Structure and tribological behavior of electro-spark deposited TiC based coatings

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Abstract. This work gives an analysis of the coating obtained by electro-spark alloying using TiCNIr electrode regarding their composition, structure, morphology, roughness, and mechanical properties. Tribological properties were studied by pin-on-disk test against different counterparts without lubricant. Soft materials like Cu, 100Cr6 steel are not damaging the coating and hard materials are either a good couple like with WC-Co, or characterized by a aggressive wear like with SiC, Si₃N₄, Al₂O₃. Detailed microscopic investigations of the tracks were done after tribo-tests.

1. Introduction

Raw materials present basic tribological characteristics. Coating deposition is an efficient and economical way using a low quantity of matters and energy [1] to improve the wear and the corrosion resistance for metallic alloys. As an example, a lifetime of cutting tools can be improved by 1.5 to 1.8 [2].

Three major processes exist: Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD) and Electro-Spark Alloying, also known as Electro-Spark Deposition (ESD). PVD and CVD are two technics adopted by companies for high quality coatings. The process required an inert atmosphere or in vacuum to produce a coating, resistant to delamination and fractures [3]. Otherwise, without the special atmosphere, it will produce thick coatings and a fragile interface [4].

ESD is cheaper than PVD and CVD, and industrially attractive because of its easier process. It works under any atmosphere. Using Argon is faster but optional [5]. Its process uses alternative current. The coating material is transferred from the electrode to the surface with an electrical pulse leading to a local melt (elevated temperature and high pressure) [6] [7]. A frequency sometimes bellows \( \tau = 100 \mu s \) conducts to the extreme rapid heating and cooling (up to \( 10^9 \) K/s [8]) of the coating creating a specific microstructure in the coating. First the solidification is parallel to the surface characterized by a high tensile strength then perpendicular [9].

The TiC is commonly used as coating agent because of its high hardness. Its melting point is 3 257 °C, reached locally with EDS [10].

A wide combination of parameters is possible, letting the porosity and the size of grains definable. For example, the shape of the electrode is related to its electrical resistance and its electric field intensity [11] [12]. Thus, a 6 mm diameter electrode TiC based produces specific form of 5 µm ball surrounded by Fe [13]. The size of grains composing the electrode affects the hardness of the coating. Nano and micro-structured electrode increase the hardness by three in comparison with standard electrode; the Young modulus by 2.4 times for the nano-structured electrode; the density increase to 98 and 90 % for nano and micro-structure electrodes respectively, and the thickness of the coating to 40 and 30 µm respectively [14].
The composition of the electrode also impacts the coating. Introducing Ni, acting like a binder, in the electrode decrease the number of defect in the coating. The deposition of a multilayer of Ni / (TiC/Ni) / Ni also reduces the number of cracks but also the hardness from 1000 to 500 Hv in comparison with (TiC/Ni).

Laser treatment can also reduce the number of cracks and improve the toughness of coating [15]. Tribological tests revealed a lower level of mechanical properties for the interface between coating and substrate, since it is the case for the interface between MAX phase Cr2AlC based coatings on titanium alloy [5,16].

TiC based electrodes with Chromium are not enough investigated for now, and this work will bring light over the correlation of the morphology of the wear-resistant coating and its tribological behavior against varied materials.

2. Materials and methods

The synthesis of electrodes was carried out by the force Self-propagating High-temperature Synthesis (SHS)-pressing technology starting from the precursor powder (in mass percent: 57.6 % Ti, 16.8 % C, 15.6 % Cr and 10 % Ni). Force action of 15 tonnes upon hot SHS products (immediately on completing the gas-free combustion process) followed by cooling in sand. Polished substrate was made of the Russian steel 40X with a composition in mass percent: 97 % Fe, 0.95 % Cr, 0.65 % Mn, 0.4 % C, 0.3 % Cu and Ni, 0.27 % Si, 0.035 % S and P.

| Element (mass %) | Fe  | C  | Ti  | Cr  | Ni  | Mn  | Others |
|------------------|-----|----|-----|-----|-----|-----|--------|
| Substrate        | 97,00 | 0,40 | 0,00 | 0,95 | 0,30 | 0,65 | 0,70 |
| Coating          | 49,7 | 22,4 | 19,5 | 5,2  | 2,8  | 0,4  | /      |

Table 1. EDS composition analysis.

