

On the Synthesis and Characterization of Mixed (Mo,W) Carbides

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Abstract

Different pathways for the synthesis of mixed (Mo,W) carbides are presented and discussed. Thin mixed carbides films were deposited by the reactive cosputtering of W and Mo in a CH₄ (10%)/Ar gas mixture. Bulk carbides were prepared from various precursors during carburization reactions at different temperatures under a constant control of the gas flow rate of CH₄ (10%)/H₂. The principal aim of this work was to achieve an as good as possible homogeneity of the samples, at low temperatures, in comparison with the melting point of the tungsten (~3900 K). The structure of the samples was determined by X-ray and electron diffractions, and their composition by scanning Auger electron spectroscopy. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Because of their high mechanical and thermal stability, transition metal carbides have been used for a long time in a large field of industrial applications.

The dissolution of carbon in the lattice of transition metals like Cr, Mo and W leads to new physico-chemical properties^{1–5} that are not observed with the above mentioned pure metals.

During the incorporation of carbon in the metal, usually of cubic body centered (bcc) structure, its lattice changes and adopts cubic face centered, hexagonal simple or hexagonal close-packed conformations, according to Hägg's rule.⁶ The carbon atoms occupy the interstitial sites of the metallic lattice.

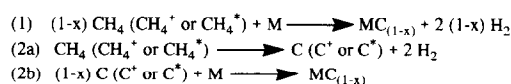
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Some years ago, the possibility of using tungsten, molybdenum and mixed molybdenum/tungsten carbides as catalysts instead of platinum group metals in some catalytical^{7–13} and electro-catalytical^{14–18} reactions opened new outlooks for this kind of materials. For this reason, the number of studies focused on the synthesis and characterization of new transition metal carbides have increased during the last decades.^{19–21}

One point of interest in this research is to find the way of preparing mixed molybdenum/tungsten carbides at low temperatures. First of all, low temperatures of synthesis are required for economical reasons and industrial engineering. A second reason is the possibility of using these materials in catalytical reactions. Too high temperatures of preparation lead to the sintering of the catalyst powder that diminishes its surface area.

The purpose of our work is to synthesize and characterize thin films and bulk (Mo,W) carbides through different pathways allowing low temperatures of preparation. Thin films were prepared by the reactive cosputtering of Mo and W in a CH₄ (10%)/Ar atmosphere. The methodology adopted here is based on the experimental conditions elaborated by Reniers *et al.*^{22–25} for the reactive sputtering of W and by Maoujoud *et al.*^{25–28} for the one of Mo.

When one refers to the literature, two models exist for describing the reactive sputtering. The first model proposed for the synthesis of β -WC_(1-x)²⁹ assumes the formation of the carbide on the target and has been generalized to a metal M:



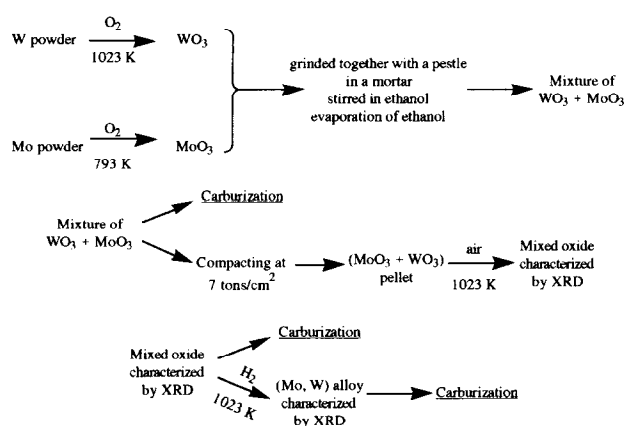
1. Describes the direct reaction on the surface of the target between the metallic atoms and the methane molecules which may be ionized or excited.

- Describes the decomposition of CH_4 in the plasma followed by the reaction between the metallic atoms and the carbon (C^+ or C^*) colliding with the target.

The second model consists of the reaction between the sputtered metal and the excited carbon (C^*) during the deposition on the substrate.^{30,31}

These two models were corroborated by experimental results so that it was concluded that the two phenomena occur during the reactive sputtering.

Bulk carbides were synthesized from different precursors following dry and wet pathways. The dry pathways for the synthesis of precursors for carburization are summarized in the following scheme:

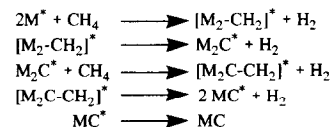


The mixed (Mo,W) oxide was prepared according to Oyama's methodology.^{32,33} In fact, this pathway was influenced from Volpe and Boudart's work^{34,35} in which they mentioned that the oxidation of Mo and W powders leads to the increase of their surface area and to the breakup of their structure. Therefore, reactions at the solid/gas interface become easier. Oyama made evidence that it also allows the interdiffusion of the oxidized forms of tungsten and of molybdenum, leading to a monophasic mixed oxide.

