Effect of the temperature variation on the hardness and microstructure of TiSiNO coatings obtained by sputtering

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Abstract. Titanium-Silicon Oxynitride (TiSiNO) coatings were synthetized by reactive co-sputtering technique on stainless steel 304 substrates varying the substrate temperature during the deposition. Two targets were used simultaneously, the first one of Ti on a DC source at 100 W and the second was a Ti-Si-O target on a pulsing RF source at 180 W. X-ray diffraction identified three crystalline phases: titanium nitride (TiN), titanium oxide (TiO) and silicon oxide (SiO_2), where the SiO_2 phase presented compressive stresses at low temperatures and tension stresses at higher temperatures, along with a change in the preferential orientation. The coating obtained at 200 °C showed the higher hardness value of 14.8 GPa, attributed to a lower grain size and high compressive stress. Finally, all coatings presented high fracture toughness, since the was a lack of any type of crack for all applied load values.

1. Introduction

In recent years, the research to develop hard materials has been increased, mainly because the mechanical applications as cutting tools, aerospace and industrial applications are very attractive [1]. Generally, a single hard material could present problems due to their low fracture toughness, however, to combine two or more materials as a coating, can provide enhanced mechanical properties without losing the original properties of the substrate.

From the vast amount of materials that exist to form coatings, a lot of attention has been paid to binary ceramic materials like the titanium nitride (TiN) and silicon oxides (SiO_2), but it has been reported that composite coatings could improve considerably the mechanical properties [1], [2], [3], some of the most important composite quaternary systems are the Ti-Al-N-O or the Ti-Si-N-O, where the Ti-Si-N-O reached values up to 32 GPa [4]. Nevertheless, the high hardness values in quaternary systems are not easy to reach, since most of the Ti-Si-N-O works report values between 5 and 6 GPa [5]. Therefore, to find a path to reach high hardness values of these coatings could be very important. Moreover, there is a small amount of works regarding this matter, owing the difficulty to produce these high-quality quaternary systems is hard.

Between the different techniques to fabricate these coatings are the chemical vapor deposition (CVD) and physical vapor deposition (PVD), where the PVD are well accepted because they provide a better control of the coating growth and it does not generate a lot of contaminant waste. The sputtering is a very versatile PVD technique, that allows the deposition of metallic or ceramic materials at the same time, having the possibility to control the growth of composite materials. In this sense, some works report the growth of composite quaternary systems using the sputtering, however, most of these works try to control the growth by making changes of the atmosphere inside the chamber during the deposition, whether varying the gases flow [6] or altering the power of the sources during the process [4]; moreover, most of these works use two reactive gases, nitrogen and oxygen, during the sputtering deposition process; additionally, the effect of the substrate conditions, like the temperature, hasn't been studied. The employment of temperature during the deposition on binary systems has had a positive effect, because they promote a better atom movement and diffusion on the substrate to form better crystalline phases [7].

For the above, in this work, quaternary TiSiNO coatings are synthetized using the Sputtering technique, without the use of oxygen as reactive gas, varying the substrate temperature during the deposition process. The effect of the temperature of the coatings in its microstructure and hardness are studied by X-ray diffraction (XRD) and Vickers microhardness respectively.

2. Methodology

2.1. Substrate preparation and coating synthesis

Steel substrates 304 were used, with dimension of 2 in $\times$ 1 in. The steel plates where then polished to obtain a mirror finish with chromium oxide. Finally, the steel was cleaned using ultrasonic baths of liquid soap, a mixture of xylene ethanol and acetone in (1:1:1) proportion and a pure ethanol bath, the samples were dried with nitrogen and placed inside the sputtering chamber afterwards. A sputtering system intercovamex V3 was used for the growth of the coatings, where two targets were used, the first target was a pure Ti target (99.95%) placed in a direct current source (DC) with 100 W, while the other target was a Ti-Si-O target (99.98%) on a radiofrequency source (RF) with 180 W. Two gases were used, an inert Ar gas set at 18 sccm and a reactive nitrogen gas set a 2 sccm, leading to a working pressure of 3.5×10^{-2} Torr. The substrate temperature during the deposition was varied by 100, 150, 200, 250 and 300 °C. All samples were growth until their thickness reached 1 μm. This configuration allowed the dispense of the oxygen gas during the deposition process.

