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Journal of Solid State Chemistry 174 (2003) 1–10

JOURNAL OF
SOLID STATE
CHEMISTRY

<http://elsevier.com/locate/jssc>

Study of the reaction of tungsten carbide in molten alkali metal nitrates. Syntheses of divalent (s and d blocks) metal tungstates

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Received 28 May 2002; received in revised form 2 October 2002; accepted 23 October 2002

Abstract

WC is tested as precursor to synthesize metal tungstates by reaction in molten alkali metal nitrates. This constitutes a complex redox system with two reducing agents, W and C, and an oxidizer having several oxidation states. The mass loss due to the evolution of gases reveals the reaction steps. The infrared analyses of the gas phase show what kind of reaction develops according to the temperature. WC produces a water-soluble alkali metal tungstate. The reaction of a mixture of WC and a divalent metal chloride (Mg, Ca, Ba, Ni, Cu, Zn) leads to water-insoluble metal tungstates. As the reactivity of the cations increases in the order Zn, Ni, Cu, the reaction of WC is modified by their presence. The physico-chemical characterizations of the products show that some of them are contaminated either by WC or by metal oxide. Some others are rather pure products. These differences, in relationship with the other analyses, allow to propose first reaction pathways of the tungsten carbide in molten salts.

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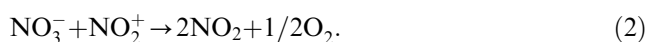
Keywords: Divalent metal tungstates; Tungsten carbide oxidation; Molten salts; Reactivity in alkali metal nitrates

1. Introduction

Until now, the syntheses of simple or multiconstituted metal oxides in molten alkali metal nitrates (in the text FS means Molten Salts) have been performed using metal chlorides, nitrates or sulfates as precursors [1–3]. These anions may promote one kind of crystal growth or polymorph of the oxide rather than another. Redox reactions of the anions, chloride ions namely, are not necessarily involved. The formation of the oxide corresponds to an acido-basic reaction [4] in which NO_3^- is the base (Eq. (1)).



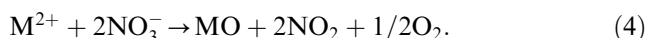
The nitryl ion reacts very fast with the nitrate ions according to the following:



The metal cation is the acid, it displaces the equilibrium (Eq. (1)) toward the right and forms the metal oxide,



The overall reaction is



If the metal ion undergoes oxidation, Eq. (4) is modified (Eq. (5)) to fit the TGA results [5]:



On the one hand, as the oxidation number of the metal increases in the precursor, the commercially available compounds become rarer and rarer. On the other hand, the inner 2nd and 3rd row transition element chlorides and fluorides are too volatile to be used in FS. The few oxychlorides supplied are expensive and retain some volatility (WOCl_4 bp. 227°C NbOCl_3 subl. 400°C). Among the commercially available non-volatile, inexpensive compounds, WC was the easiest to obtain and the most interesting because of its ability to yield

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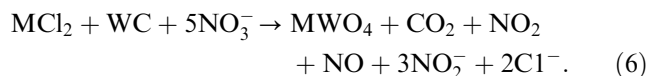
relatively well defined tungstates. Dmitruk et al. [6] have already presented this kind of reaction as a method for recycling hard tungsten–cobalt alloys. Using WC, the volatility is no longer a problem but the reactivity of this refractory compound in FS is unknown, particularly the chemical behavior of the carbide ion towards the nitrates.

If the reaction occurs, the works of Kerridge on high oxidation states in molten salts [7–9] allow to predict the formation of water-soluble alkali metal tungstates, and we shall have to introduce divalent ions to obtain insoluble metal tungstates. These ions have been chosen for their redox stability, their regular and well-known acido-basic properties. The alkaline earth metal ions which are feebly or very feebly acid in FS, do not react with the medium, while divalent transition metal ions, acid or weak acid (Cu^{2+} , Ni^{2+} , Zn^{2+}) produce oxide in every case [10].