A close mixture of WO_3 and MoO_3 was also prepared by the coprecipitation of the two metal oxides, following the wet pathway developed by Leclercq *et al.*^{36,37}

All those precursors were carburized in a gas mixture of CH_4 (10%)/ H_2 (90%). From the literature, it is known that the carburization of Cr, Mo and W requires their metallic state. Therefore, the oxide precursors of Cr, Mo and W have been first reduced. The oxide precursors of Mo and W can be reduced either by the hydrogen or by the methane contained in the reactive gas mixture of CH_4 and H_2 .³⁸ On the other hand, chromium oxides are reduced only by CH_4 , in order to form CO and Cr,³⁹ and not by hydrogen, as it is the case for W and Mo.

The reaction scheme proposed here for the carburization of M, which can be Mo, W or the (Mo,W) alloy, was based on the works of Davidson⁴⁰ and Leclercq.³⁸ The carburization results from the catalytical dehydrogenation of the hydrocarbon molecules as follows:



The structural characterization of the intermediates of reaction and of the final carbides was performed by X-ray diffraction (XRD) and electron diffraction. Auger electron spectroscopy (AES) was also used in order to determine the composition of some of the carbides.

2 Experimental

Thin carbide films were deposited on titanium foils (99.98% of purity from Johnson Matthey) by dc reactive sputtering of different targets. The targets used were a tungsten foil (99.97% of purity from Johnson Matthey), a molybdenum foil (99.97% of purity from Johnson Matthey) and a molybdenum foil for which half of the surface was covered with sputtered tungsten. The gas ratio used for the reactive sputtering was 90% Ar (N57)/10% ($\pm 1\%$) CH_4 (N45) (Air Liquide). The experimental procedure and a drawing of the setup were already described.²²⁻²⁵

Bulk carbides were synthesized in a high temperature furnace during a 15 h chemical reaction of various precursors with a 90% H_2 (N40)/10% ($\pm 1\%$) CH_4 (N45) (Air Liquide) mixture, under constant control of the gas flow rate.

The tungsten and molybdenum powders used were 99.9% of purity from Johnson Matthey. Ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ from Janssen Chimica and ammonium tungstate $[(\text{NH}_4)_{10}(\text{W}_{12}\text{O}_{41})\cdot 5\text{H}_2\text{O}]$ from Johnson Matthey were also used for the coprecipitation reaction leading to a mixture of molybdenum and tungsten oxides.

The structure of the samples was characterized by RHEED (apparatus constant $\lambda_1 = 26.9 \text{ mm } \text{\AA}$) and X-ray diffraction (using Berthold's goniometric method and Co monochromatized K_α radiation. Silicon was taken as standard.). Their composition was determined by Auger spectrometry. The Auger spectrometer used was a Perkin-Elmer PHI 650, with an incident exciting electron beam of 2.5 keV. Before the acquisition of the Auger spectra, the surface of the samples was cleaned up by a 5 kV Ar^+ sputtering.

3 Results and Discussion

3.1 Preparation of thin carbide films

The advantage of the dc reactive sputtering lies in the possibility of synthesizing compounds of variable stoichiometry that usually exist at high temperatures. This technique of synthesis allows the kinetic stabilization of metastable phases at low temperatures.²⁵

In order to get a basis for comparison, tungsten carbide and molybdenum carbide were deposited on titanium foils according to the pathway described in our previous works.²²⁻²⁵ The titanium substrate was heated at 793 K in an ultra high vacuum chamber at $3.9 \cdot 10^{-4}$ Pa. The mixture of CH₄ (10%)/Ar was introduced at 6.65 Pa. The 3 kV voltage applied to the target induced an ionic current of 1 mA.

The interreticular parameters $d(hkl)$ of the tungsten carbide and of the molybdenum one revealed by RHEED were in agreement with the cubic face centered structures of β -WC_(1-x) ($a_0 = 0.4248$ nm, see JCPDS folder no. 20-1316) and of δ -MoC_(1-x). ($a_0 = 0.4281$ nm determined by Rudy *et al.*⁴¹)

The molybdenum target for which half of the surface was covered with tungsten was sputtered in the same conditions as those described above and a thin mixed molybdenum/tungsten compound was deposited on a titanium substrate. Figure 1 shows the RHEED diagram performed on the deposit.

