

THE CORROSION CHARACTERIZATION OF Ti-Si-C THIN FILMS OBTAINED BY MAGNETRON SPUTTERING DEPOSITION

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Abstract. Nano-composite layers, formed by a mixture of crystalline or amorphous nano-phases, which include Ti-Si-C type layers, obtained with the help of the PVD process, have attracted lately a wide interest both in research, and in the industrial applications, because of their possibility to form a protective coating with physical and chemical unique properties. With this process there can be obtained hard coatings with a high degree of toughness, with an excellent wear resistance, characterized by a low friction coefficient and a good corrosion resistance. The present paper contains both general data about the Ti-Si-C system, and the experimental results obtained from the deposition of Ti-Si-C layers on a rapid steel substrate, at low temperatures. This way, there can be seen some correlations between the deposition method used, the chemical composition and the corrosion resistance, determined using the salt fog (salt spray) chamber method.

Keywords: thin layers, deposition, Ti-Si-C, corrosion

1. Introduction

The scientific effort towards the development of this new field of research with a multi disciplinary character was determined by the fact that taking mechanical parts out of use is caused by three phenomenons, wear, fatigue and corrosion, which take act especially on the surface zone, where the wear and tear is more intense and more complex. The material's destruction caused by corrosion and wear, both direct and indirect, costs the state's economy hundreds of billions of dollars each year [1]. Having this in mind, the goal is , by the deposition of thin layers, the destructive effect limitation of the above factors, by the increase of wear resistance, the contact fatigue, the oxidation and the corrosion.

The research involving the Ti-Si-C system starts from the phase diagram learning. The Ti-Si-C system's ternary phase diagram determined theoretically or experimentally, is present in a big number of speciality papers [2, 3, 4, 5, 6].

In paper no [3] there is presented an isothermal section, from a phase diagram, published by Arunajatesan and Carim, in which we positioned, compositional wise, the probes used.

Contrary to binary phase diagrams, which are plane representations in composition-temperature coordinates and where for any composition and temperature the equilibrium phases can be seen, a ternary diagram, because the

presence of three components, is a spatial representation, the temperature being shown by these isothermal sections (surfaces) [8]. In figure 1, Ti-Si-C system's phase structure, is presented by a section situated at 1200°C. There can be observed that at this temperature, function of the Ti content ,the Si content and the C content, a few ternary phases: MAX (Ti_3SiC_2), $Ti_5Si_3C_x$ (contains dissolved carbon), and binary TiC_x , SiC, TiSi, $TiSi_2$ and Ti_5Si_4 can be present.

The ternary phase diagram, as shown in figure 1, needs to be interpreted with great caution, because of the completely different thermodynamical phase forming conditions. It needs to be underlined that the Ti-Si-C thin layers analyzed in this paper are obtained by magnetron sputtering deposition at low temperatures, process that requires not only different pressures an temperatures than those needed to obtain the Ti-Si-C ternary phase diagram, but the presence of important magnetic and electric fields which modify a great deal the system's energy potential.