The Alier-303-Metal stands for the ESD. It is used in experiments afforded regulating the following parameters: intensity I = 120 A, duration of pulse \(\tau = 100 \mu s\) and frequency \(f = 640 \text{ Hz}\). Depositions of the coating were carried out in a 0.25-liter box under argon. ESD was made in manual mode with an opposite polarity current with a rectangular rod of 2.5x2.5x30 mm³.

Sliding tests were made with a Tribometer (CSM Instruments, Switzerland) [17] in a reciprocating linear cycle of 4 mm with maximal speed of 5 cm/s applying a constant force of 5 N. Counterparts, used during 20 000 cycles, are 3 mm balls made of hard metal (94 % WC, 6 % Co), SiC, Al₂O₃, Si₃N₄, during 10 000 cycles for Steel (100Cr6) and during 4 000 cycles for Copper.

X-Ray Diffraction (XRD) was carried out with a D8 Advanced (Bruker, US) with Copper K-\(\alpha\) radiations. Images of counterparts and the cross-section were made thanks an Axiovert CA25 optical microscope (Carl Zeiss, Germany). Microstructure and elemental compositions of coatings were characterized by a S-3400N scanning electron microscope (SEM) (Hitachi, Japan) equipped with an UltraDry energy-dispersive detector (EDS) and Silicon Drift X-ray detector (Thermo Fisher Scientific, US). Profilometry was made by a Wyko NT1100 optical profiling system (Veeco, US).

Hardness are calculated thanks imprints made with Nano-hardness Tester (CSM, Switzerland) over the cross-section mirror polished. Each imprint is separated by 8 μm and sequences are separated by 10 μm. Approach speed is 2 000 nm/min with a maximum load of 30 mN with a program of loading/unloading rate of 60 mN/min with a pause of 5 s. Microhardness of coatings was measured via a DuraScan70 microhardness tester (Emco-Test Prüfmaschinen GmbH, Austria) with loads of 25, 50, 100, 300 and 500 g.

3. Results and discussion

3.1. Structure and phase composition of coating
The constraint apply to the coating during fast heating and fast cooling will affect the coating in two ways: the surface appears molten, with holes, cracks from 80 to 200 µm and high points, comparable to lumps (Figure 1). Roughness is Ra = 3.84 µm, Rq = 4.69 µm with maximum high points of 50 µm. The composition of the coating is measured with EDS (Table 1).

![Figure 1. Top view and cross-section of the Fe-Ti-Cr-Ni-C coating.](image)

XRD analysis (Figure 2) shows that the deposition affects the morphology of the substrate. First, it is composed of two phases, α-Fe in majority, the stable phase of iron, and γ-Fe, its metastable form. After deposition, the amount of α-Fe reduces from 79.5 to 1.1 % (volume %) with a cell parameter of 0.288 nm to an undetermined value; and the amount of γ-Fe rises from 20.5 to 66.2 % (volume %) with a cell parameter from 0.3609 to 0.3620 nm. The coating is composed of 32.7 % (volume %) of TiC with a cell parameter of 0.4283 nm, corresponding to a concentration of TiC < 0.4 [18].

