

Structural characterization of co-sputtered W–C–Fe films

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Abstract

R.f. sputtered films of W–C–Fe were obtained by co-sputtering a WC target with different sizes of iron foils. The films were analysed by energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction and Mössbauer spectroscopy. X-ray diffraction results showed that iron contributes to the amorphousness of the films. Mössbauer results revealed that iron is chemically bonded in the W–C sputtered films. Furthermore, the values of the Mössbauer hyperfine parameters obtained for crystalline samples are consistent with the existence of a f.c.c. β -WC₁ phase, detected by X-ray diffraction.

1. Introduction

WC–Co cemented carbides have been found to be suitable for hard and wear-resistant materials with a wide application on cutting tools [1, 2]. In these hard metals, cobalt is used as a binder element and contributes to the improvement of their mechanical properties. It appears as a structural phase between the WC grains, and the chemical bond is confined to the grain boundaries.

Concerning W–C–Co sputtered films the situation is not clear. In these films, the main role of cobalt seems to be not to actuate as a binder but to guarantee a good toughness of the coatings [3]. In previous work on W–C–Co sputtered films, X-ray photoelectron spectroscopy (XPS) results showed that the Co 2p^{3/2} peak was situated at binding energies associated with non-bonded cobalt [3, 4]. Nevertheless, this element was not detected, as a structural phase, either by energy-dispersive X-ray spectroscopy (EDXS) X-ray maps or by X-ray diffraction.

Mössbauer spectroscopy is a useful technique to distinguish chemical phases in materials and it can be a valuable aid to determine the chemical bonding state of cobalt in the W–C films. However, the study of these films by this technique would require radioactive samples which would be difficult and expensive to obtain. To overcome this problem, cobalt was replaced by iron in the preparation procedure of the films. This was done having in mind two aspects. Firstly, although the affinity of iron to carbon is superior than that of cobalt, these two elements are neighbours in the periodic table and they have comparable properties. Secondly, it is known that the non-utilization of iron in the production of WC cemented carbides is attached to the sinter process and not to their properties.

The aim of this work is to study the role of iron on sputtered W–C films, in order to compare the results with those previously obtained for the system W–C–Co. Furthermore, to determine by Mössbauer spectroscopy the chemical bonding state of iron in the W–C sputtered films and thus to predict the behaviour of cobalt in the W–C–Co system.

2. Experimental details

Thin films (2 to 3 μm) were deposited by r.f. diode sputtering a WC target onto high-speed steel M2 (AISI), a substrate mainly used to deposit W–C–Co films [3, 4], and glass discs. Iron foils with different areas were placed on the target in order to obtain samples with different compositions. The deposition rate was about 3 \AA s^{-1} with an argon pressure of 0.3 Pa.

Samples on M2 steel substrates were used for EDXS, XPS and X-ray experiments and on glass substrates for Mössbauer spectroscopy.

A Jeol 35C scanning electron microscope operated at 20 kV, connected to an energy-dispersive X-ray detector, EDXS (Tracor Instruments), was used to determine the composition of the films. A semiquantitative computer fitting programme was applied to the peaks corresponding to the Fe K lines and W L lines, considering that Fe + W = 100% due to the impossibility of determining light elements, such as carbon, with the spectrometer utilized. To overcome this restriction and with the aim of determining the bonding state between the elements, XPS experiments on some W–C–Fe films were carried out on a Leybold–Heraeus LH11 spectrometer using Mg K α radiation, operating at 100 W (10 keV; 10 mA). The composition of the films was obtained from the intensities of the C 1s, O 1s, Fe 2p

and W 4f peaks, after subtraction of the background, corrected by relative sensitivity factors.

The X-ray results were obtained with a Siemens diffractometer (30 kV; 40 mA), equipped with a monochromator, with Cr K α radiation. The ^{57}Fe Mössbauer measurements were performed in transmission geometry by means of a spectrometer with a constant acceleration. The spectra were recorded at room temperature. Velocity calibration was done with a metallic iron foil.