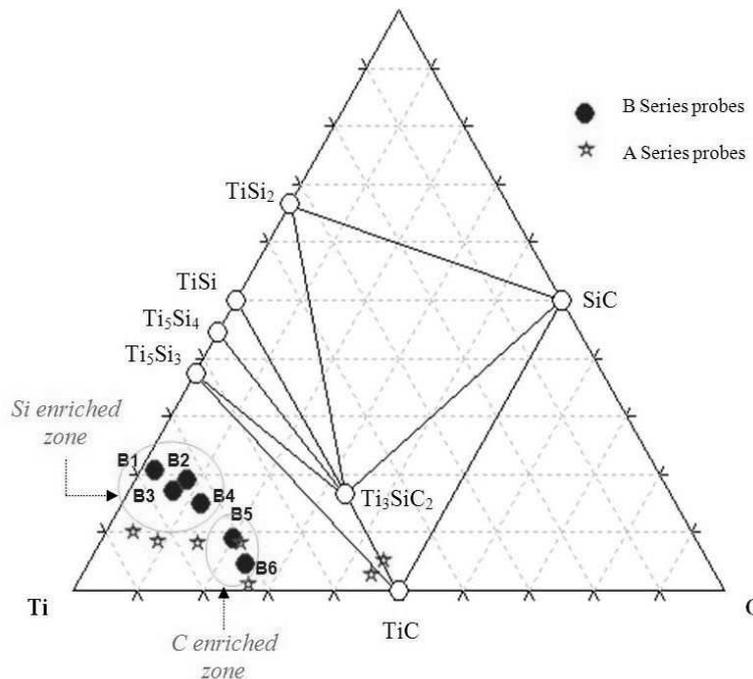


Figure 1. Analysed probes' positioning in the Ti-Si-C phase diagram at 1200°C

2. Experimental data

The Ti-Si-C thin films obtained by magnetron sputtering deposition were made by using two different sputtering systems and two different settings. This way, function of the deposition parameters and the installation configuration (magnetron positioning, target positioning, substrate positioning), the experimental probes were divided into two series with different characteristics: **A Series and B Series**. The A series probes were deposited

using the Alcatel - SCM 650 equipment, presented in figure 2. This equipment allows the deposition both by direct current sputtering (DC) and radiofrequency sputtering (RF – 13.56 MHz), allowing this way the deposition of conductive, semiconductive and insulating materials. The equipment consists of the following parts: the deposition chamber, the vacuum system, the power sources and an automated control system (command system).

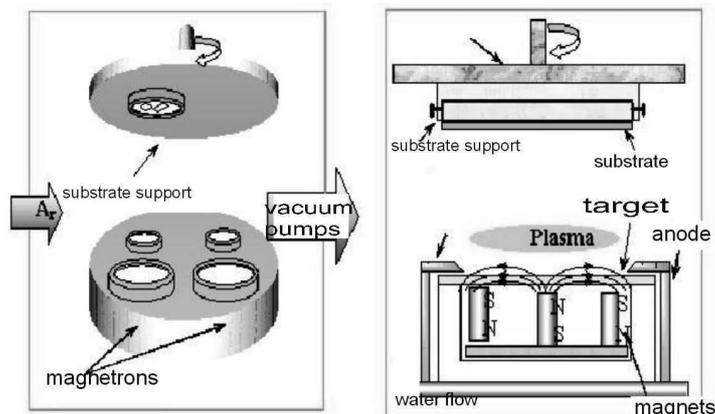


Figure 2. A sketch of Alcatel – SCM 650 system's deposition chamber used for the deposition of A Series probes.

For the A Series deposition there were used both the DC magnetron sputtering and the RF magnetron sputtering, by the simultaneous use of two targets:

- A Ti target on which there were placed Si tablets, connected to a DC power source, with current densities varying from 1.6 to 3.2 mA/cm²;
- A C target, on which there were placed Si tablets, connected (because of the low carbon conductivity rate) to a radiofrequency power source, with applied power densities varying from 0.32 to 1.59 W/cm²;

There could be seen that in order to obtain Ti-Si-C layers with a different Si content, the Si tablets placed on the Ti or C-graphite targets were in different numbers, 5 or 10 tablets, on the target erosion zone .

Table 1. Deposition parameters – A Series

Probe	A1	A2	A3	A4	A5	A6	A7
Substrate	300						
Temperature, (°C)	300						
Substrate Tension, (V)	-50						
Argon gas flow, (sccm)	100						
System	TiSiC						
Target – substrate distance, (mm)	65						
Substrate rotation speed	5 rpm						
I _{Ti} , (A)	1.0	1.0	1.0	1.0	1.0	0.5	0.5
P _C , (W)	100	200	300	400	500	500	500
Si tablet number on the Ti target	10	10	10	10	5	5	5
Si tablet number on the C target	5	5	5	5	5	5	10
Deposition time (h)	8	8	8	8	8	8	8

where: I_{Ti} = Current intensity at the Ti target;
P_C = RF power applied at the C target;

For the B Series deposition there was used laboratory equipment, designed and made by the Physics Department of Minho University, as shown in figure 3.