Although that the coating is formed of phases of the electrode, the substrate and the combination of both, the XRD analysis with a grazer angle of measurement confirms the absence of other phases. In the case of a WC92–Co8 electrode used, Fe, absent in the electrode, is found in phases of the coating [19].
Figure 2. XRD of the sample varying angle of attack from frontal (a) to grazer angles (b)(c).
### 3.2 Tribological tests and properties investigations

| Counterpart | $HV$ (GPa) | $E$ (GPa) | $\nu$ | Hertz stresses (GPa) | Wear rate (mm$^3$/N/m) | CoF | Ball ($10^{-6}$) | Disk ($10^{-3}$) | Start | Max |
|-------------|------------|-----------|-------|----------------------|--------------------------|-----|------------------|-----------------|-------|-----|
| WC          | 15.5       | 610       | 0.24  | 3.16                 | 7.06                     | 0.10| 0.10             | 0.22            |
| SiC         | 24-28      | 310       | 0.14  | 2.57                 | 7.89                     | 0.13| 0.12             | 0.35            |
| Al$_2$O$_3$ | 19         | 380       | 0.22  | 2.71                 | 1.52                     | 0.10| 0.11             | 0.64            |
| Si$_3$N$_4$ | 15.5-16    | 320       | 0.27  | 2.57                 | 7.89                     | 0.13| 0.11             | 0.66            |
| Copper      | 2.1        | 121       | 0.35  | /                    | 487                      | No track | 0.28 | 0.67           |
| Steel       | 0.832      | 210       | 0.30  | /                    | 33.1                     | No track | 0.06 | 0.51           |

Table 2. Tribological data of wear test.

Nano-indentation gives a Young modulus evolving according to the depth with 245 GPa for the substrate, from 150 to 200 GPa for the interface and a mean value of 205 GPa for the coating (Figure 3). Hardness seems to follow a schematic behavior (Figure 3c) with a minimum at interphase layer. Hardness is 1200 Hv for the substrate, 500 Hv for the interface and 800 Hv for the coating (Figure 3).

Micro-indentation shows that top-layer has got a hardness of 800 HV, with values decreasing with increasing of the penetration depth (Fig 3d). In the literature, TiCNi coating is harder than this TiCCrNi coating [15,21].
Figure 3. Nanoindentation of the cross section (a), (b). Schematic dependence of hardness from surface to bulk (c). Microindentation data (plan) (d).
The response of the coating to the sliding test is characterized in three distinct types of behavior with damages either one-sided or equitable distributed (figure 4).

SiC, $\text{Al}_2\text{O}_3$ and $\text{Si}_3\text{N}_4$ are defined by a highly scratched coating. The CoF of $\text{Si}_3\text{N}_4$ evolves linearly, which makes its evolution more predictable. Cross-section of the sample shows that $\text{Si}_3\text{N}_4$ sands the coating without chemical adherence showed by a round shape of the imprint of the counterpart. $\text{Si}_3\text{N}_4$ counterpart did a 600 µm groove with a depth of 10 µm. Si atoms can be found in the coating. The coating is ripped off and oxides of iron are gluttéd on the counterpart. The present of black oxides and the acceleration of the CoF proves that the friction creates a rapid heating. This leads to a cascade of events responsible for a rapid abrasive behavior.

$\text{SiC}$ counterpart pulled away the entire coating over a width of 315 µm and with a maximal depth of 5 µm. As $\text{Si}_3\text{N}_4$ test, the shape of the scratch is a perfect round ball trace, which shows no adhesion of the counterpart. No oxide is formed in $\text{SiC}$ counterpart showing no increase of temperature. The damage of the test is the lowest of all the three.

$\text{Al}_2\text{O}_3$ counterpart, relatively intact after test, results the most destructive one. Two stages of groove are visible: one with a width of 500 µm with a maximal depth of 10 µm and one central one thinner of 74 µm, 2 µm deeper. The coating appears teared off, showing either a strong chemical interaction or an elevated temperature, transforming debris into red oxides of iron.

