with 14.0% copper has increased only in one order of magnitude and the limiting wear is observed. The pressure increase from 1 to 5 MPa leads to 2 times decrease of friction coefficient of studied alloys.

3.3 The Results of Wear Tests of Alloys under Boundary Friction

The tribotests of the alloys under boundary friction at sliding velocity 1 m/s and the pressures of 1 and 5 MPa have shown (Figure 3) that the wear rate of studied alloys at pressure of 1 MPa is practically equal to the one observed under dry friction, and the wear in this case is classified as fatigue wear. The alloy with 14.0% copper has minimal wear rate (like under boundary friction) and wear rate is 2.2 and 1.4 times less, than that of the alloys with 0 and 0.4% copper, respectively. The increase of the pressure to 5 MPa leads to significant wear rate increase (4.5 and 3.2 times) of alloys with 0 and 0.4% copper, but the wear rate increase (1.6 times) of the alloy with 14.0% copper is minimal.

Such variability of wear rate of the alloys results, probably, from the original structure differences determined by differences of copper content, modes of heat treatment, and peculiarities of redistribution of alloying elements on friction surfaces of specimens and counterbodies, as well as subsurface structure formation in friction layers.

Figure 2. Wear rate of studied Fe-Cr-C alloys alloyed by 0 (1), 0.4 (2), and 14.0% Cu (3) in dry friction at sliding velocity 1 m/s and the pressures of 1 (a) and 5 (b) MPa
3.4 The Chemical Composition of the Contacting Surfaces of the Friction Members

The results of determination of chemical composition changes in specimen and counterbody surfaces are given in Table 2. Analyzing the data in Table 2, we can note that the chemical composition of a surface after friction depends not only on the copper content in an alloy and their initial structure, but on the friction conditions as well.

On the surface of the alloy without copper after dry friction (pressure of 1 MPa), there is decrease in Al, Si, Cr and Mn content relative to the ones in the original state. The content of alloying elements after dry friction (pressure 5 MPa) is practically not changed relative to the original state. The boundary friction tests of the alloys at pressure of 1 MPa have shown decrease in Al, Si, Cr content and increase in Mn content on its friction surface. The content of alloying elements after boundary friction at pressure of 5 MPa is practically not changed relative to the ones at pressure of 1 MPa.

On the friction surface of the alloy with 0.4% copper after dry friction at pressure of 1 MPa, there is a decrease in Si, Cr, Mn, and Cu content, but an increase in Al content relative to the original state. The content of alloying elements after dry friction at the pressure of 5 MPa is practically not changed relative to the one at the pressure of 1 MPa. The wear tests of this alloy under boundary friction at pressure of 1 MPa show a decrease in Al, Mn, Cr content and an increase in Si, Cu content on its surface. The content of alloying elements after boundary friction at the pressure of 5 MPa is increased relative to the original state, but the content of Mn is decreased.

On the surface of an alloy with 14.0% copper after dry friction at the pressure of 1 MPa there is an increase in Al, Si, Mn content and a decrease in Cr and Cu content relative to the original state. The content of alloying elements after dry friction at the pressure of 5 MPa is practically not changed relative to the one at the pressure of 1 MPa. The wear tests of this alloy under boundary friction at the pressure of 1 MPa show the decrease on the friction surface content Al, Si, Cr and Cu, but an increase in Mn content. The content of alloying elements after boundary friction at the pressure of 5 MPa is increased in Mn and Si, but decreased in Al, Cr, and Cu on the friction surface.
Table 2. The chemical composition of surface of specimens of Fe-Cr-C alloys containing 0, 0.4, and 14.0% copper and counterbodies made of steel 20Cr13 in an original state and after sliding friction (V=1 m/s, P=1 and 5 MPa)

<table>
<thead>
<tr>
<th>Cu, wt%</th>
<th>Surface state of specimen and counterbody</th>
<th>Chemical composition*, **, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>0</td>
<td>original</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>P=1 MPa</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>ffiction</td>
<td>0.28</td>
</tr>
<tr>
<td>0.4</td>
<td>original</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>P=1 MPa</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>ffiction</td>
<td>0.74</td>
</tr>
<tr>
<td>14.0</td>
<td>original</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>P=1 MPa</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>ffiction</td>
<td>0.65</td>
</tr>
</tbody>
</table>

* - The carbon content in steel 20Cr13 is 0.23%, in the alloys (C ~ 1.2 %, Cr = 17-19 %) alloyed with 0, 0.4, and 14.0% copper–1.19, 1.21, and 1.21% respectively. The micro-analyzer characteristics have not allowed determining the content of carbon on specimen and counterbody surfaces after friction.