The $d(hkl)$ stemmed from the diffraction rings are in agreement with those calculated for the lattice parameter $a_0 = 0.426$ nm. This value results from the application of Vegard's law for a 50-50 'alloy' of β -WC_(1-x) and δ -MoC_(1-x), and also corresponds to the lattice parameter of

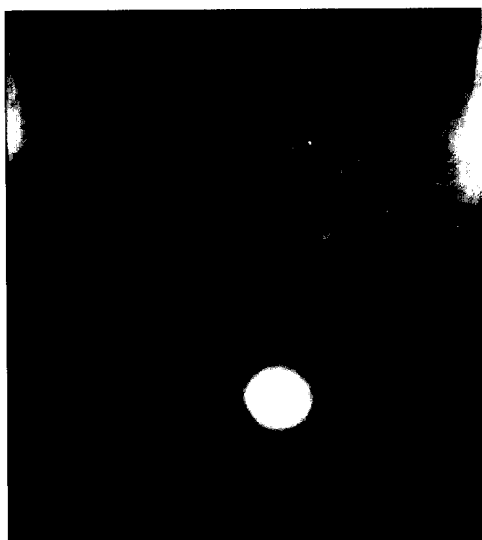


Fig. 1. RHEED diagram of the deposit obtained from the reactive cosputtering of Mo and W in a CH₄/Ar atmosphere.

α -(Mo, W)C_(1-x) obtained by Schuster.⁴² But taking into account the low resolution of the diffraction rings and the close values of the lattice parameters of β -WC_(1-x), δ -MoC_(1-x) and α -(Mo, W)C_(1-x), the sputtered thin film can also correspond to a mixture of β -WC_(1-x), and δ -MoC_(1-x). Table 1 shows the comparison of the experimental values of $d(hkl)$ of the deposit with the $d(hkl)$ data of β -WC_(1-x), δ -MoC_(1-x) and α -(Mo, W)C_(1-x).

In fact, the two existing models for the reactive sputtering predict that the sputtered thin film may be composed by any of these three carbides mentioned above. The first model describing the reaction of carburization on the target indicates that with the molybdenum foil for which half of the surface is covered with tungsten, the two carbides β -WC_(1-x) and δ -MoC_(1-x) are separately sputtered. The second one describing the reaction of carburization during the deposition of the thin film explains the formation of α -(Mo, W)C_(1-x) for such a target.

Figure 2 exhibits one of the superimposable Auger spectra performed on three different points of this sample showing its metallic homogeneity. The Auger peaks of both metals (Mo and W) appear in an energetic window included between 100 and 230 eV. The typical triple Auger peak of carbon confirms the presence of the carbide in the sample. It is important to note that a high oxygen peak also appears between 495 and 515 eV. The presence of oxygen in the sample can modify the interpretation of the diffraction analysis. If one refers to the tungsten compounds, it is known that β -WC_(1-x) and the oxycarbide W₂(C,O) present the same cubic face centered structure with very close lattice parameters [$a_0 = 0.4248$ nm for β -WC_(1-x) and 0.424 nm for W₂(C,O) (JCPDS folder no. 22-959)].

Therefore, at this stage of the analysis, one cannot make any distinction between a mixed carbide α -(Mo, W)C_(1-x), a mixture of β -WC_(1-x) and δ -MoC_(1-x), the presence of W₂(C,O) in the sample, a kind of new mixed oxycarbide, or a mixture of all these compounds.

Table 1. Comparison of the $d(hkl)$ (Å) of the deposit obtained by the reactive cosputtering of Mo and W in a CH₄/Ar atmosphere with some existing data

(hkl)	Deposit	β -WC _(1-x)	δ -MoC _(1-x)	α -(Mo,W)C _(1-x)
(111)	—	2.429	2.471	2.46
(200)	—	2.107	2.140	2.13
(220)	1.51	1.495	1.514	1.51
(311)	—	1.277	1.291	1.29
(222)	1.24	1.221	1.236	1.23
(400)	1.07	1.061	1.070	1.07
(331)	0.98	0.973	0.982	0.98
(420)	0.95	0.948	0.957	0.95

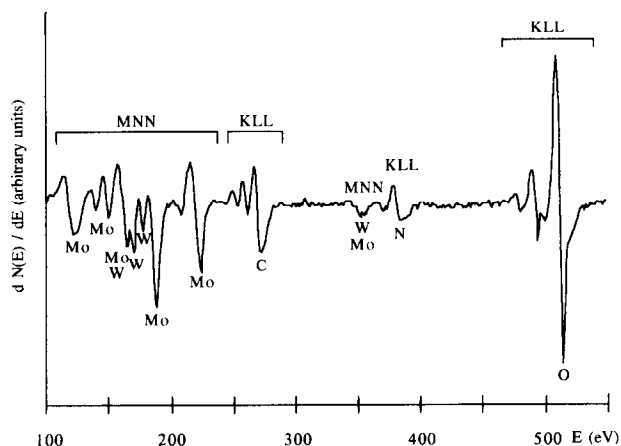


Fig. 2. One of the superimposable Auger spectra recorded on three different points of the deposit obtained from the reactive cosputtering of Mo and W in a CH_4/Ar atmosphere.

