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A new approach to the synthesis of intermetallic compounds: mild synthesis of submicrometric Co_xM_y (M = Mo, W; $x:y$ = 3:1 and 7:6) particles by direct reduction of freeze-dried precursors

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A simple processing route to cobalt–molybdenum and cobalt–tungsten intermetallics (Co_xM_y, where M = Mo and W, and $x:y$ = 3:1 and 7:6) has been developed, on the basis of the use of precursors resulting from freeze-drying of aqueous solutions of the appropriate common metal salts. The influence of the preparative variables on the outcomes of this procedure is examined. These compounds are prepared as single phases by thermal reduction of amorphous freeze-dried powders under a hydrogen–argon atmosphere (8% H_2), followed by slow cooling of the samples. The materials have been characterised by X-ray powder diffraction, metal analysis, scanning electron microscopy and thermogravimetry under an oxygen flow. Co_xMo_y and Co_xW_y grains are aggregates of submicrometric spherical particles.

Introduction

Intermetallics constitute a unique class of metallic materials composed of two or more metals, sometimes with the addition of some non-metallic component, in definite proportions. As opposed to random solid solutions, they form long-range ordered crystal structures, which usually differ markedly, as well as their properties, from those of their constituents. Alloys based on ordered intermetallic compounds have experienced a considerable increase in interest over the last years due to both the never ending search for novel properties and emerging applications.[1] Although advances in preparation and characterisation techniques have favoured significant progress in this field,[1,2] the production of intermetallics in a relatively pure form usually implies complex and vigorous synthetic methods, which are controlled by a great diversity of procedural variables.[3]

Some years ago, H. Schäfer wrote an exceptional report about the preparative work in the solid state chemistry of his time, mainly based on the use of procedures as "primitive" as the ceramic method.[4] Since then, a great deal of ingenuity was put in the service of designing alternative routes for solid state synthesis which obviate the need for the use of high temperatures.[5] Now, there is no doubt that a relevant part of the legacy of the enormous worldwide effort devoted to research on high temperature superconductors is the redrawing of the frontiers of synthetic (and structural) solid state chemistry.[6] Among the diversity of procedures and techniques developed to reach low temperature synthesis of complex (polymetallic) systems, those based on the use of chemical precursors take advantage of the quasi-atomic level mixing of the involved metals in the precursor, which decreases the diffusive distances and usually results in very small sized particles.[7]

The search for simple processing routes (as an alternative to conventional solid state reactions) to complex polymetallic systems (from high T_c superconducting materials[8] to polymetallic nitrides and oxynitrides,[9] among other materials) has constituted a relevant part of the research work of our group in recent years. In this context, the use of precursors obtained by freeze-drying of aqueous solutions of the appropriate metal salts has proved to be a very versatile soft method for obtaining stoichiometrically controlled complex polymetallic systems.[10]

Indeed, we have recently approached, by this procedure, the preparation of $CoMoO_4$.[11] In the course of the characterisation of the resulting nanostructured material (consisting of spherical particles with a typical diameter of 10 nm), a result powerfully attracted our attention. Thus, thermal treatment of this material under a hydrogen–argon mixture (8% H_2) resulted in the formation, at relatively low temperature (*ca.* 800 °C), of the intermetallic Co_7Mo_6 together with metallic Mo. At this point, our immediate goal was to explore the possibility of adjusting the synthetic parameters to obtain pure Co–Mo intermetallics (and the analogous Co–W intermetallics) by direct reduction of precursors under a hydrogen–argon mixture. These compounds are components of Co–Mo alloys that have been used in orthopaedic implants (Co–Cr–Mo alloys),[12] as electrodes for hydrogen evolution in alkaline water electrolysis,[13] and as catalysts (silica-supported Co–Mo) for CO hydrogenation with improved alkene selectivity.[14]

In the present work, we report on how the use of freeze-dried bimetallic precursors has allowed us to prepare pure Co_xM_y (M = Mo, W; $x:y$ = 3:1 and 7:6) compounds.