2. Experimental procedure

Tungsten carbide is an ACROS product 99% pure. Analytical grade metal chlorides (Prolabo) are used as received, a dehydration was performed as the first step of each experiment. The alkali metal nitrates are commercial salts (Prolabo Normapur). They are dehydrated for 24 h at 120°C and then preserved in a drying oven at 100°C.

The eutectic NaNO_3 – KNO_3 (mol/mol), melting point 228°C, is used in this study. The mass of precursor (WC or $\text{WC} + \text{MCl}_2$), determined to obtain 0.5 or 2.5 g of tungstate, is mixed with an excess of alkali metal nitrate which constitutes the molten medium. The ratio between nitrate and metal ions is estimated, assuming a priori reaction (6), and fixed at seven times the stoichiometry.



The ratio is maintained at the value 35/1 when the reaction involves WC alone, this allows to work at a constant volume of liquid in both kinds of experiments.

All the reactions are carried out, under flowing air, with the same heating program. The heating rate is 150°C h^{-1} , a first plateau is maintained for 1 h at 100°C to dehydrate the metal chlorides and a second for 4 h at the reaction temperature of 470°C, which is the temperature required to achieve the formation of the transition metal oxides [10]. At the end of the reaction the molten medium is allowed to cool according to the natural temperature decrease of the furnace. The solidified block is treated with water in order to dissolve the alkali metal salts. The residue is washed with water until chloride ions have been eliminated (AgNO_3 test) and finally oven dried at 100°C for 24 h.

Most of the reactions have been followed by TGA with a Setaram B 70 digitalized balance with Pyrex crucible allowing to introduce large amounts of reactants, typically WC 25.4 mg, NaNO_3 193 mg and KNO_3 230 mg. The losses of mass are expressed in g mol^{-1} of WC (or theoretical metal tungstate MWO_4) to allow direct comparison between the different reactions. The gases released during the reaction of WC and transition metal chlorides in nitrates have been analyzed by FTIR spectroscopy in a 100 mm gas cell equipped with KBr windows mounted in a Magna 550 Nicolet spectrometer. For these analyses the reactor was flowed with nitrogen, the samples were taken with a temperature interval of 25°C approximately.

The powders obtained (MWO_4) were analyzed using the following techniques: chemical analysis performed by the CNRS Central Service of Analysis at Vernaison, scanning electron microscopy (Hitachi S800 microscope, CMEAB of Claude Bernard University), X-ray diffraction (Siemens D500 diffractometer for powders working with $\text{CuK}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$, at the Henri Longchambon Center of Claude Bernard University). The XRD patterns were recorded in the 2θ range 15–50° (step 0.02°, step time 1 s).

3. Results and discussion

3.1. Reaction of WC with alkali metal nitrates

First of all, the solidified cake resulting from the reaction dissolves totally in water. The product formed during the reaction is not an oxide of tungsten but, as predicted, a soluble alkali metal tungstate.

The TG curve (Fig. 1) shows a one-step reaction with poorly significant events at 230°C and 370°C. It starts as the eutectic begins to melt, speeds up until 325°C where

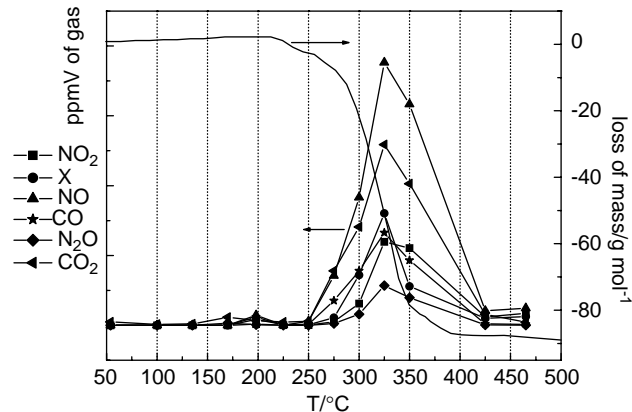


Fig. 1. TGA of the reaction of WC with nitrates and the respective compositions at given temperatures of the gas phase determined by IR spectroscopy.