** - The numerator shows the composition of the specimen surface, and the denominator-counterface.

The results show increase of Si content on friction surfaces of the alloys with different copper contents after dry friction at the pressure of 5 MPa are in accordance with the data given in work (Eyre & Maynard, 1971). The copper content in the alloys exerts significant influence on distribution of alloying elements on its surfaces after boundary friction (pressures of 1 and 5 MPa). The increase in Si content on the friction surface is observed only for alloys containing copper (Markovskiy & Kirievskiy, 1974), and the decrease in Si content for an alloy
The wear rate of the alloy with 14.0% Cu is minimal, and there is a minimal lattice parameter in the alloy without copper is observed.

The content of chromium on the friction surface after dry and boundary frictions also depends on the copper content in an alloy, and its content is decreased at the copper content of 0% and 14.0%, while an insignificant content of copper (0.4%) in an alloy leads to increase of chromium content on friction surfaces (boundary friction at the pressure of 5 MPa). An increase of chromium content on friction surfaces of specimens was observed by us earlier by alloying a similar alloy with a small amount of vanadium (Gorskiy et al., 1981).

The content of Mn on friction surfaces after boundary friction at the pressures of 1 and 5 MPa is increased for alloys with 0% and 14.0% copper and is decreased for the alloy with 0.4% copper. The copper content on the friction surface (after boundary friction at the pressures of 1 and 5 MPa) has the tendency to increase slightly for the alloy with 0.4% copper and to decrease for the alloy with 14.0% copper, when there is an appearance of copper on the counterbody surfaces (3.3 and 4.8% respectively), depending on test conditions. The change of copper content in an alloy also results in change of phase composition and thin structure both the original state and after friction.

3.5 The Characteristics of Structures of Studied Alloys before and after Sliding Friction

The quenching and tempering of alloys has resulted in significant changes in their original structure. The structure of the alloys with 0 and 0.4% copper content is troosto-sorbite (Figure 1). In the alloy with 14.0% copper, besides α-phase in matrix, there is a significant quantity of residual austenite (30%) (Figure 4, I). The maximal lattice parameter of α-phase is observed for the alloys alloyed with copper (0.4 and 14.0%); and their lattice parameter is independent on copper content in an alloy (Figure 4, II). The obtained results are in accordance with the data given for Fe-Cu system (Sokolovskaya & Guzey, 1986; Wassermann & Wincierz, 1958). The maximal value of microdistortions of the II kind (Δa/α), size of coherent particles (Dα), and a total concentration of stacking faults (1.5α + β) for α-phase is observed in the alloy with 0.4% copper (Figure 4, IV, VI, VIII). The value of microdistortions of the III kind (√2), and the value of dislocations density ρα are depended on copper content in alloy, and their value is maximal for the alloy with 14.0% copper (Figure 4, V, VII).

Tests of alloys in dry friction conditions showed that after friction at the pressure of 1 MPa in the surface layer of the alloy without Cu, the 25% γ-phase appears; for the alloy with 0.4% Cu, the γ-phase is not formed; and for the alloy with 14% Cu the amount of γ-phase has not changed relative to the original state, and is 30% (Figure 4, I). Because of fuzziness of interference line (311) it is impossible to determine the changes of other parameters of thin structure in γ-phase.

The wear rate of the alloy with 14.0% Cu is minimal, and there is a minimal lattice parameter in the α-phase, while the microdistortions of the II kind (Δa/α) and the microdistortions of III kind (√2), are maximal, and values of dislocation density ρα, the size of coherent particles (Dα), and total concentration of stacking faults (1.5α + β), are practically not changed relative to the original state. The lowest wear rate of the alloy with 14.0% Cu under dry friction and the minimal changes of both the phase composition and thin structure of subsurface friction layers can be explained by formation of plating copper film on the counterbody surface (2.9% copper), that significantly changes subsurface layer structure formation under dry friction. The obtained results are in accordance with the data (Ránea, 2003), where the presence of a plating film deposited on one or both friction surfaces exerts influence friction energy dissipation and minimizes probability of thermomechanical wear commencement.