The Ti-Si-C layers of B Series were obtained using a different configuration as the one presented above, meaning the DC co-sputtering of two high purity Ti targets. On the two Ti targets,

placed one in front of the other, there were placed on the erosion zone, both Si tablets and C-graphite tablets. Having this in mind, the targets will be named the Ti-Si target (Ti with Si tablets), and the Ti-C target (Ti with graphite tablets).

Table 2. Deposition parameters – B Series

Probe	B1	B2	B3	B4	B5	B6
Substrate	200					
Temperature, (°C)	200					
Substrate Tension, (V)	-70					
Argon Gasflow, (sccm)	60 - 85					
System	TiSiC					
Target-substrate distance, (mm)	65					
Substrate rotation speed	7 rpm					
I _{Ti-C} , (A)	0	0.5	1.1	0.8	0.7	1.5
I _{Ti-Si} , (A)	2.5	2	2.75	1.5	0.5	0.5
Basic pressure, (Pa)	1.2x10 ⁻⁴ – 3.9x10 ⁻⁴					
Deposition time (h)	8					

where: I_{Ti-Si} = Current intensity at Ti-Si target (A);
I_{Ti-C} = Current intensity at Ti-C target (A);

The A and B Series were deposited at a -50 and -70 V substrate polarisation tension and a substrate temperature of 300 and 200 °C.

During the deposition period there have been used different intensity I_{Ti} and power P_C values (for the A series) and different target current ratios I_{Ti-C/Ti-Si}, (for the B series), resulting in different structures and different chemical compositions.

There has to be specified the fact that by using the Scanning Electron Microscopy (SEM), at a 10.000X increase, there were shown significant differences regarding the structural morphology, the A series probes presenting a tendency of amorphisation and a crystalline/columnar-like character less showing, different from the B series, where the crystalline/columnar-like character is more evident [6].

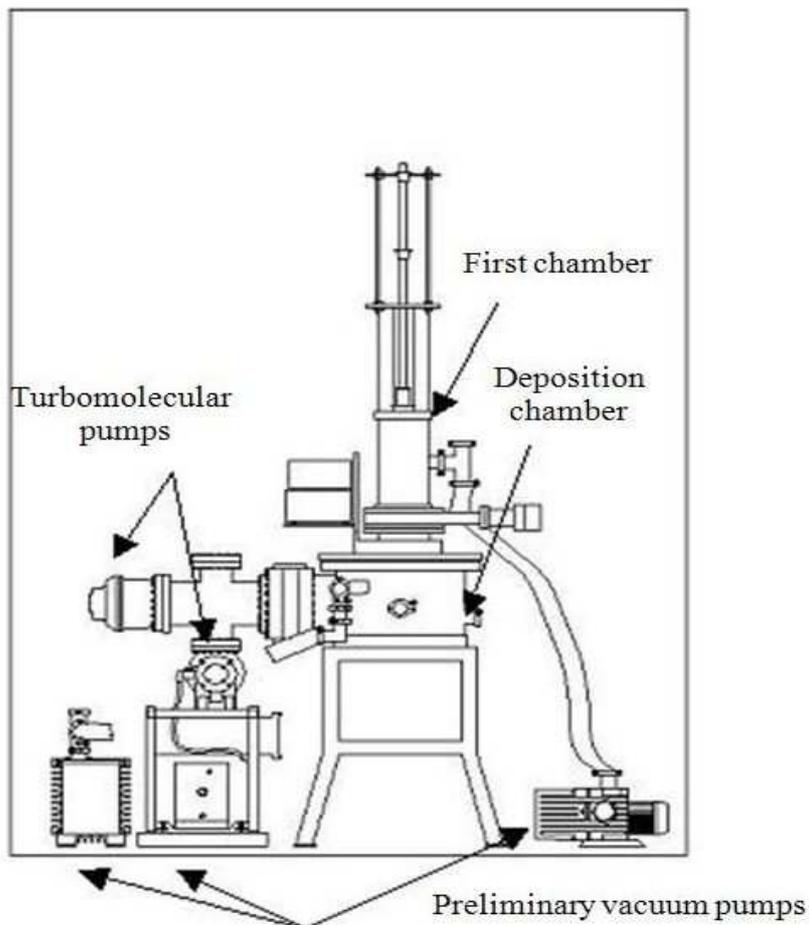


Figure 3. The deposition installation simplified sketch.