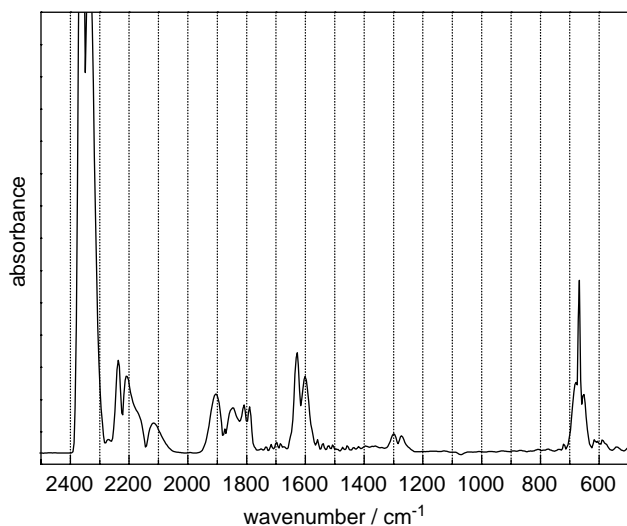


Fig. 2. FTIR spectrum of the gas phase evolved by the reaction of WC with nitrate melt at 300°C.

Table 1
Characteristic infrared bands of the gases and their extinction coefficient

Compound	Band /cm ⁻¹	Coeff*10 ⁻⁵ /ppmV
CO ₂	2360	8
CO	2117	0.6
N ₂ O	2237	9
NO	1905	0.5
NO ₂	1627	5
X	1789	1(assumed)

the greatest rate is reached and reaches completion at 400°C. The loss of mass is 88 g mol⁻¹.

The IR spectra show the regular evolution of the gaseous mixture on heating. All the bands but two are already known (Fig. 2), they are assigned to CO₂ (2360–2337–667 cm⁻¹), CO (2117 cm⁻¹), N₂O (2237–2210–1300–1273 cm⁻¹), NO (1905–1847 cm⁻¹), NO₂ (1627–1600 cm⁻¹). The bands at 1806, 1789 cm⁻¹ do not correspond to any known nitrogen or carbon oxides which could be, beside inactive N₂ and O₂, the unique gaseous compounds released by the reaction, especially in this reaction WC-ANO₃. They correspond to the region of the vibration of N=O or (NO)₂ [11].

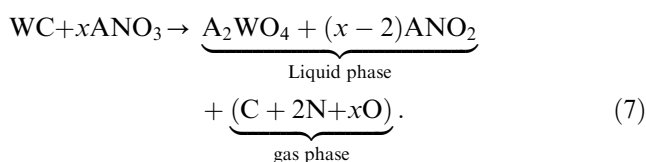
The volumic extinction coefficients have been tentatively determined from spectra of gaseous mixtures prepared in the laboratory for DeNO_x catalysis purposes and from the thesis works of C. Aneur [12]. The retained values, listed in Table 1, are not accurate enough to determine the composition of the gaseous mixture, they allow to take into account the wide ratios of the extinction coefficients

Fig. 1 shows the correlation between the TG analysis and the composition of the gas phase. Even though both experiments are technically so different, they point to the same conclusion. The reaction is complete and

immediate. The maximum rate and the maximum gas release are reached at 325 (±10)°C.

This is a redox reaction from the beginning until completion as shown by the presence of, roughly, the same proportions of nitrogen oxides and carbon oxides. This implies that the actual reaction cannot be described by any simple formula, such as reaction (6) which, moreover, does not fit with the experimental loss of mass.