3.2 Synthesis of bulk mixed carbides

3.2.1 Preparation of different precursors for carburization

The synthesis of mixed carbides requires the close mixing of both metals. In order to achieve the homogeneity, dry and wet pathways were developed in this work. The common point of all these methodologies is the necessity to get the oxidized forms of both metals that allow their interdiffusion.

Synthesis of precursors following dry pathways (see Scheme 2): A tungsten oxide was obtained by oxidation of a tungsten powder during 6 h at 1023 K. A molybdenum oxide was also prepared by a 6 h oxidation of a molybdenum powder at 793 K. The X-ray diffraction performed on these samples [Fig. 3(a) and (b)] revealed an orthorhombic structure for both of them, in agreement with the JCPDS folder no. 20-1324 of WO_3 and with the JCPDS folder no. 5-0508 of MoO_3 .

The masses of these two oxides were chosen to get a 50–50 molar ratio of the two metals. WO_3 and MoO_3 were grinded together with a pestle in a

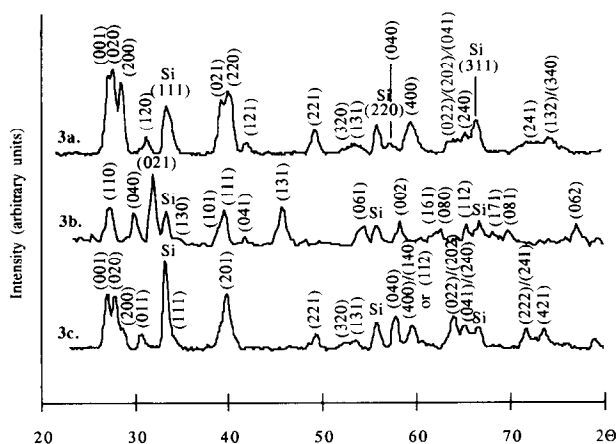


Fig. 3. Comparison of the X-ray diffraction diagrams of (a) WO_3 , (b) MoO_3 and (c) of the mixed oxide.

mortar, and then stirred in ethanol. Once the ethanol was evaporated, this mixture could be used as precursor for carburization. Another technique consisted in compacting at 7 tons cm^{-2} and heating at 1023 K this mixture in order to obtain a mixed oxide according to Oyama's methodology.^{32,33}

The X-ray characterization [Fig. 3(c)] revealed the mixed (Mo,W) oxide after the compacting and heating treatments as mentioned by Oyama.

As the X-ray diffraction diagram of this mixed (Mo,W) oxide does not correspond to any existing JCPDS folder, its interpretation proposed by Oyama was based on a comparison with those of WO_3 and MoO_3 . It was concluded that the product of reaction has to be a monophasic mixed oxide, because the main diffraction peaks of MoO_3 do not appear in its X-ray diffraction diagram. Moreover, the similarity in shape of the diagram of the mixed (Mo,W) oxide with the one of WO_3 strongly suggests that the atoms of Mo replace up to 50% atoms of W in the metallic lattice of WO_3 .

This comparison can be investigated further. The similarity of the X-ray diffraction patterns of WO_3 and of the mixed (Mo,W) oxide should mean that the lattice of the mixed oxide is orthorhombic as the one of the tungsten trioxide. It is therefore possible to assign the Miller indices (hkl) to some of the main diffraction peaks of the mixed oxide. These Miller indices (hkl) and their corresponding interreticular parameters $d(hkl)$ are used in the quadratic form of the equation for a (hkl) plane of an orthorhombic lattice:

$$Q(hkl) = (h/a_0)^2 + (k/b_0)^2 + (l/c_0)^2 \text{ in which}$$

$$Q(hkl) = 1/d(hkl)^2$$

So the parameters of the orthorhombic lattice of the mixed oxide a_0 , b_0 and c_0 are extracted from the appropriate combinations of those (hkl) equations and their averages are compared with those of the orthorhombic WO_3 in Table 2.