Their wear test starts with the same coefficient of friction (CoF) as counterpart not affecting the coating like WC and Steel, but it grows up faster to a high value (Figure 4b). First acceleration will appear after 1 000 cycles with $\text{SiC}$ counterpart, 2 000 cycles with $\text{Al}_2\text{O}_3$, and 10 000 cycles with $\text{Si}_3\text{N}_4$. After 10 000 cycles, the CoF of $\text{Al}_2\text{O}_3$ and $\text{Si}_3\text{N}_4$ are over 0.4, while the CoF of $\text{SiC}$ is about 0.24. Then the CoF grows slowly to 0.47 and 0.50 respectively. This behavior shows a scratching as three steps: first a small CoF, due to the surface of contact increasing because of the increase of depth of groove and slowed by the roughness of the coating; then a rapid growth of CoF, corresponding to a minimum roughness and a surface of contact increasing with depth of groove. This stage continues until the complete suppression of coating; and finally, a slow growth.

The second behavior corresponds to a good couple of friction with few damages over the coating and the counterpart. WC/TiC based coating does not show any visible groove according to microscopy despite the profilometry shows one. WC appears also a good friction partner because of the low CoF (Figure 4a). The third body is not built of the counterpart as proved with an absence of $\text{W}$ and $\text{Co}$ over the coating. It is formed with oxidation of iron high concentrated in Oxygen (58 atoms%) showing absorption of the humidity, coatings or high carbon concentrated particles (92 atoms%). MgO was observed over the scratched ball.

Two different areas are visible; the Ti-coating sanded surrounded by dusts and oxidations accumulated. Because of the heat, the uncoated part becomes oxidised and brittle as has been highlighted by cracks seen by the SEM. Cracks in the coating show that the substrate also absorbs a part of the movement.
And the third behavior shows no damage in the coating and the deep sanded counterpart (Figure 5c). Neither profilometry nor cross-section show any track for Copper test and almost invisible one for Steel test of 126 µm.

Steel wear test shows low CoF from 0.6 to 0.18 in 2 000 cycles and stays constant. Highest value corresponds to the moment until high points become enough flat to have a stable surface of contact against the ball, becoming able to sand the counterpart without variation. In comparison, WC counterpart evolves slowly but constantly growing to 0.18. There is no signal indicating an eventual future high constant value of CoF.

According to profilometry analysis, one high point of 400 µm damaged is the only visible trace of the track of the Steel. This counterpart is the one most affected with a high surface of contact in only 10 000 cycles or two times less than other experiences. This coating can also be a viable alternative to the cutting of steel.

Copper wear test presents a stable instantly high CoF of 0.48 during all the test (Figure 4c). A stable third body uniquely composed of oxides of copper due to a high heating is immediately created. Debris is under the form of little balls or parts ripped, comparable as rubber debris. After 4 000 cycles, or 5 times less cycles than other experiences, the counterpart is already deeply sanded.

Their wear tests define uniquely the behavior of the counterpart because no change is observable in the coating, thus only heating and time of the formation of the third body is observable.

Other publications, because of the use of lubricant present significant lower CoF with lower damages of the coating [19].
Figure 5. Wear track of the Fe-Ti-Cr-Ni-C coating and contact spot of counterpart for SiC (a), Al₂O₃ (b) and Copper (c).

4. Conclusion

The coating is composed of 66.2 % of $\gamma$-Fe and 32.7 % (volume%) of TiC with interstitial Cr, Ni, and Mn. The coating presents cracks, points higher than 5 µm and holes smaller than a few micrometers; is rough with $Ra = 3.84$ µm and its thickness ranges from 10 to 25 µm.
The hardness of the coating is about 800 Hv and Young modulus about 200 GPa. Tribological behavior of the coating against hard metal (WC-Co) is very good with a CoF under 0.2 during 20 000 cycles with negligible wear rate.

Indeed, the coating cannot support friction against Al₂O₃. 20 000 cycles are enough to remove the coating with advanced tear off damages. Si₃N₄ and SiC counterparts damage corresponds to an intermediate behavior with damages over the counterpart and the coating.

Soft metals made of Steel and Copper are destroyed after less than 4 000 cycles of the same wear test, and do not hurt at all the coating.

Acknowledgements
This work was carried out with financial support from the Ministry of Education and Science of the Russian Federation in the framework of state assignment No.11.7172.2017/8.9.

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