As the pH of the solution obtained by dissolution of the cake is close to 7, we can conclude that no carbonate ions are formed during the reaction. In this case, the only anions able to balance the positive charge of the alkali metal ions are WO₄²⁻ and NO₂⁻. The most general form of the equation related to the mass loss and without any assumption on the composition of the gas phase is

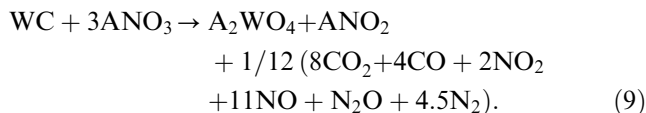


x does not depend on the excess of nitrate salts used in the experiment. The ratio 35/1 is high enough to ensure a large volume of liquid phase even if x rises to 8 or 9. The mass loss equal to (40 + 16 x) g mol⁻¹ is determined by TGA and leads to the x value. For this reaction, TG loss is equal to 88 g mol⁻¹, consequently x is equal to 3.

According to Eq. (7) we can write:



This formalism contains as much information as Eq. (9), which considers the FTIR results. Fig. 1 shows that, at 325°C, the gas phase contains twice more CO₂ than CO and 1.5 times more NO than CO₂ and then



The reaction of the tungsten carbide with molten nitrates is easy to carry out and to understand. This is a single-step redox reaction leading from W(IV) to W(VI). The various oxidation states of nitrogen does not allow to determine the composition of the gas phase which should also evolve with the temperature of reaction.

3.2. Reaction of WC and alkaline earth metal (Ae) chlorides with nitrates

Each experiment leads to a crystalline powder, insoluble in water, identified from the XRD patterns (Fig. 3) with the corresponding Ae tungstate described on ICDD files : 27-0789 for MgWO₄, 41-1431 for CaWO₄ and 43-0646 for BaWO₄.