Experimental

Synthesis

Materials used as reagents in the current investigation were $CoC_4H_6O_4 \cdot 4H_2O$ (Panreac, 98.0%), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Panreac, 99.0%) and $(NH_4)_6W_{12}O_{39} \cdot H_2O$ (Panreac, 99.0%). The starting Co-, Mo- or W-containing solutions were prepared by dissolving their respective salts in distilled water. Then, they were combined to obtain Co–Mo and Co–W source solutions whose total cationic concentrations were 0.3 M. The masses of the different reagents were adjusted to give 3 g of the final product. In all cases, to avoid precipitation, a small amount of nitric acid was added to the solution (until pH *ca.*

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Table 1 Chemical analysis for Co_xM_y (M = Mo, W; $x:y$ = 3 : 1 and 7 : 6) intermetallics

	Nominal composition (% Co molar)		Homogeneity range for the solid solutions[a]		Experimental (% Co molar)[b]	
	Mo	W	Mo	W	Mo	W
$Co_3Mo_{1\pm x}$	75	75	74.48–75.47	74.68–77.09	75	75
$Co_7Mo_{6\pm x}$	53.84	53.84	50.80–58.78	51.50–56.85	54	55

[a] The ideal nominal compositions Co_3M and Co_7M_6 correspond in practice to solid solutions $Co_3M_{1\pm x}$ and $Co_7M_{6\pm x}$, for which the compositional range is narrow. Data in this table have been taken from refs. 15 (Co–Mo) and 15*a* (Co–W). [b] ±2%.

1–2) after mixture. The compositions of these source solutions were adjusted to have metal ratios Co : M = 3 : 1 and 7 : 6 (M = Mo, W). Droplets of these solutions were flash frozen by projection on liquid nitrogen and then freeze-dried at a pressure of 1–10 Pa in a Telstar Cryodos freeze-drier. In this way, dried solid precursors were obtained as amorphous (X-ray diffraction) loose powders.

Co–Mo and Co–W intermetallics were synthesised by thermal treatment, under a hydrogen–argon mixture (8% H_2), of the stoichiometrically adequate precursor. A sample of the selected precursor (*ca.* 0.2 g) was placed into an alumina boat, which was then inserted into a quartz flow-through tube furnace. The front end of the tube furnace was connected to the gas line. Prior to initiating the thermal treatment, the tube furnace was purged for 30 min with the reductor gas mixture. Several experiences under different experimental conditions were performed in order to determine the appropriate conditions for the preparation of each one of the intermetallics. The precursor powder was heated at 5 K min^{-1} to a final temperature (T_f) that was held for a period of time (t_{hold}) under flowing reductor gas (50 cm^3 min^{-1}). Then, the resulting solid was cooled down leaving the sample inside the furnace. All products were stored in a desiccator over $CaCl_2$.

Characterisation

Metal analysis. Metal ratios in the solids (Table 1) were determined by energy dispersive analysis of X-ray (EDAX) on a Jeol JSM 6300 scanning electron microscope, using an Oxford detector with quantification performed using virtual standards on associated Link-Isis software. The operating voltage was 20 kV and the energy range of the analysis 0–20 keV. It must be remarked that the metal analysis results in Table 1 fit in well with the homogeneity ranges previously established for the solid solutions of the intermetallics we are dealing with (see below).

X-ray diffraction. X-ray powder diffraction patterns were obtained from a Siemens D501 automated diffractometer using graphite-monochromated Cu K_α radiation. Powder samples were dusted through a sieve on the holder surface. Routine patterns for phase identification were collected with a scanning step of 0.08° in 2θ over the angular range 20–80° in 2θ with a collection time of 5 s per step. All graphical representations relating to X-ray powder diffraction patterns were performed using the DRXWin Program.[16]

Microstructural characterisation. The morphology of the intermetallics was observed using a scanning electron microscope (Hitachi S-4100) operating at an accelerating voltage of 30 kV.

Oxidation behavior. The oxidation of the intermetallics have been studied by means of thermogravimetry in a PerkinElmer TGA 7 system. The compounds were heated at 5 K min^{-1} under oxygen flow (50 cm^3 min^{-1}).

Results and discussion

According to the bibliographic data,[15] the ideal compositions, Co_3M and Co_7M_6, correspond to the two intermetallics, stable at low temperatures, which have been characterised in both the Co–Mo and Co–W systems. In fact, there are two solid solutions with compositions $Co_3M_{1\pm x}$ and $Co_7M_{6\pm x}$ in which the structure of the compounds Co_3M and Co_7M_6 remains unaltered. It seems evident that the stoichiometry constitutes a key question concerning isolation of the intermetallics Co_xM_y (M = Mo, W; $x:y$ = 3 : 1 and 7 : 6) we are dealing with, as well as the uselessness of searching for a single definite precursor for each composition (without prejudice from the features of the respective phase diagrams of these systems).[15]