These parameters allow the calculation of the interreticular distances $d(hkl)$ for each plane of the orthorhombic lattice of the mixed oxide. Table 3 shows the comparison between the calculated interreticular distances, $d(hkl)$, and all those measured on the X-ray diffraction diagram of the mixed oxide. The (hkl) planes assigned thanks the comparison of the XRD diagram of the mixed

Table 2. Comparison between the averages of a_0 , b_0 , c_0 calculated for the mixed oxide and those of WO_3

	Mixed oxide	WO_3 (JCPDS 20-1324)
a_0 (nm)	0.725 ± 0.001	0.7384
b_0 (nm)	0.745 ± 0.001	0.7512
c_0 (nm)	0.382 ± 0.002	0.3846

oxide with the one of WO_3 are also mentioned in Table 3.

Moreover, since no mass loss was detected after the synthesis of the mixed oxide in comparison with the initial masses of WO_3 and MoO_3 , this mixed oxide may correspond to the $(\text{Mo}_{0.5}\text{W}_{0.5})\text{O}_3$ stoichiometry. This mixed (Mo,W) oxide and also its reduced form can be used as precursor for carburization.

The reduction of the mixed oxide was performed under hydrogen at 1023 K during 15 h. Prior to their reduction, the mixed oxide pellets were grinded. Figure 4 shows the comparison of the X-ray diffraction diagram of the reduced mixed oxide with the one of a mixture of Mo and W. The diffraction peaks (hkl) of the reduced mixed oxide lie exactly in the middle of the corresponding diffraction peaks (hkl) of Mo and W. This is in agreement with Vegard's law for a 50–50 (Mo,W) alloy.

Synthesis of precursors following a wet pathway: The methodology described here was elaborated by Leclercq *et al.*^{36,37} The close mixing of the two metal oxides is obtained by their coprecipitation. Therefore ammonium paratungstate and ammonium molybdate were dissolved together in water in order to get a 50–50 molar ratio of both metals. Then, hydrochloric acid (12 N) was added dropwise to the solution under stirring. After a 6 h reaction, the precipitate obtained was filtered and dried at 393 K.

No X-ray diffraction diagram could be obtained for this sample, due to the too small size of the oxides particles. But the authors of this pathway proposed that it leads to a mixture of MoO_3 and

Table 3. Comparison between calculated and experimental $d(hkl)$ of the mixed oxide

(hkl)	Calculated $d(hkl)$ (Å)	Experimental $d(hkl)$ (Å)	(hkl)	Calculated $d(hkl)$ (Å)	Experimental $d(hkl)$ (Å)
(001) ^a	3.82	3.84	(400)	1.81	1.80
(020) ^a	3.72	3.73	(140)	1.80	1.80
(200) ^a	3.62	3.63	(112)	1.79	1.80
(011)	3.40	3.40	(022)	1.70	1.70
(120)	3.31	—	(202)	1.69	1.70
(111)	3.08	3.08	(041)	1.67	1.67
(021)	2.67	—	(240)	1.66	1.67
(201)	2.63	2.63	(401)	1.64	—
(220)	2.60	—	(420)	1.63	—
(121)	2.50	—	(141)	1.63	—
(221) ^a	2.15	2.15	(331)	1.58	—
(031)	2.08	—	(222)	1.54	1.53
(320) ^a	2.03	2.03	(241)	1.52	1.53
(131) ^a	2.00	2.00	(421)	1.50	1.50
(311)	1.97	—	(132)	1.48	—
(002)	1.91	—	(312)	1.47	—
(040) ^a	1.86	1.86			

^aIndexation of the Miller indices (hkl) of some of the main diffraction peaks of the mixed oxide by comparison of its XRD diagram with that of WO_3 . These peaks were used to determine the lattice parameters of the mixed oxide.

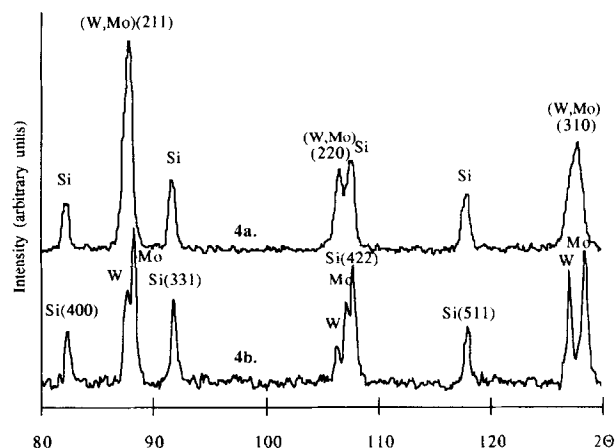


Fig. 4. Comparison of the X-ray diffraction diagram (a) of the reduced mixed oxide with (b) the one of a mixture of Mo + W.

WO_3 according to the chosen ratio. This coprecipitate was used as precursor for carburization.