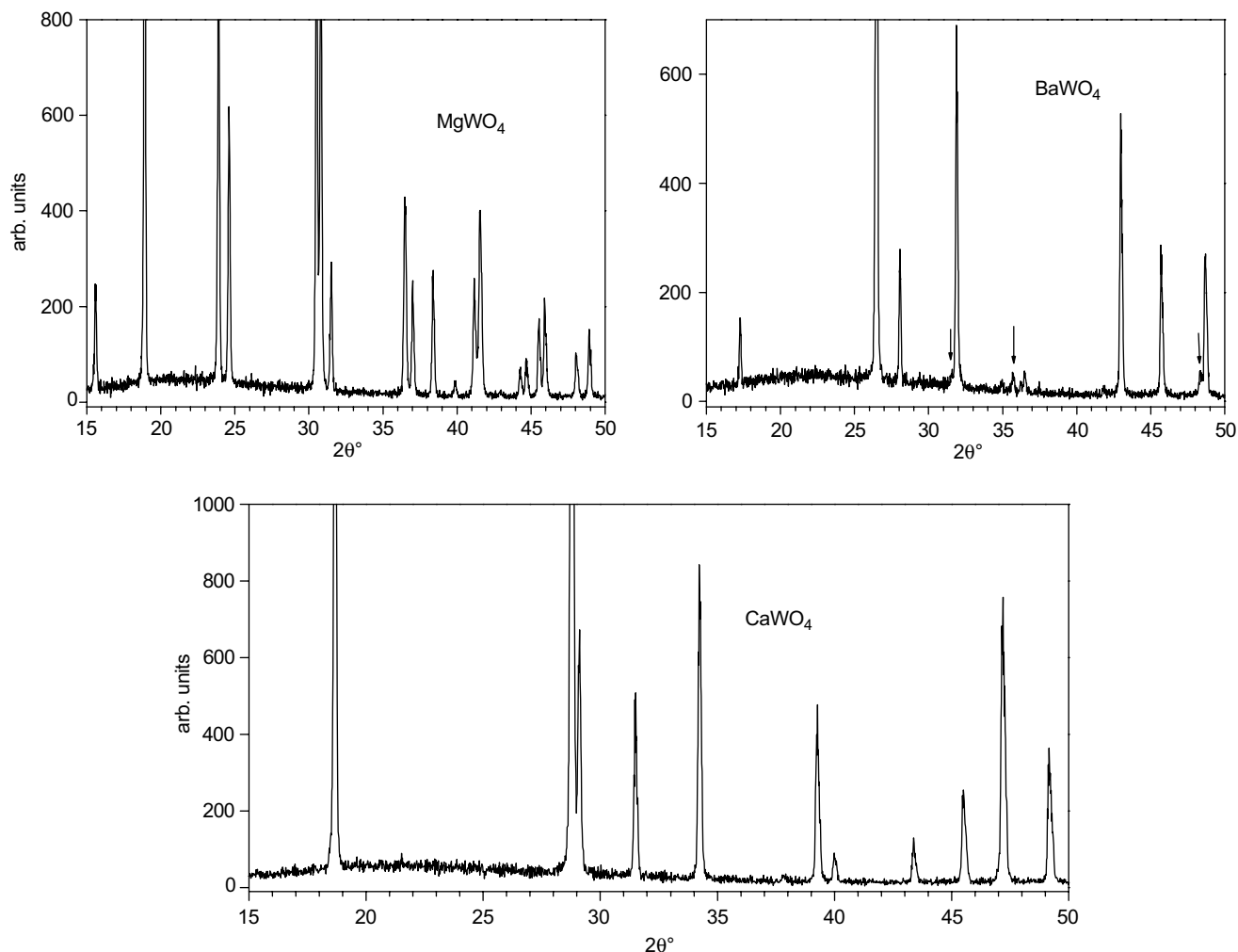


Fig. 3. XRD patterns of alkaline earth metal tungstate. On BaWO_4 arrows point at WC.