The wear rate of studied alloys at the pressure of 5 MPa has increased by up to two orders of magnitude as compared to the one at the pressure of 1 MPa, but again the minimal wear rate is observed for the alloy with 14% of copper. The increase of pressure leads to minimizing of lattice parameter, dislocation density in α-phase, and to maximal values of lattice parameter in γ-phase, microdistortions of III kind (√2), and total concentration of stacking faults (1.5α + β). On the surface of the counterbody the appearance of 7.6% copper is noted.

The boundary friction tests of alloys at pressure of 1 MPa have shown, that the wear rate of studied alloys is practically equal to the one obtained under dry friction and the minimal wear rate is observed for an alloy with 14.0% of copper (Figure 3). It is worth mentioning, that if the γ-phase is appeared in subsurface friction layers in the alloys with 0% and 0.4% of copper after boundary friction as compared to the ones in original state, the amount of γ-phase in subsurface friction layer for the alloy with 14.0% copper has decreased and dislocation density (ργ) has minimal value as compared to the other alloys. Because of fuzziness of interference line (311) it is impossible to determine the changes of other parameters of thin structure in γ-phase. The increase of amount of α-phase in subsurface friction layer of the alloy with 14.0% copper leads to maximal values of the lattice parameter α-phase, the microdistortions of III kind (√2), and dislocation density (ρα), while the...
microdistortions of the II kind ($\Delta a/\alpha$), the size of coherent particles ($D_\alpha$), and total concentration of stacking faults ($1.5\alpha + \beta$) have minimal value (Figure 4, II, IV, VI, VII, VIII).

Figure 4. The subsurface structure characteristics of Fe-Cr-C alloys containing Cu in quantity 0 (1), 0.4 (2), and 14.0% (3) under conditions: in original state (a), after dry (b, c), boundary (d, e) friction and at specific load 1 (b, d) and 5 (c, e) MPa

I-quantity of $\gamma$-phase, %; II-lattice parameter of $\alpha$-phase ($a_\alpha$), nm; III-lattice parameter of $\gamma$-phase ($a_\gamma$), nm; IV-microdistortions of the II-kind ($\Delta a/a$); V-microdistortions of the III-kind ($u_2$), nm; VI-size of coherent particles ($D$), nm; VII-dislocation density ($\rho$), cm$^{-2}$; VIII-total concentration of stacking faults ($1.5\alpha + \beta$);

□-the value for $\alpha$-phase; ■-the value for $\gamma$-phase;

•, ••-the data were not obtained because of fuzziness of interference line (220) and correspondingly (311).
The wear rate at the pressure of 5 MPa is severely increased for alloys with 0% and 0.4% of copper, while the wear rate of the alloy with 14.0% of copper is insignificantly increased relative to the one obtained at the pressure of 1 MPa (Figure 3). In this case the amount of $\gamma$-phase has increased 2 times in subsurface friction layer, while the lattice parameter of $\alpha$-phase and the microdistortions of the II ($\Delta a/a_0$) and of III kind ($\sqrt{\Delta a^2}$) don’t change (Figure 4, I, II, IV), which can be explained by formation of plating copper-bearing film formed on the counterbody surfaces (4.8% of copper). This copper-bearing film divided the contacting surfaces and promotes more equal distribution of loading in the contact zone, thus decreasing structure stress in the subsurface friction layers of the alloy with 14.0% copper.

4. Conclusion

1) The different contents of copper (0, 0.4, 14.0%) in cast alloys Fe-Cr-C (1.2% C, 17-19% Cr) had a significant influence on the characteristics of the structure of the alloys in the initial state and subsurface friction layers, and thus influence the tribological characteristics of these alloys.

2) During the friction process there is a change of chemical composition of friction surfaces of the alloys, which depends on the original chemical composition of alloys and the test conditions.

3) The alloy with 14.0% of copper has minimal wear rate in dry friction at the pressures of 1 and 5 MPa. In this case there is the least change of amount of $\gamma$-phase in subsurface friction layers relative to the original state and optimization of thin structure parameters in these layers.

4) The alloy with 14.0% of copper has minimal wear rate in boundary friction. The wear rate of this alloy at the pressures of 1 and 5 MPa is practically equal due to the equality of parameters of thin structure of $\alpha$-phases and plating effect of copper transferred from the specimen to the counterbody.

References


