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Study of structural and mechanical properties of tungsten carbides coatings

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Abstract

Hard coatings of tungsten carbides have been obtained by the deposition of tungsten thin layers, on steel substrates (containing 0.7% wt. carbon), according to the cathodic magnetron sputtering held at temperature of 500°C. It is established by X-rays diffraction that, in the temperature range 500-800°C, no formation of tungsten carbides was observed. However, the annealing at a temperature greater than or equal to 900°C promotes the reaction between the constituents of the samples (W, Fe, C) and hence the formation of W_2C carbide. No other compounds were detected. The micro-hardness measured by Vickers tests, increases with the rise in temperature, particularly from 900°C. The morphology of the surface samples depends on the temperature and duration of thermal annealing.

Key words: Thin films, RF magnetron sputtering, Coating, tungsten carbides.

1. Introduction

Carbides, particularly of the transition metals, have a number of valuable properties, which make them the most promising materials for use in various new fields of technology [1]. They are widely used in cutting tools, tools resistant to wear, abrasive and hard coatings [2]. They are also used for catalytic applications, (similar to the noble metals) [3]. Tungsten carbide is one of these carbides throughout these years. The coatings of pure tungsten carbide, or alloyed with cobalt or iron tungsten carbide, exhibit high wear resistance and low friction [4,5]. Furthermore, their hardness at high temperatures is out standing [6]. Tungsten carbide is also highly corrosion-resistant in acidic media. Owing to its high-temperature stability, chemical inertness and good electrical conductivity, tungsten carbide is a promising thin film diffusion barrier material for the microelectronic devices designed to function at sustained elevated temperature and in hostile environments [7].

The investigation of thin layers for hard coatings or electrical applications requires the preparation of a homogeneous material. However, tungsten carbide exists in different phases, most important are WC and W_2C [8]. Although the W_2C phase is unstable below 1300°C [8], normally a mixture of both WC and W_2C was found by most of the thin layer techniques like sputtering [9,10] and reactive sputtering [11,12], chemical vapor deposition (CVD) [13], solid-phase reaction [14] and ion beam synthesis [15].

In the present work, we have formed thin hard coatings of tungsten carbides. The samples are thin layers of tungsten deposited by RF magnetron sputtering on steel substrate. The samples were submitted to thermal annealing in vacuum, at various temperatures (500-1000°C). The formation of tungsten carbides, the evolution of the microstructure and the morphology of the surface of samples were followed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The measurements of micro-hardness were carried out by Vickers tests.

2. Experimental

One series of samples (thin layer of tungsten / steel substrate XC70) are prepared. The thin layers of tungsten (6 µm) are deposited by RF magnetron sputtering in a vacuum 10^{-7} mbar at 500°C.

After the deposition process, samples (W layer & substrate) were submitted to thermal annealing in vacuum, at various temperatures (500-1000°C) and during different times.

3. Results and discussion

3.1 Analysis by X-rays diffraction (XRD)

Figure 1 shows the XRD patterns for the samples. The spectrum of the not-annealed samples shows the existence of only one phase of W, represented by 3 peaks with 40.6°, 73.6° and 115.16°, corresponding to the plans (110), (211) and (222) respectively. On the other hand the annealing during 30min at 700°C samples does not make any structural modification compared to the state "not annealed", where we noted the existence of the three peaks of W with a texture of the layer according to the direction <222>.

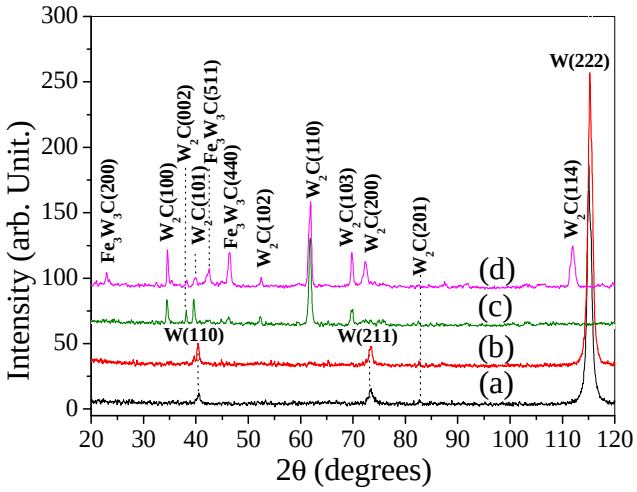

Fig. 1: XRD spectra of the samples [W (6µm)/XC70]: before (a) and after annealed during 30 min at 700°C (b), 900°C (c) and 1000°C (d).

However, the annealing of 30 min at 900°C, allows the observation of new peaks with the disappearance of two peaks of tungsten W(110) and W(211). These new peaks indicate the formation of two new phases: the binary phase W_2C and ternary Fe_3W_3C.

The annealing of 30 min at a higher temperature, 1000°C, does not change anything in the composition of samples, except that it supports the growth of the phases formed previously (W_2C and Fe_3W_3C).

3.2. Study of surface morphology

The study of the morphology of the samples by SEM also shows that the surface morphology of samples changes with the time and the temperature of annealing.