Co–Mo system

Shown in Fig. 1 and 2 are the X-ray powder diffraction patterns of the Co–Mo intermetallics (and/or intermediate phases) that result from the reduction of the corresponding precursors. After preliminary experiments, the reaction time

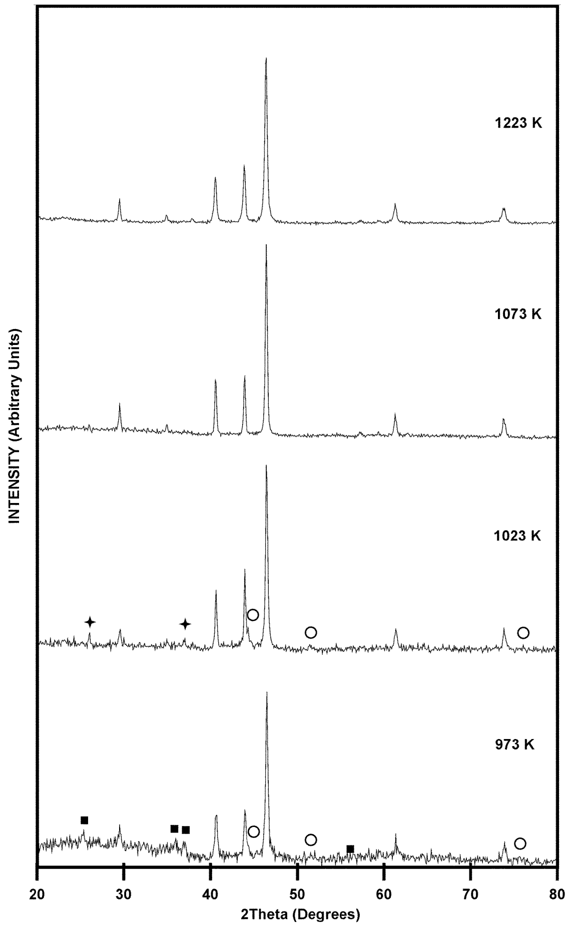

Fig. 1 X-ray diffraction patterns of the products resulting after thermal treatment in the conditions described in the text of the freeze-dried precursor of nominal stoichiometry Co_3Mo (○ Co JCPDS 15,0806; ■ $Co_2Mo_3O_8$, JCPDS 34,0511; ♦ MoO_2, JCPDS 32,0671).

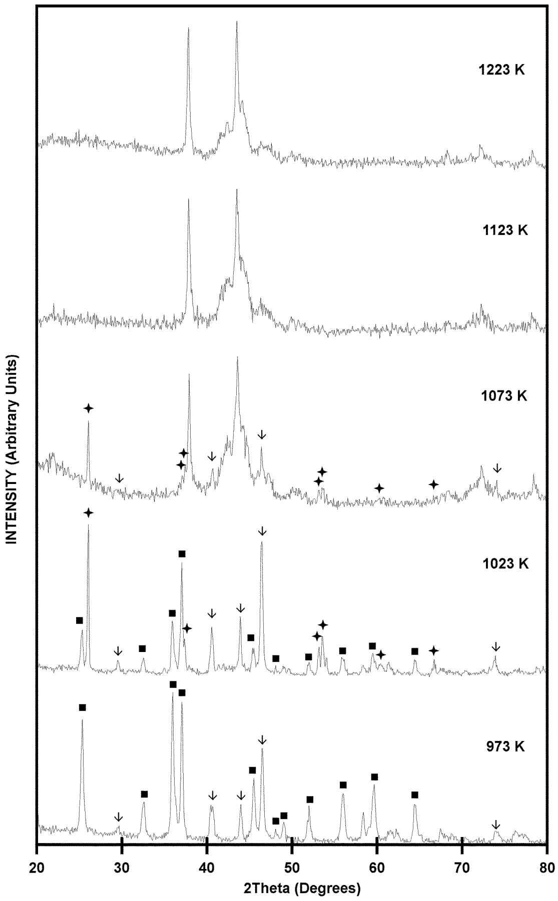

Fig. 2 X-ray diffraction patterns of the products resulting after thermal treatment in the conditions described in the text of the freeze-dried precursor of nominal stoichiometry Co_7Mo_6 (○ Co, JCPDS 15,0806; ■ $Co_2Mo_3O_8$, JCPDS 34,0511; ♦ MoO_2, JCPDS 32,0671; ↓ Co_3Mo, JCPDS 29,0488).