3.2.2 Reaction of carburization

Before carburizing the different precursors for the synthesis of mixed (Mo,W) carbides, standards of Mo and W carbides were prepared in the same conditions of constant control of the reactive gas flow rate (31 ml/min of a mixture of CH_4 (10%)/ H_2) and temperatures during 15 h.²⁴ Table 4 summarizes the main results obtained by X-ray diffraction on these standards.

Carburization of different mixed precursors at 1023 K:

- (a) Mixture of $\text{WO}_3 + \text{MoO}_3$ —Prior to carburization, the mixture of the two oxides was pressed at 7 tons cm^{-2} into pellets.

The X-ray diffraction diagram (Fig. 5) reveals that the mixture of WO_3 and MoO_3 carburized at 1023 K leads to hexagonal simple (hs) and hexagonal close-packed (hc) structures. Moreover, diffraction peaks corresponding to a metallic lattice also appear, indicating that uncarburized metal still exists in the sample. Because of the diffraction angles investigated here, it is not possible to assign this metallic lattice to Mo, W or to the (Mo,W) alloy.

The hexagonal simple structure can be attributed to the mixed carbide (Mo,W)C because this structure does not appear after

Table 4. Influence of $T(K)$ on the synthesis of standard carbides

Initial reactants	T (K)	Final products	Lattice	JCPDS
WO_3	1023	W	bcc	4-0806
WO_3	1173	α -WC	hs	25-1047
MoO_3	1023	α - Mo_2C	hc	35-787
MoO_3	1173	α - Mo_2C	hc	35-787

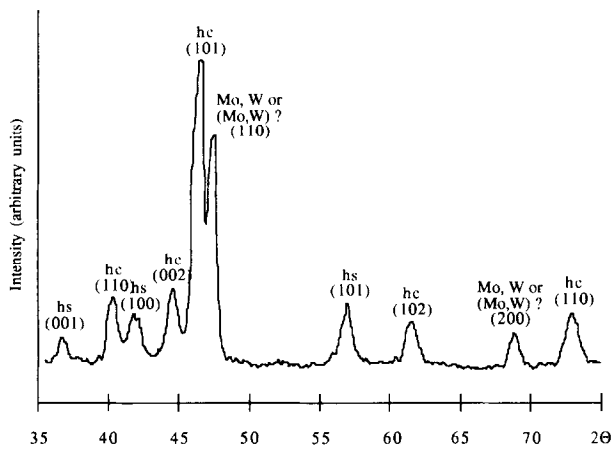


Fig. 5. X-ray diffraction diagram obtained after carburization of a $\text{MoO}_3 + \text{WO}_3$ mixture at 1023 K (hs: hexagonal simple; hc: hexagonal close-packed).

the carburization of WO_3 and even not after the carburization of MoO_3 in the same reaction conditions (Table 4). On the other hand, the hexagonal close-packed structure can be attributed either to $(\text{Mo,W})_2\text{C}$ or to $\alpha\text{-Mo}_2\text{C}$.

Moreover, the Auger spectra recorded for three different points of this sample (Fig. 6) reveal its heterogeneity. Therefore, this kind of precursors for the synthesis of mixed carbide was given up for further experiments. An important contamination by oxygen is also observed. The typical triple peak of carbon between 225 and 275 eV confirms the presence of carbide in the sample.

- (b) Mixed (Mo,W) oxide—The X-ray diffraction diagram recorded after the carburization of the mixed oxide at 1023 K is similar to that presented in Fig. 5. The hexagonal simple structure was attributed to $(\text{Mo,W})\text{C}$ but, in this case, the hexagonal close-packed structure was assigned only to $(\text{Mo,W})_2\text{C}$. There are two reasons why the hexagonal close-packed structure can be attributed here only to $(\text{Mo,W})_2\text{C}$. The first one is that the

precursor for the carburization is the monophasic mixed oxide, for which the reduction leads to the (Mo,W) alloy, showing the close mixing of the two metals. The second one is that the Auger spectra recorded for three different points of the sample are identically the same. Figure 7 shows one of these superimposable Auger spectra. Therefore, it can be concluded that the carburization of the mixed oxide at 1023 K leads to a homogeneous metallic composition of the carbide, contrary to the $\text{MoO}_3 + \text{WO}_3$ mixture.

Carburization at 1173 K of the mixed oxide and of its reduced form (Mo,W): The mixed oxide precursor was carburized as the pellet obtained after its formation. Its reduced powder form was pressed at 7 tons cm^{-2} into pellets.

The X-ray diffraction diagrams and the Auger spectra obtained after the carburization of these two kinds of precursors are identical. So, the reduction of the mixed oxide leading to the (Mo,W) alloy is not, in this case, a necessary step before the carburization.