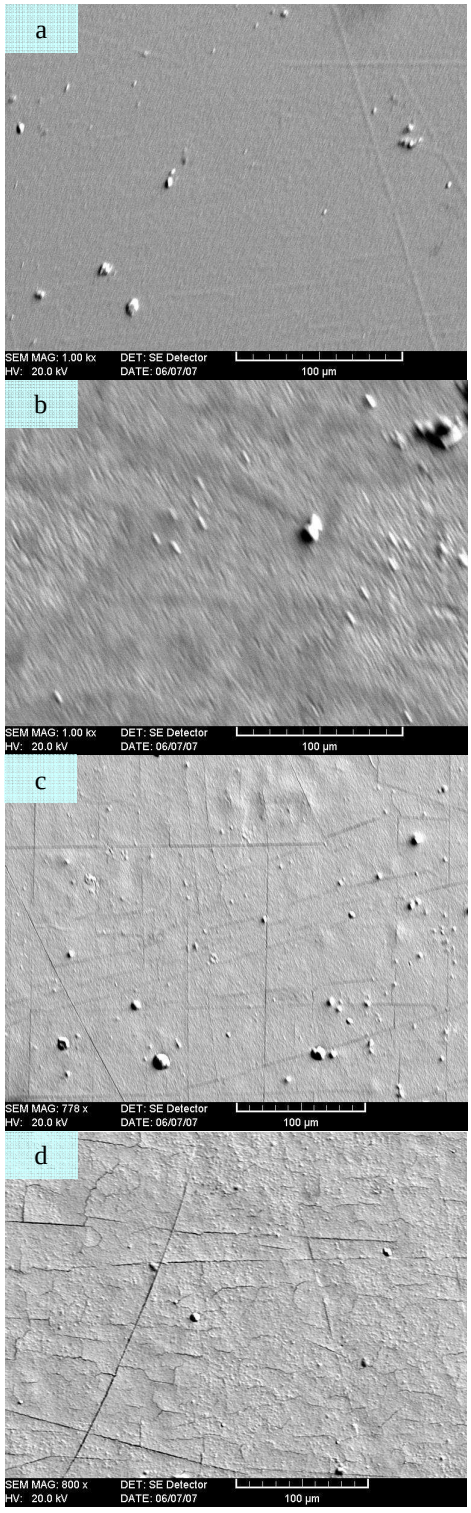

Fig.2: SEM surface images of the samples [W (6µm)/XC70]: before (a) and after annealed during 30 min at 700°C (b), 900°C (c) and 1000°C (d).

The figure 2 illustrates the images obtained with the SEM. In the case not-annealed and annealing at 700°C during 30 min (fig. 2.a & b) the surface of the samples is relatively smooth, but it presents small white particles. After an annealing with 900°C during 30 min (fig. 2.c), the surface

morphology changes with the appearance of the cracks on the surface of the samples W (6µm)/XC70.
The annealing at 1000 ° C for 30 min caused a remarkable increase of the cracks (fig. 2.d). This may be related to the reaction between the substrate and the thin layers of W

3.3. Micro-hardness measurements

Figure 3 shows the variation of microhardness (Hv) of the samples as a function of annealing temperature. It is clear that micro-hardness increases slightly with annealing temperature. The value of micro-hardness of not-annealed sample equals 312 kg/mm^2 (value comparable to that of solid tungsten) [8]. However, after annealing the values of microhardness are distinct: for example the samples annealed at 900°C for 30 minutes increased the microhardness up 392 kg/mm^2. At 1000°C/30min micro-hardness was maximum and takes the value 442 kg/mm^2. This increase is due, probably, to the formation and growth of W_2C carbide. On also note that the values of microhardness throughout the annealing temperatures are lower than those of massive carbides WC (~2000 kg/mm^2), [16,17] and W_2C (~ 3000 kg/mm^2), [17].

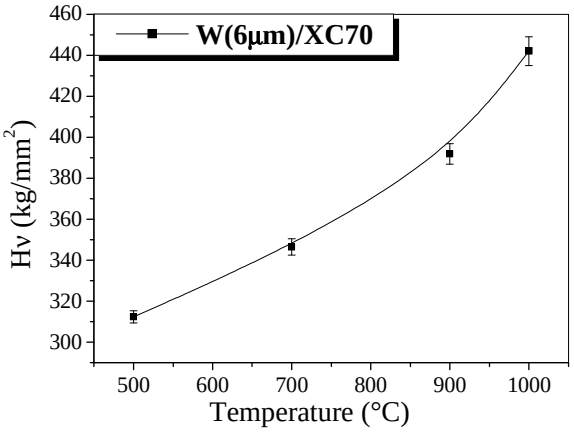

Fig. 3: Variation of the micro-hardness in function of the temperature of annealing.

4. Conclusion

According to the results obtained in this study, we can conclude that it is possible to work out hard tungsten carbide coatings by indirect method consists the coating of a steel substrate, rich in carbon by a layer of tungsten, then the annealing of together to support the diffusion of carbon and the formation of carbides with tungsten. The thermal annealing of the samples leads to the formation of the carbide W_2C but with a lower growth rate for the thin layer of thickness 6 µm. The morphology of surface and the micro hardness also depends on the thicknesses of the thin layers of tungsten.

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