2.2. Characterization techniques

The microstructure, hardness and fracture toughness were studied on the TiSiNO coatings with the X-ray diffraction (XRD) and Vickers microhardness. The XRD measurements were made on a Bruker D8 advance diffractometer using a graze angle configuration, with a Göbel mirror and a 1° incident angle, step size of 0.03° and 1 s step time in a 2θ swept from 35 to 95°. Further XRD analysis were performed using the PDF-02 database from the ICDD [8], additionally, the Scherrer formula was used to compute the grain size of the coatings [9]. The hardness was studied in a Vickers indentator Mitutoyo H-125, a load swept was made from 500 grf to 0.5 grf. With the complete load swept it was possible to obtain the real hardness value of the TiSiNO coatings, by eliminating the contribution of the substrate. This was performed using the Korsunsky model [10] according to equation 1.

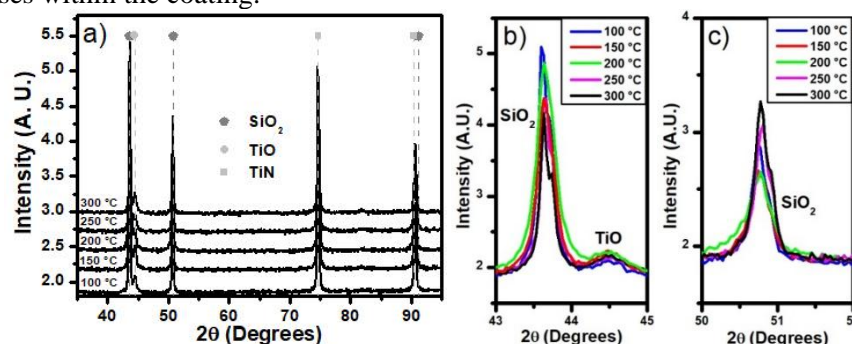$$Hv_c = Hv_s + \frac{Hv_f - Hv_s}{1 + \kappa\beta^2} \qquad (1)$$

Where H_{vf} is the hardness of the coating, H_{vs} is the hardness of the substrate and H_{vc} is the hardness of the composite substrate-coating. k is a dimensionless parameter that relates the material response to the indentation and the coating thickness, and β is the relative indentation depth.

3. Results and discussion

3.1. Microstructure

The X-ray diffractograms of the TiSiNO coatings are shown in Figure 1.a, there, it is possible to observe the formation of well-defined peaks, which correspond to crystalline phases that could be identified in the database as a silicon oxide (SiO_2), titanium oxide (TiO) and titanium nitride (TiN), according to the cards PDF 01-070-2540, PDF 01-073-9742 and PDF 00-002-1159, respectively. It is possible to appreciate that the most intense peak is formed at about ~ 43.6° in 2θ, that correspond to the plane (011) of the SiO_2 phase, the same phase also shows another well-defined but lesser intense peak at about ~ 50.7 ° corresponding to the plane (200). The second most intense peak is located at ~ 74.7 ° that is related to the TiN phase along with the peak at ~ 90.6 °. Finally, the less intense peaks at ~44.5 and ~90.9 ° correspond to the TiO phase. Due to the higher intensity of the SiO_2 and TiN phases, they could be related to a better phase formation and can be referred as the primary phases, which -as a whole- they form the quaternary system Ti-Si-N-O. It is important to notice that there is the formation of two titanium phases against only one from silicon, this could happen because during the deposition process two targets that contained Ti were used, and it is very likely that the nitrogen gas had better affinity to the metallic Ti target than the ceramic Ti-Si-O target, where the SiO_2 was detached.