Figure 8 shows the X-ray diffraction diagram typical for a carburized mixed (Mo,W) oxide and for a carburized (Mo,W) alloy. The hexagonal simple structure appears as a unique phase. This structure cannot be obtained for MoO_3 in the same conditions of carburization using a CH_4/H_2 gas mixture.

Because of the homogeneity of the precursors, and of the impossibility to obtain an hexagonal simple structure by the carburization of MoO_3 in these conditions, this structure is attributed to $(\text{Mo,W})\text{C}$. As the lattice parameters of $\alpha\text{-WC}$ ($a_0 = 0.29062 \text{ nm}$ and $c_0 = 0.28378 \text{ nm}$) and of $\gamma\text{-MoC}$ ($a_0 = 0.2898 \text{ nm}$ and $c_0 = 0.2809 \text{ nm}$)⁴³ are very close, it is difficult to check from the diffraction diagram presented here if the lattice parameters of (Mo,W)C follow Vegard's rule.

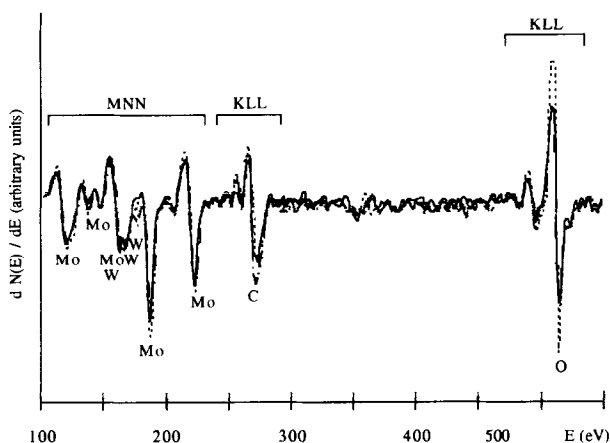


Fig. 6. Auger spectra recorded on three different points of the carburized $(\text{MoO}_3 + \text{WO}_3)$ mixture at 1023 K.

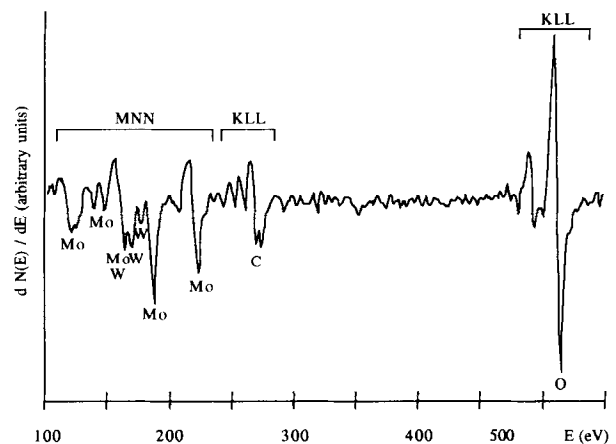


Fig. 7. One of the superimposable Auger spectra recorded on three different points of the carburized mixed oxide at 1023 K.

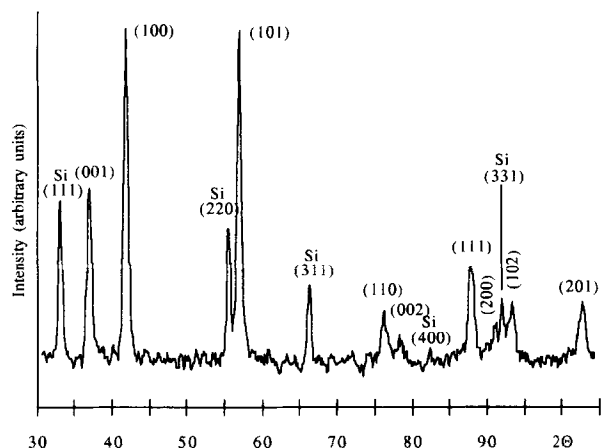


Fig. 8. X-ray diffraction diagram obtained after carburization of a (Mo,W) mixed oxide at 1173 K. The XRD of a carburized (Mo,W) alloy at 1173 K presents the same feature.

Nevertheless, from the comparison of this diffraction diagram with the one obtained for α -WC, it is possible to assign a plane to each peak.

The similar Auger spectra recorded for three different points of a carburized mixed oxide confirm the presence of Mo and W in these two homogeneous samples. Figure 9 shows one of these superimposable Auger spectra. The Auger spectra recorded for the carburized (Mo,W) alloy are identically the same as those of the carburized mixed oxide. The typical triple peak of the carbon for a carbide compound is also present. Moreover, its morphology dismisses the possibility of unbound carbon in the sample.^{44,45} A slight contamination by oxygen also appears, but taking into account the great sensitivity of oxygen in Auger spectroscopy, it can be neglected here.