3. Results and discussion

3.1. EDXS and XPS

The results of EDXS are summarized in Table 1. The C 1s and W 4f XPS spectra, recorded for samples A, C and E, are similar to those obtained in earlier studies concerning the deposition of W-C-Co sputtered films [3–7]. The positions of the carbon and tungsten peaks correspond to the binding energies characteristic of tungsten carbide compounds [3–7]. Neither of the Fe 2p $^{1/2}$ and Fe 2p $^{3/2}$ peaks shows any important feature when compared with those of the standard sample spectrum [7]. However, in all the XPS spectra, the Fe 2p $^{3/2}$ peak is located at binding energies slightly higher than that assigned to non-bonded iron (≈ 707.10 eV against 706.75 eV, respectively). Furthermore, for all the samples, the distances between the energies of the two Fe 2p peaks are lower than the value of 13.2 eV reported in the literature [7] for pure iron. This is particularly true for sample A, where this distance is 12.6 eV. In spite of this discrepancy being of the order of that observed in the W-C-Co sputtered films, it may indicate a probable chemical bonding between the Fe and one or both elements W/C. Unfortunately, no data on W-C-Fe compounds were found in the XPS literature.

Taking into account the intensities of the iron, tungsten and carbon peaks (I_{Fe} , I_{W} and I_{C}) a good agreement is achieved between the XPS $I_{\text{Fe}}/I_{\text{W}}$ ratio and the ratio of the atomic percentage of iron and tungsten obtained by EDXS (Fig. 1).

In order to correlate the chemical composition of the films obtained by EDXS and XPS, sensitivity factors were applied at the iron, tungsten and carbon peak

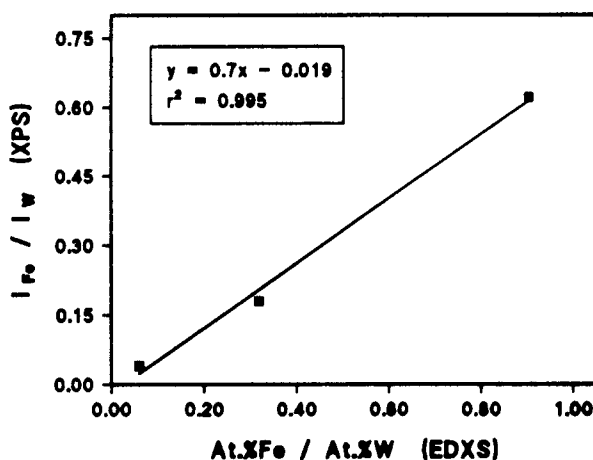


Fig. 1. Relation between XPS $I_{\text{Fe}}/I_{\text{W}}$ and EDXS at.% Fe/at.% W ratios.

intensities. However, since it was not possible in this study to compare the peak intensities obtained for W-C-Fe films and those of standards with known chemical composition, we considered the sensitivity factors of tungsten and carbon indicated in the literature [7]. Thus, considering a linear relation between the XPS $I_{\text{Fe}}/I_{\text{W}}$ ratio and the EDXS at.% Fe/at.% W, and the sensitivity factor 2.2 for tungsten, a value close to 1.4 is obtained for the sensitivity factor of iron, which is rather different from the value 4.6 proposed in the literature. This might be due either to the fact that the latter value concerns a spectrum of an iron standard sample, while the former refers to W-C-Fe films, or to the preferential sputtering of iron [4] during the ion bombardment cleaning procedure before surface analysis. It is important to remark that the value of the sensitivity factor of cobalt in W-C-Co films [4] is also very different from what one would expect for a spectrum of a cobalt standard sample.

The compositions of samples A, C and E, obtained by XPS, are listed in Table 2. In the same table, XPS values of the iron percentage and the ones corrected obtained by EDXS, considering that at.% W/at.% C = 1, can also be compared.

3.2. X-ray diffraction

The X-ray spectra of the W-C-Fe films can be classified into two groups (Fig. 2). The first one includes samples C, D and E, and is characterized by spectra with a broad peak close to the $2\theta = 60^\circ$ angle, which suggests the existence of an amorphous structure; the other one includes samples A and B. The X-ray diffraction spectrum of sample B shows traces of a crystalline structure, owing to the appearance of some more or less broad peaks, which were indexed as $\beta\text{-WC}_{1-x}$ f.c.c. carbide. However, the crystallites of this phase must be of small size in order to explain the large widths of the peaks. The

TABLE 1. Chemical composition of the films (EDXS results)

Sample	W	Fe
A	94.6	5.4
B	92.6	7.4
C	76.0	24.0
D	64.5	35.5
E	52.2	47.8

TABLE 2. Chemical composition of the films (XPS and EDXS results)

Sample	XPS				EDXS
	W	C	Fe	W/C	Fe
A	49.6	47.2	3.2	1.05	2.8
B	48.2 ^{a)}	46.0 ^{a)}	5.8 ^{b)}	1.05	6.1
C	44.6	42.7	12.7	1.04	13.8
D	40.3 ^{a)}	38.4 ^{a)}	21.3 ^{b)}	1.05	20.1
E	34.1	32.6	33.3	1.05	30.3

^{a)}Estimated considering that W/C = 1.05, as obtained for samples A, C and E by XPS technique.