Table 3. A and B Series layer's chemical compositions:

Probe	Ti (%at.)	Si (%at.)	C (%at.)	C/Ti	Si/Ti	Probe	Ti (%at.)	Si (%at.)	C (%at.)	C/Ti	Si/Ti
A1	81.5	9.5	3.9	0.05	0.12	B1	72.9	19.7	2.0	0.03	0.27
A2	79.0	8.1	8.4	0.11	0.10	B2	68.9	18.1	7.5	0.11	0.26
A3	73.9	8.0	14.3	0.19	0.11	B3	72.6	16.5	6.3	0.09	0.23
A4	67.5	7.9	20.8	0.31	0.12	B4	70.2	14.4	11.6	0.17	0.21
A5	70.1	1.0	25.4	0.36	0.01	B5	68.3	8.6	19.4	0.28	0.13
A6	51.1	2.6	43.1	0.84	0.05	B6	68.8	4.5	23.4	0.34	0.06
A7	48.8	5.0	44.2	0.91	0.10						

- The difference up to 100 atomic percents is represented by the oxygen residual percents.

The corrosion characterization is more of a novelty, because the existing written data about this property of the Ti-Si-C system layers is relatively of small size.

For the corrosion characterization it was used the salt fog chamber. The experiment consists of a highly corrosive artificial salt fog attack with a defined composition, in well known temperature and pressure conditions. The deposited surface degradation is appreciated visually through the

appearance of corrosion points and finally by the relative measurement of the corroded area.

The experiment took place in a chamber containing salt fog with the following characteristics:

- the sodium-chloride concentration in water: 50±5 g/l;
- the saline solution density at 20±2°C: 1.025-1.040 g/cm³;
- the saline solution pH: 6.5-7.2;

- work temperature: $35 \pm 2^\circ\text{C}$;
- the pressure and spraying are kept constant and they are set in such manner as the result should be a quantity of 1-2 ml/h of solution on a surface of 80 square centimetres.

There was studied the showing of the first traces of corrosion and the corrosion evolution level, at different intervals (24, 48 and 240 hours). The data presented in table 4 is referring at the corrosion level after 240 hours, because after 24 and 48 hours there were not any signs of corrosion, and therefore, no different corrosion activity in order to make any conclusions.

Table 4. A and B Series corrosion grade

A Series	A1	A2	A3	A4	A5	A6	A7
Ti concentration (% at.)	81.5	79.0	73.9	67.5	70.1	51.1	48.8
Corrosion grade (surface percents)	1	1	2	4	3	4	5
B Series	B1	B2	B3	B4	B5	B6	
Ti concentration (% at.)	72.9	68.8	72.6	70.2	68.3	68.8	
Corrosion grade (surface percents)	4	7	4	5	5	15	

3. Results and discussions

There is known that the main forms of corrosion that can appear in the salt fog method's case, function of the chemical composition and the alloy structure are: uniform corrosion, when the corrosion reaction starts on the whole surface and continues evenly in depth, localized-pitting corrosion when the base metal is attacked in particular areas, intergranular corrosion, which proceeds on the grain boundaries or intragranular corrosion which proceeds within the grains. The visual observations over the both series' probes, showed that the surface corrosion starts (figure 5) with a localized corrosion, which eventually increases in size.

Missing a comparison chart in order to show a certain corrosion resistance level, the most important conclusions that can be drawn by comparing the two series of probes, obtained with different installations and in different conditions, is that the A series probes had a better corrosion resistance compared with the B series probes (table no. 3).