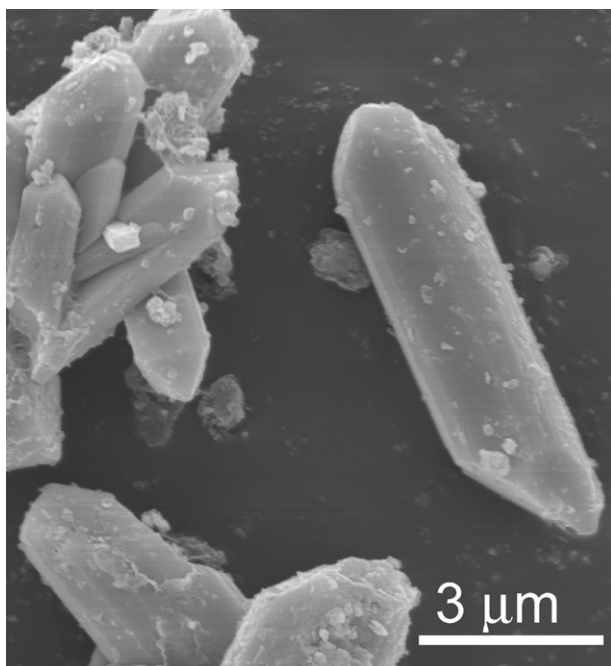
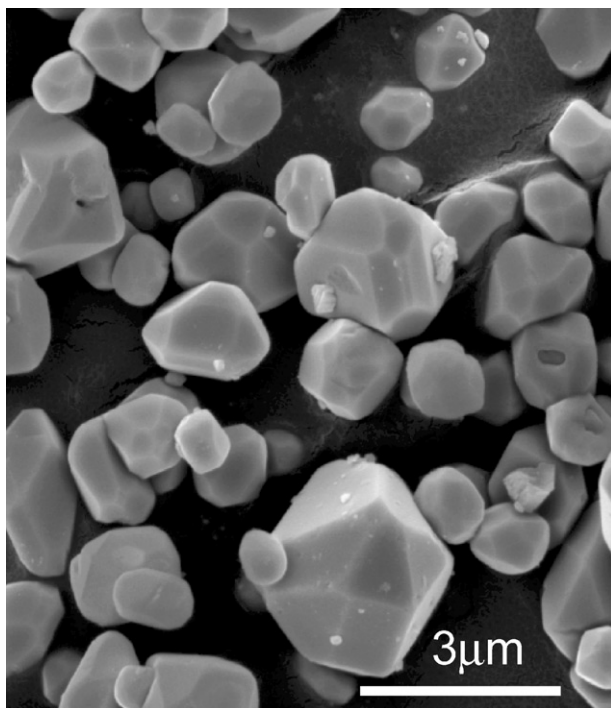
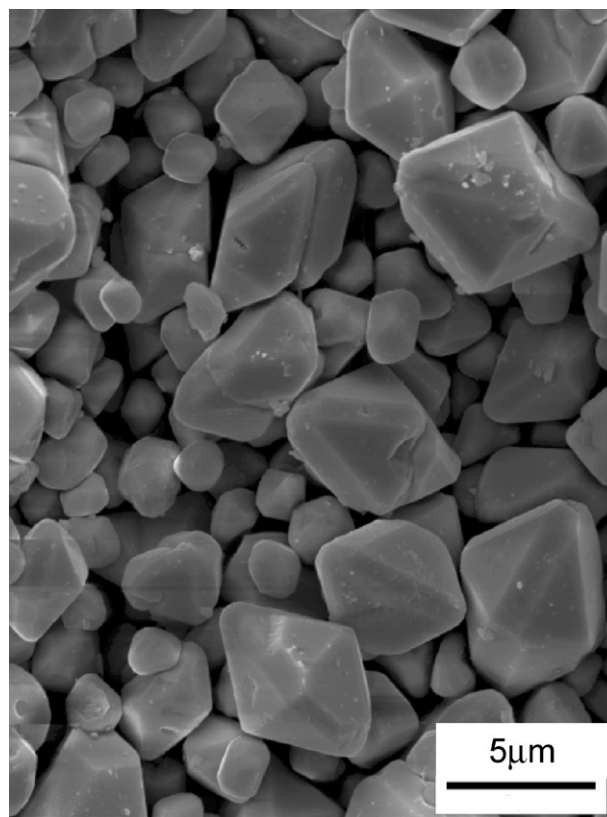
SEM micrographs (Figs. 4–6) reveal two kinds of crystallization according to the space groups of the tungstates given by ICDD files: $P2_1/c$ for MgWO_4 and $I4_1/a$ for the others. The crystals of MgWO_4 (Fig. 4) are typically elongated, over about $6\ \mu\text{m}$. They do not appear really well-defined, elsewhere on the micrographs they appear as though immersed in foam. CaWO_4 (Fig. 5) and BaWO_4 crystals (Fig. 6) are in contrast, well individualized. The distribution in sizes ($1\text{--}3\ \mu\text{m}$) and shapes are homogeneous. The facets look glossy and clean.

However, these nice crystals of BaWO_4 are not pure. On the pattern (Fig. 3), three weak diffraction lines indicated by an arrow characterize unreacted WC. Such extra lines do not exist on Ca and MgWO_4 patterns and chemical analyses are required to examine the purity of the compounds.

The results are summarized in Table 2. They show that the amount of carbon is very low. For BaWO_4 , they confirm the XRD observation. The ratio Ba/W is smaller than one; this indicates that some barium, which

cannot form BaO, has been eliminated on washing. On the opposite, the results show that the ratio Mg/W is much more greater than one. The value 1.38 corresponds to a powder of composition $\text{MgWO}_4 + 0.38\text{MgO}$. The magnesia could be what we named “foam” on the SEM micrographs. It is not revealed by XRD because it is constituted only from light elements and should be amorphous. In contrast to BaWO_4 and MgWO_4 , CaWO_4 is a pure compound, the M/W ratio is equal to one.