^{b)}Estimated considering a linear relation between the values of iron composition obtained for samples A, C and E by EDXS and XPS techniques.

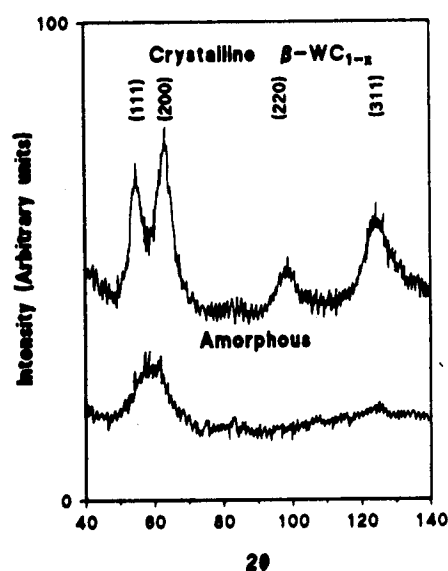


Fig. 2. X-ray diffraction spectra of samples A and E (see text).

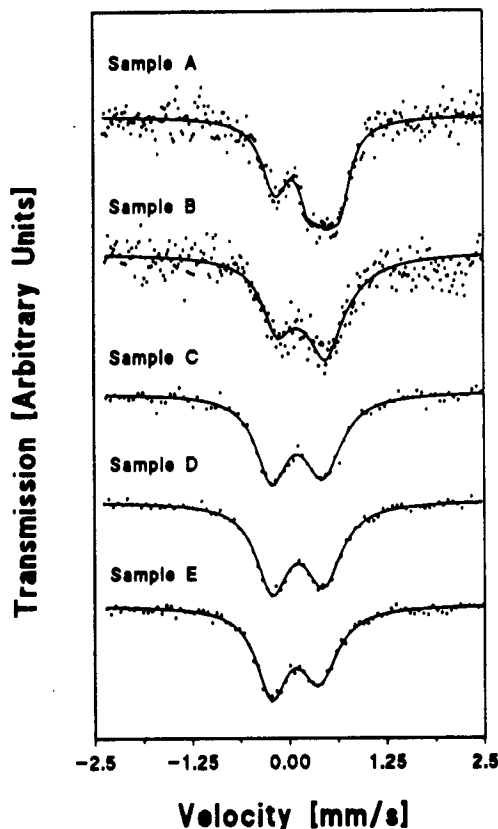


Fig. 3. Mössbauer spectra of W-C-Fe films.

solid lines stand for spectra synthesized by least-squares fit to examine the local environmental effect.

Taking into account the X-ray results, the spectra of samples A and B were fitted by two symmetric doublets. Spectra of samples C, D and E were described by fitting the two peaks to two independent Lorentzian line shapes.

Visual analysis shows that the spectra are composed of one or more doublets which is not compatible with the existence of an α or γ iron single phase; in this case, a sextuplet or a single line spectrum would be expected, respectively.

The mean line widths of the peaks differ with increasing iron content. For samples A and B the line width of the doublet I (Γ_I) increases with increasing iron content while the corresponding value of doublet II (Γ_{II}) remains constant. However, within experimental error, no significant differences in the line widths of the quadrupole doublet were observed for the amorphous films (samples C, D and E); the value of 0.5 mm s^{-1} obtained for these samples is larger than the one expected for a single site absorption line, meaning a distribution of both the isomer shift and the quadrupole splitting.

The values of the average hyperfine parameters of the W-C-Fe series of sputtered films are listed in Table 3. As it can be seen, there is a systematic decrease of the isomer shift (IS) with increasing iron content in the films,

spectrum of the sample A shows well defined peaks which were also identified as $\beta\text{-WC}_{1-x}$. It is important to point out that no other single, binary or ternary phases were detected in any of the samples studied, meaning that if they exist they must be arranged in small size aggregates not detectable by X-ray diffraction.