(t_{hold}) was fixed at 5 h, once it was verified that longer reaction times did not measurably alter the results. Reactions were carried out at temperatures (T_f) ranging from 973 (at which intermetallics begin to be detected in significant proportion) to 1223 K.

As can be observed in Fig. 1, when starting from the Co : Mo = 3 : 1 precursor, Co_3Mo (JCPDS Card 29,0488) is already the majority phase at 973 K. The minimum temperature at which Co_3Mo is obtained as single phase is 1073 K, while no change is detected by XRD at higher reaction temperatures (until the highest temperature reached in our experiments, 1223 K). Although the elucidation of the possible pathways leading to Co_3Mo formation is out of the scope of this work, it can be noted that $Co_2Mo_3O_8$ (JCPDS Card 34,0511) and metallic Co (JCPDS Card 15,0806) are detected as impurities at 973 K, while the mixed oxide has disappeared at 1023 K [MoO_2 (JCPDS Card 32,0671) and metallic Co are the observed impurities at 1023 K].

In the case of the Co : Mo = 7 : 6 precursor, the evolution of the phases with temperature is a little more complicated than in the above case. As shown in Fig. 2, Co_7Mo_6 (JCPDS Card 29,0489) is obtained as a single phase at a minimum temperature of 1123 K, and remains unchanged at least until 1223 K. Co_7Mo_6 formation is preceded by that of Co_3Mo. Thus, Co_3Mo is already observed together with $Co_2Mo_3O_8$ (majority phase) at 973 K. When the temperature is increased to 1023 K, Co_3Mo remains as an important phase, while MoO_2 becomes the majority phase at the expense of $Co_2Mo_3O_8$ (the relative intensity of its diffraction peaks is very low). Co_7Mo_6 is already the majority phase at 1073 K, the temperature at which Co_3Mo and MoO_2 are observed as impurities.

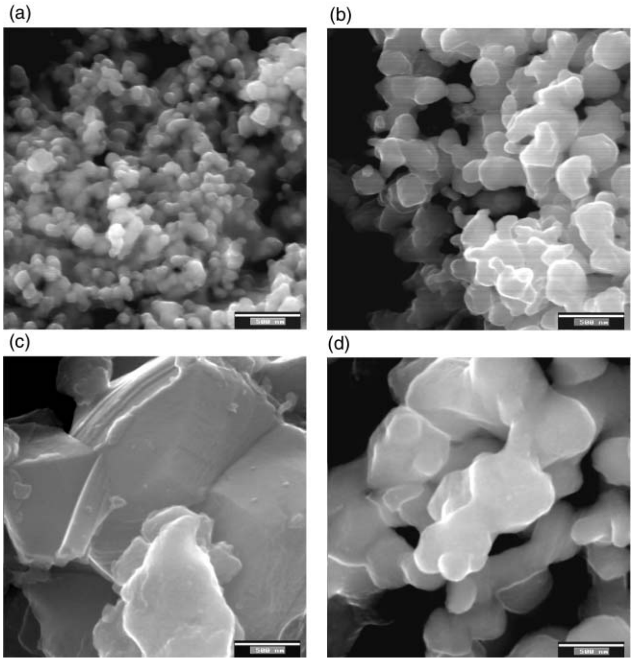

Fig. 3 SEM images showing the microstructure of Co_3Mo obtained at (a) 1073 and (c) 1223 K and Co_7Mo_6 obtained at (b) 1123 and (d) 1223 K.

The morphology of both Co–Mo intermetallics was observed using scanning electron microscopy (SEM). Fig. 3 shows characteristic SEM images corresponding to representative samples. At the minimum temperatures at which single phases are obtained (1073 K and 1123 K for Co_3Mo and Co_7Mo_6, respectively), both solids are formed by aggregates of rounded particles [Fig. 3a, 3b] with typical diameters around 125 nm for Co_3Mo and 225 nm for Co_7Mo_6 (it should be noted that, regardless other factors, Co_7Mo_6 is prepared at a temperature 50 K higher than Co_3Mo). As expected, a progressive increase in the particle sizes is observed by increasing the reaction temperature. At 1223 K [Fig. 3c, 3d], the materials show mainly polyhedral faceted particles, with mean particle sizes around 500–1000 nm.

Co–W system

Shown in Fig. 4 and 5 are the X-ray powder diffraction patterns of the Co–W intermetallics. As above, t_{hold} was fixed at 5 h, and the T_f range was from 973 to 1223 K.