Carburization of the coprecipitate of MoO_3 and WO_3 at 1173 K: The X-ray diffraction diagram obtained after the carburization of the coprecipitate is the same as that presented in Fig. 8 and can be attributed to (Mo,W)C. If one refers to the XPS

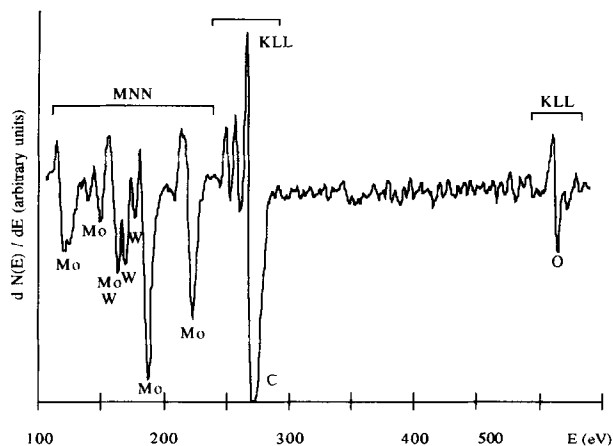


Fig. 9. One of the superimposable Auger spectra recorded on three different points of a carburized mixed oxide at 1173 K. The AES of the (Mo,W) alloy carburized at 1173 K presents the same shape.

Table 5. Main results presented in this work for the synthesis of bulk mixed carbides

Precursors for synthesis of bulk mixed carbides	T (K)	Carbides obtained	Metallic homogeneity determined by AES analysis
Mixture of $\text{MoO}_3 + \text{WO}_3$	1023	(Mo,W)C + (Mo,W) ₂ C or α -Mo ₂ C	Poor
(Mo,W)O ₃	1023	(Mo,W)C + (Mo,W) ₂ C	Good
(Mo,W)O ₃	1173	(Mo,W)C	Good
(Mo,W) alloy	1173	(Mo,W)C	Good
Coprecipitate of $\text{MoO}_3 + \text{WO}_3$	1173	(Mo,W)C	—

analysis performed by Leclercq *et al.*,^{36,37} the close mixing due to the coprecipitation seems to lead to quite homogeneous samples. It is not surprising that the carbides so obtained at 1173 K are homogeneous, because it is known that the carburization of MoO_3 at 1173 K in a CH_4 (10%)/ H_2 (90%) gas mixture leads to α -Mo₂C (hc). So, the fact that the carburized coprecipitate presents an hexagonal simple structure as the unique one indicates that the tungsten and the molybdenum have to be close mixed. Otherwise, as the sample contained some sites enriched with Mo, a hexagonal close-packed structure corresponding to α -Mo₂C should appear in the diffraction diagram for these conditions of carburization (Table 4).

4 Conclusions

This work has shown that it is possible to prepare mixed (Mo,W) carbides at low temperatures in comparison with the melting point of W.

Thin films of mixed carbides were synthesized by reactive sputtering on Ti substrates in a CH_4 (10%)/Ar atmosphere. The low resolution of the diffraction rings does not allow to conclude if the thin films correspond to α -(Mo,W)C_(1-x), or to a mixture of β -WC_(1-x) and δ -MoC_(1-x). Moreover, the presence of oxygen in the samples could mean that they contain $\text{W}_2(\text{C},\text{O})$ or a mixed oxycarbide.

Bulk carbides were synthesized from different precursors. The precursors consisted in a mixture of MoO_3 and WO_3 , a mixed oxide (Mo,W)O₃, a (Mo,W) alloy and a coprecipitate of MoO_3 and WO_3 . Table 5 summarizes the main results obtained in this work for the synthesis of bulk carbides.

From all these data, it appears that the mixed (Mo,W) oxide, its reduced form and the coprecipitate of $\text{MoO}_3 + \text{WO}_3$ are good precursors for the synthesis of homogeneous mixed (Mo,W) carbides.

It can also be noted that their carburization leading to the monophasic hexagonal simple mixed carbide (Mo,W)C requires a temperature of 1173 K. At the temperature of 1023 K, a mixture of hexagonal close-packed and hexagonal simple phases is obtained.

Some of the pathways presented here could be of a great interest for metallurgical engineering because of their economical advantages. Moreover, low temperatures of preparation, avoiding the sintering of the powder particles, allow the use of these materials in catalytical and electrocatalytical applications.

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