To resume, in BaWO_4 unreacted WC is detected, CaWO_4 is a pure compound and MgO contaminates MgWO_4 . This evolution of the purity is an interesting feature of the synthesis in the present experimental conditions. It could be related to the reactivity of Ae ions towards nitrate and tungstate ions. Ae^{2+} ions alone do not react in molten nitrates because the basicity of the medium is too low, the spontaneous decomposition of nitrate ions (Eq. (1)) is not sufficient to precipitate the oxide. However, Mg^{2+} (the smallest ion) requires a lower basicity to precipitate as oxide than Ba^{2+} (the

Fig. 4. Scanning electron micrograph of MgWO₄.Fig. 5. Scanning electron micrograph of CaWO₄.Fig. 6. Scanning electron micrograph of BaWO₄.Table 2
Chemical analysis of alkaline earth metal tungstates

	%w.	Ae	W	C	M/W at.
MgWO ₄	Theor.	8.9	67.5		
	Exp.	10.1	59.1	0.27	1.38
CaWO ₄	Theor.	13.9	63.8		
	Exp.	14.0	63.9	0.13	1.00
BaWO ₄	Theor.	35.6	47.7		
	Exp.	34.0	49.2	0.32	0.93

in the medium. These later form alkali metal tungstates which dissolve on washing.

The difference between Ca and Ba results could probably be explained by diffusion process. As the crystals of WC are attacked by nitrate ions the Ae²⁺ ions precipitate AeWO₄ on the surface. A shell of tungstate is gradually formed through which the ions have to diffuse to continue the reaction. The bigger the ion, the more difficult the diffusion. Ca²⁺ (0.99 Å), which is much smaller than Ba²⁺ (1.34 Å), diffuses more easily and allows the reaction to go to completion. This phenomenon could be modified by changing the experimental conditions. Heating rate, level temperature and duration are effective parameters in these syntheses, and their optimization should lead to pure alkaline earth

largest ion) does. When WC is added, the medium becomes much more basic, for example, nitrite ions appear (Eq. (7)), whereupon the basicity allows the precipitation of MgO and not that of CaO or BaO. Once MgO is formed, it cannot react with WO₄²⁻ ions existing