The X-ray results are in agreement with those obtained for W-C-Co films [3]. However, the value of 10 at.% Co presented as the amorphous/crystallinity threshold content for W-C-Co films seems to be slightly higher than the corresponding value of iron for the W-C-Fe system, which must be close to 6 at.%, the composition of sample B.

3.3. Mössbauer spectroscopy

Experimental Mössbauer spectra of the W-C-Fe sputtered films are presented by dots in Fig. 3. The

TABLE 3. Isomer shifts (IS) and quadrupole splittings (QS) of the films

Sample	IS (mm s^{-1})	QS (mm s^{-1})
A	0.29 (Site I = 0.42, Site II = 0.16)	0.53 (Site I = 0.40, Site II = 0.65)
B	0.28 (Site I = 0.40, Site II = 0.16)	0.52 (Site I = 0.39, Site II = 0.63)
C	0.11	0.65
D	0.10	0.61
E	0.08	0.58

meaning an increasing charge density at the iron nucleus, and indicating that this element must be bonded to a W, C or W-C phase. This does not exclude, however, a hypothetical existence of finely divided iron-rich clusters, small enough to be superparamagnetic. Low-temperature Mössbauer experiments would be necessary in order to elucidate this question.

The discrepancy between the values of the quadrupole splitting of samples B and C might be attributed to different structural behaviours of these W-C-Fe films. Similar behaviour was observed by Blum *et al.* [8] in Fe-B samples. These authors, when comparing their values of the isomer shift and quadrupole splitting of a Fe-50B sample (prepared by r.f. sputtering) and the corresponding ones of a Fe-50B crystalline sample, found a significant difference between the two results. They justified this behaviour in terms of different chemical orderings in the film structures.

In agreement with the results of X-ray diffraction, the values of the quadrupole splitting obtained for W-C-Fe r.f. sputtered samples point towards the existence of a structural transition from a crystalline to an amorphous state for an iron composition close to that of sample B. This conclusion is also supported by the quadrupole splitting probability curves, $P(QS)$, extracted from Mössbauer experimental data by the method of Le Cäer [9]. In fact, very broad $P(QS)$ curves were obtained for samples C, D and E while samples A and B presented more sharp distributions. Moreover, the Mössbauer hyperfine parameters obtained for samples A and B may correspond to a cubic NaCl-type structure, which is consistent with the presence of the metastable f.c.c. $\beta\text{-WC}_{1-x}$ phase, indexed by X-ray diffraction.

In a recent work on mechanically driven synthesis of carbides with a vibratory mill, equipped with tungsten carbide balls, Le Cäer and co-authors [10] found by Mössbauer spectroscopy a metastable paramagnetic Fe-C compound. According to the authors it could correspond to Fe_{1-x}C carbide with a NaCl-type structure. The existence of an Fe-C phase in the W-C-Fe sputtered films is conceivable but unexpected

since no corresponding peaks were observed in the X-ray patterns of the crystalline samples. Taking into account XPS, X-ray and Mössbauer results, in our point of view the most probable picture is that the crystalline W-C-Fe sputtered films studied are formed by a f.c.c. $\beta\text{-WC}_{1-x}$ phase in which iron is in substitution of tungsten. Moreover, if other phases are present in the structure, they must be formed by small aggregates of particles not detectable by X-ray diffraction.

Finally, we would like to mention that studies on the crystallization of samples C, D and E and on the contribution of the r.f. sputtering process in the creation of a hypothetical superparamagnetic state in the W-C-Fe sputtered films are being undertaken.

4. Conclusions

We have reported the results of a structural characterization study of co-sputtered W-C-Fe films. The results now obtained in W-C-Fe sputtered films are similar to those achieved in previous work in W-C-Co films [3, 4]. X-ray results showed that, as well as cobalt, iron contributes to the amorphousness of W-C sputtered films. An iron content close to 6 at.% was found as the amorphous/crystallinity threshold value for the W-C-Fe films, against 10 at.% Co obtained for W-C-Co films [3]. The X-ray patterns of the crystalline samples (A and B) were indexed as an f.c.c. $\beta\text{-WC}_{1-x}$ phase. Mössbauer results demonstrated that iron is chemically bonded in W-C sputtered films and, in accordance with the X-ray results, point towards the existence of a structural transition of the films for an iron composition close to 6 at.%.

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