In the A series case, the lowest levels of corrosion, less than 2% of the surface, are presented by A1 and A2 probes, characterized by a relative richer layer in Ti and Si (table no. 3). It was shown that the probes with a higher C content,

A6-A7, had a less satisfactory corrosion resistance, presenting a higher level of corrosion, of maximum 5% (table 4). There can be said that the presence of higher carbon levels affects the corrosion resistance because of the different structural layer morphology which has a higher crystalline/columnar-like character.

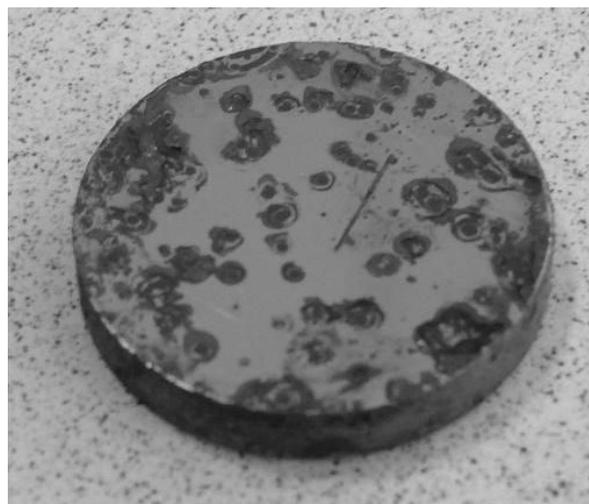
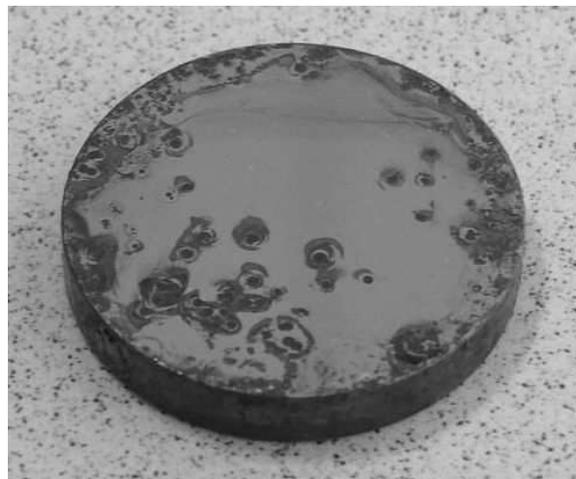


Figure 5. B2 and B6 probes after a salt fog exposure of 240 hours [5]

The different deposition conditions of the two series of probes led to layers structurally and compositionally different, characterized by a different corrosion resistance. Thus, in figure 5 there is shown the B6 probe, which presented the lowest corrosion resistance, approximately 15% of this probe's surface being corroded after 240 hours. There needs to be mentioned that this probe exhibits the highest carbon concentration from the B series, 23.4 %at C, and a low atomic content in Ti, 68.8 %at Ti, element which is characterized by a good corrosion resistance in a salt fog

environment. There can be observed that the silicon content is low, which led to a layer with a high crystalline/column-like appearance, easier to corrode. B2 probe, figure 5, although it has the same Ti content as the B6 probe, exhibits, because of a lower carbon content, a higher level of corrosion resistance, the corroded surface having an area of maximum 7%.

4. Conclusions

The goal of the present paper was to show general aspects regarding the Ti-Si-C layer deposition by magnetron sputtering, and also, to analyze the chemical composition and structure influence over the corrosion resistance of these layers. The corrosion behaviour in a salt fog environment of Ti-Si-C layers after 240 hours, analyzed without the presence of a corrosion resistance chart in order to have a comparison level, is considered generally good. There were shown differences depending especially on the Ti and C content meaning an increased corrosion resistance with the rise of Ti content in the layer's composition and a decreased corrosion resistance influenced by the C content growth. Very important is the presence of silicon which contributes to structural changes in the layer by decreasing the crystalline/column-like character, which causes, especially for a series, a significant corrosion resistance growth.

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