Due to the great crystalline quality seen, the coatings form very intense and narrow peaks, which makes it impossible to distinguish changes on Figure 1.a, however, in Figure 1.b and 1.c a closer look to the peaks of the SiO_2 phase show that there are some changes within the SiO_2 phase, neither the TiO nor the TiN phases are explained since it was harder to identify visible changes. From Figure 1.b it is possible to observe that the coatings with the low deposition temperature are more intense on the (011) direction than those with the higher temperature, in the other hand, in the (200) direction, Figure 1.c, the coatings with higher temperature are more intense than the coatings with low temperature, from here, we could say that the tend to change their crystal growing direction on the SiO_2 phase, this could be explained since the TiN and TiO phases prefer a growth in the (200) direction, so when the SiO_2 rearranges due to the extra diffusion caused by the temperature, it will try to grow as the other coexisting phases within the coating.

Figure 1: XRD diffractograms of all the TiSiNO coatings with a) the full swept in 2θ, b) a close-up to the (011) SiO_2 peak, and c) an approach to the (200) SiO_2 peak.

With the XRD information it was possible to obtain additional data on the microstructure of the coatings, i.e. the grain size and the percentage of the phases in the coating, which are reported in Table 1. Firstly, it can be observed that there is a change in the peak center, this behavior can give us good information about the stress of the coating. According to the SiO_2 card the center is at 43.622 °, and the coatings with low temperature are at the right of that value, indicating the presence of compressive stress, while the samples at higher temperature are left from that value indicating a rather tensile stress. Additionally, the intensity change was corroborated for the SiO_2 phase, where the peak related to the (011) tends to decrease at 250 and 300 ℃.

The coatings grain sizes are also reported in Table 1 for each of the phases, we can observe that the grain sizes of the samples tend to decrease as the deposition temperature increases, however, this effect occurs until a certain temperature, then the grain sizes tend to increase; for the SiO_2 phase case the grain size decreases from 46 nm at 100 ℃ to 35 nm at 200 ℃, then at 250 ℃ and 300 ℃ the

phase grow up to 45.5 nm and 50.8 nm respectively, the same occurs with the TiN phase where at 200 °C reached the lower grain size value of 26.8 nm, then grow again up to 40.9 nm at 300 °C. It is well known that quaternary samples could have a hard time to co-exist due to the different structures they possess [5], [11], so a diffusion and rearrangement process is foster with the application of the temperature, however at low temperatures between 100 and 200 °C a transitory phase could occur before initiating the crystallization process of the sample at higher temperatures.
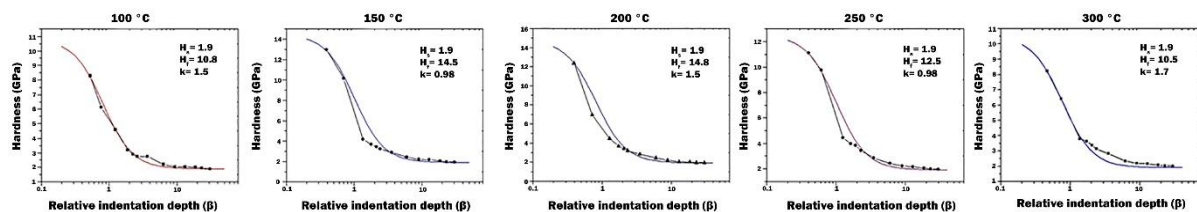
A similar effect takes place for the TiO phase, nevertheless, the lower grain size value was obtained at 250 °C instead of 200 °C but the amount of this phase is very low as seen in the phase percentage, barely reaching 1% in some cases, so it could be expected that this phase will play a minor role on the properties of the sample. Moreover, the SiO_2 is the mainly phase present in the coatings, but the TiN amount is enough to make it relevant for the properties of the coatings. Additionally, it is possible to observe that the SiO_2 phase amount decreases as the temperature increases, while the TiN phase tends to increase as the temperature increases. This effect could be explained since the TiN phase is formed in a reaction with the N_2 sputtering gas, while the SiO_2 and TiO could just be extracted from the Ti-Si-O target without the need of a reaction, and the temperature applied to the substrate could change the reaction kinetics, favoring the formation of the TiN at higher temperatures.

Table 1: Information of the center (C), intensities (I) as well as gran sizes and percentage of the phases and peaks observed in the XRD measurements.