As can be observed in Fig. 4, the minimum temperature at which Co_3W (JCPDS Card 02,1298) is obtained as a single phase is 1123 K. Co_3W is already detected as an impurity [together with WO_2 (JCPDS Card 32,1393)] at 973 K, the temperature at which the majority phase is $CoWO_4$ (JCPDS Card 15,0867). At 1023 K, Co_3W becomes the majority phase and both $CoWO_4$ and WO_2 remain as impurities. At 1073 K, Co_3W is obtained as nearly single phase (only WO_2 is additionally observed). Co_3W is obtained as a single phase from 1123 K until the highest temperature reached in our experiments, 1223 K.

As shown in Fig. 5, Co_7W_6 (JCPDS Card 02,1091) is obtained as a single phase at 1223 K. This system resembles the Co–Mo intermetallics with regard to the phase evolution with temperature, and Co_3W appears as an intermediate in the formation of Co_7W_6. At 973 K, $CoWO_4$ is the majority phase, but Co_3W and WO_2 are also observed. When the temperature is increased to 1023–1073 K, WO_2 becomes the majority phase; Co_3W is also present, together with minor amounts of $CoWO_4$ (whose peaks progressively disappear as the reaction temperature increases). At 1123, WO_2 is reduced to W (JCPDS

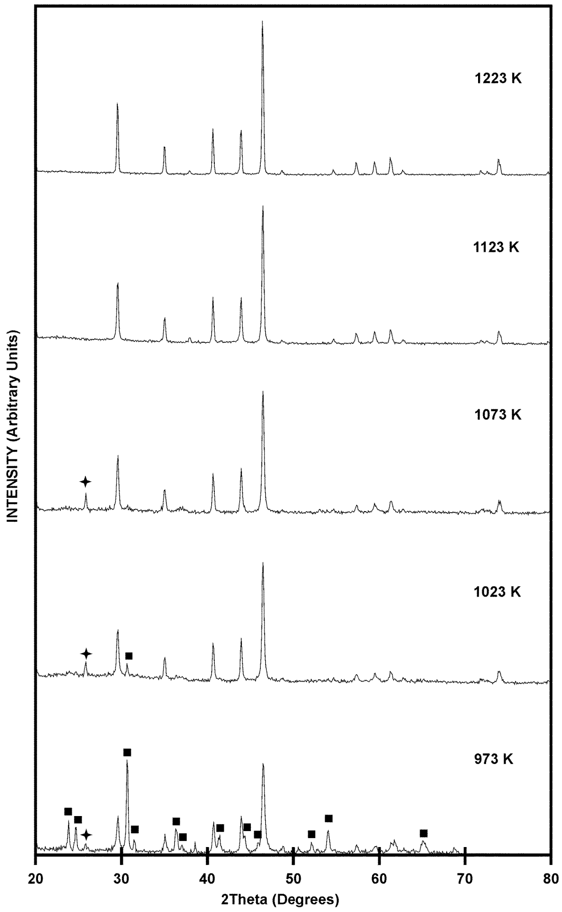

Fig. 4 X-ray diffraction patterns of the products resulting after thermal treatment in the conditions described in the text of the freeze-dried precursor of nominal stoichiometry Co_3W (■ $CoWO_4$, JCPDS 15,0867; ⧫ WO_2, JCPDS 32,1393).

04,0806). Co_7W_6 is obtained as a single phase at the highest temperature reached in our experiments, 1223 K.

With regard to the morphology of the Co–W intermetallics (Fig. 6), comments similar to those above referred to Co–Mo intermetallics should be pertinent.

Oxidation behavior

The oxidation of these compounds under oxygen flow has been characterised by means of thermogravimetry experiments. In all cases, oxidation of the bulk samples (50 cm^3 min^{-1}) occurs as a multistep process. Concerning the Co–Mo compounds, the oxidation begins at relatively low temperatures (*ca.* 450–500 K). It is nearly complete at 873 K in the case of Co_3Mo, whereas the process concludes at a significantly lower temperature (650 K) for Co_7Mo_6. In both cases, the oxidation initially occurs slowly, but it speeds up when the temperature is raised. Whereas for Co_3Mo this second stage occurs gradually between 673 and 873 K, in the Co_7Mo_6 case it proceeds almost instantaneously at 650 K. The final products are β-$CoMoO_4$ and Co_3O_4. A similar behaviour is observed for the Co–W intermetallics. Co_3W oxidation begins at *ca.* 500–550 K, and it proceeds gradually until completion ($CoWO_4$ and Co_3O_4) at 973 K. Co_7W_6 oxidation begins also at 500–550 K, and it suddenly concludes at 725 K ($CoWO_4$ and Co_3O_4). Co–Mo intermetallics are, therefore, less stable towards oxidation than their analogous Co–W counterparts, the Co_3M compounds being relatively the most stable ones.