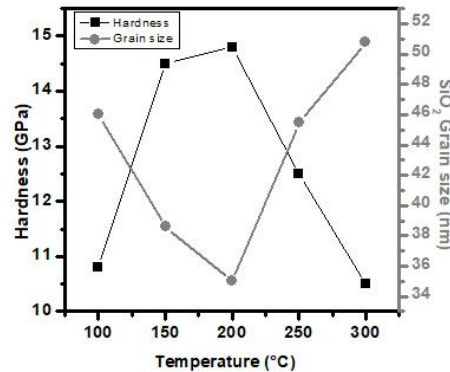| T °C	SiO_2 peak		TiO peak		TIN peak		Grain size (nm)			Phase percentage (%)		
	C (°)	I	C (°)	I	C (°)	I	SiO_2	TiO	TiN	SiO_2	TiO	TiN
100	43.62	164	44.096	6.6	74.67	52.7	46	31.1	31.1	67.1	0.7	32.2
150	43.65	132	44.507	10	74.69	39.7	38.6	28.9	28.5	63.7	1.1	35.2
200	43.66	145	44.476	6.8	74.7	36.3	35	27.8	26.8	68.6	0.9	30.5
250	43.61	124	44.512	7.1	74.72	59.8	45.5	21.6	31.8	60.9	0.6	38.5
300	43.61	113	44.202	9.1	74	70.4	50.8	24.7	40.9	58.6	0.8	40.6

3.2. Hardness

In Figure 2 the adjustment of the Korsunsky model on the Vickers measurements is visible for the coatings, on a plot of the relative indentation depth versus the experimental hardness. The form of an inverted "s" of the plots is well known, since at high load values the substrate harness values is more visible while at lower load values the contribution to the hardness is mostly from the coating, and the logarithm scale for the relative indentation depth helps to show this behavior.

Figure 2: Korsunsky adjustment model for the Vickers hardness values of the Ti-Si-N-O

From the Korsounky model it was possible to despise the hardness contribution from the substrate and to compute the hardness of the coatings, the values of this procedure are reported un Figure 3, where the TiSiNO coatings have hardness values between 10 and 15 GPa, which could be considered as hard coatings. The coatings do not show a linear dependency of the hardness, the coating with a substrate temperature of 100 °C reached a 10.8 GPa hardness, and it increases to 14.5 and 14.8 GPa for the coatings at 150 °C and 200 °C respectively, but then the hardness drops to 12.5 and 10.5 GPa for the 250 and 300 °C coatings. This behavior can be attributed to the grain sizes seen in the XRD measurements, since it is well known that at lower grain sizes the hardness in higher [12], and the

coating at 200 ℃ had the smaller gain sizes for the SiO_2 and TiN phases, which lead to the highest hardness value of 14.8 GPa. This Grain size - hardness dependency it also demonstrated in Figure 3, where the bigger the grain size is, the lower the hardness, moreover, the hardness values are also corroborated with the compressive stress seen in XRD.

Figure 3: Hardness of the TiSiNO coatings compared to the Grain sizes of the SiO_2 phase.

Finally, it is important to mention that no fracture nor fissures were seen during the measurement of the Vickers hardness, so it could be said that the samples have a high fracture toughness because of the temperature application during the sputtering process, since others works without the temperature application report that the TiSiNO coatings are easily fractured [5].

4. Conclusions

TiSiNO coatings were synthetized by reactive co-sputtering varying the substrate temperature during the deposition process. The temperature favored the formation of highly crystalline coatings where three phases where identified the SiO_2, TiN and TiO, but the amount of the TiO phase was minimal, whereas the SiO_2 and TiN act as the main phases for the sample. The temperature to rearrange the structure to the (200) preferential orientation started at 250°C where the grain sizes started to grow, before that a transition phase occurred where the grain sized decreased and the preferential orientation was (011). The changes in the microstructure caused a change in the hardness of the samples, being the sample at 200 °C the hardest, nevertheless, the temperature favored a better fracture toughness since neither coating presented visible cracks.

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