In conclusion, we have prepared cobalt–molybdenum and cobalt–tungsten intermetallic compounds, Co_3M and Co_7M_6 (M = Mo, W), at relatively low temperatures by reduction of amorphous freeze-dried precursors under a hydrogen–argon (8% H_2) atmosphere. The success in the preparation of all these four compounds as pure single phases at relatively low

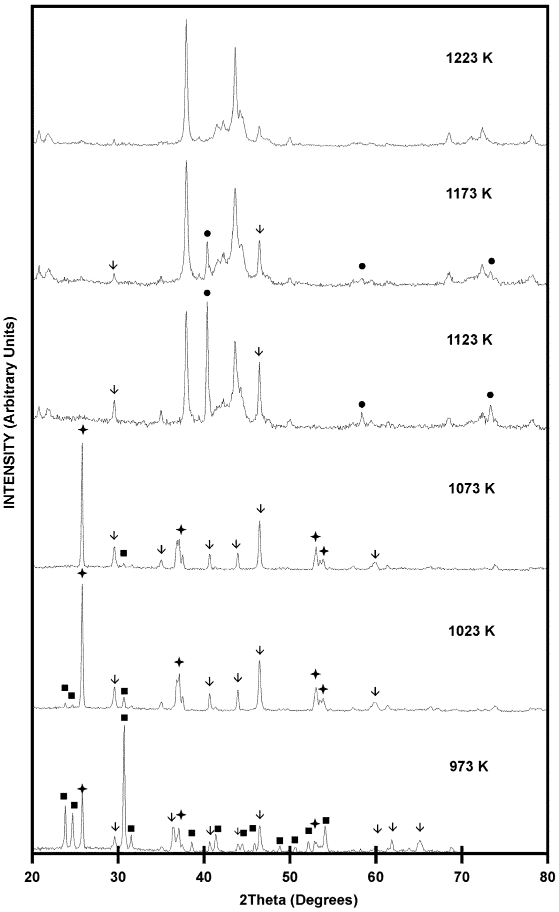

Fig. 5 X-ray diffraction patterns of the products resulting after thermal treatment in the conditions described in the text of the freeze-dried precursor of nominal stoichiometry Co_7W_6 (● W, JCPDS 04,0806; ■ $CoWO_4$, JCPDS 15,0867; ⧫ WO_2, JCPDS 32,1393; ↓ Co_3W, JCPDS 02,1298)

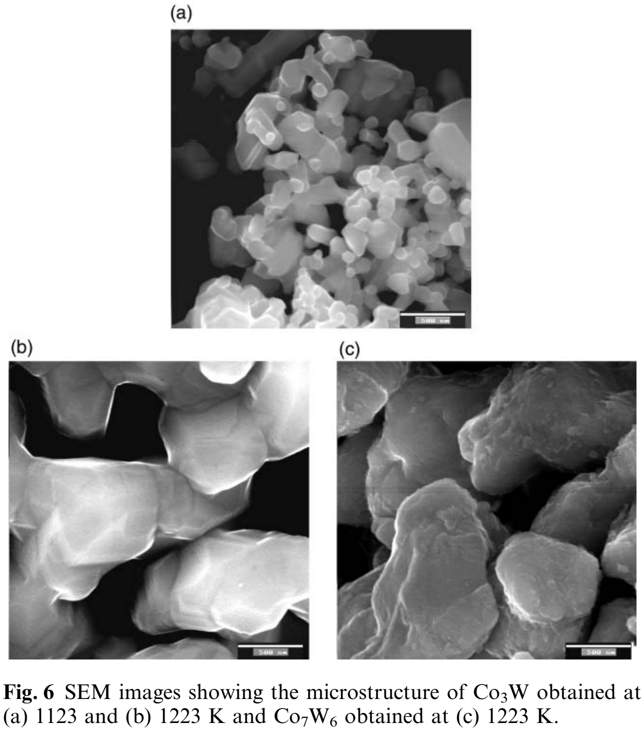

Fig. 6 SEM images showing the microstructure of Co_3W obtained at (a) 1123 and (b) 1223 K and Co_7W_6 obtained at (c) 1223 K.

temperatures is good proof of the versatility of the freeze-drying method for the obtention of a diversity of materials of different chemical nature.

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