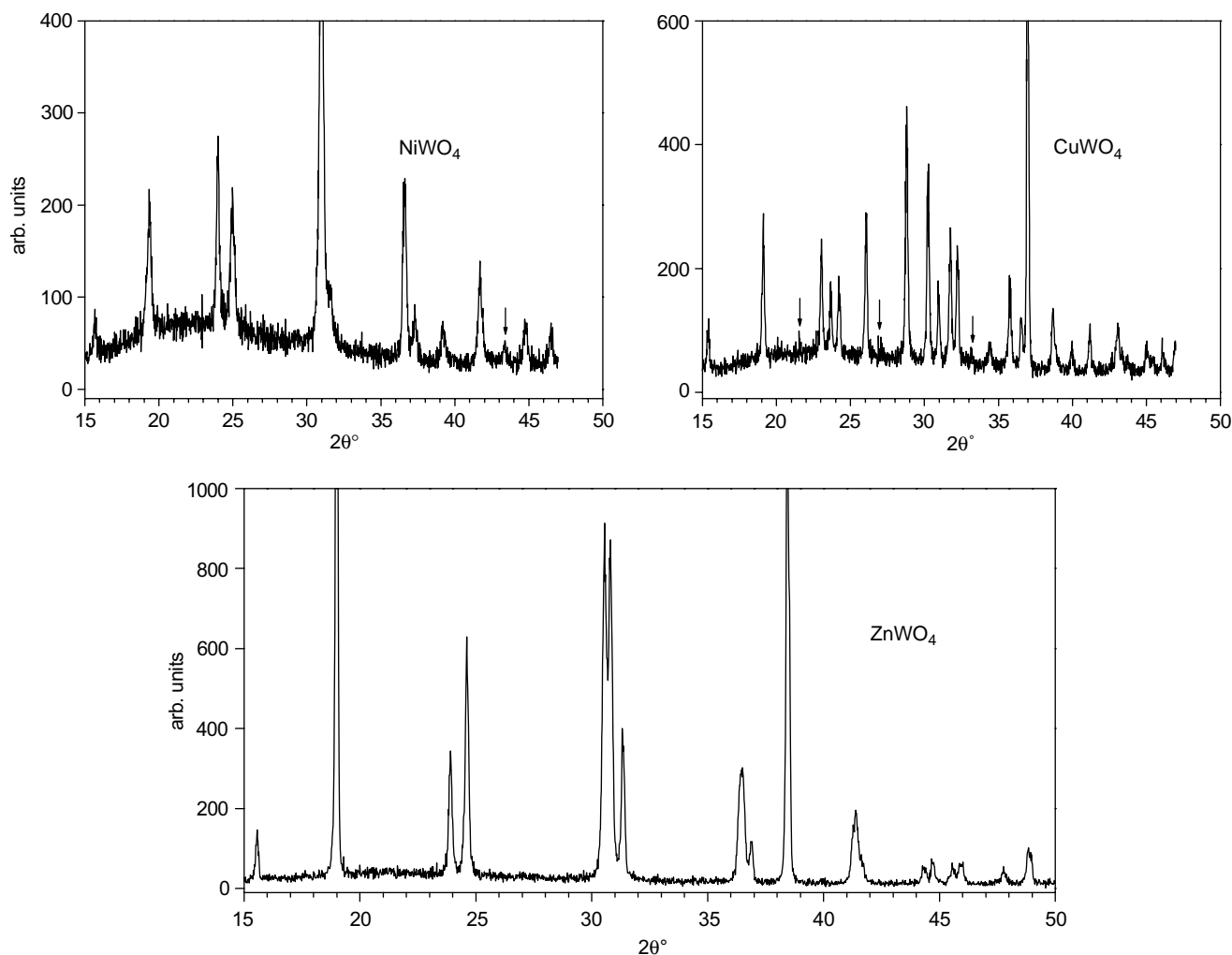


Fig. 7. XRD patterns of divalent metal tungstates. On NiWO_4 the arrow points at NiO , on CuWO_4 the arrows point at extra lines with no corresponding ICDD file.

metal tungstates. The decrease of the temperature and the shortening of the level duration would also contribute to reduce the size of the crystals.

4. Reaction of WC and transition metal chlorides with nitrates

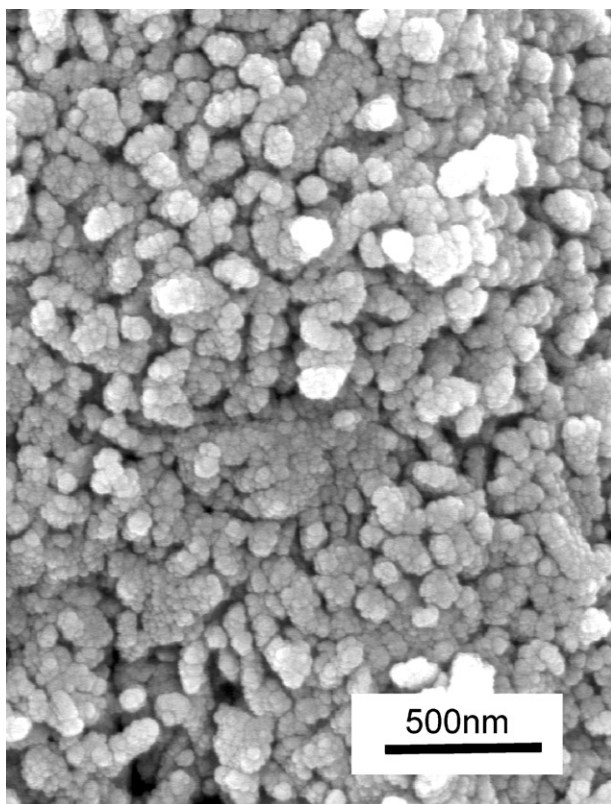
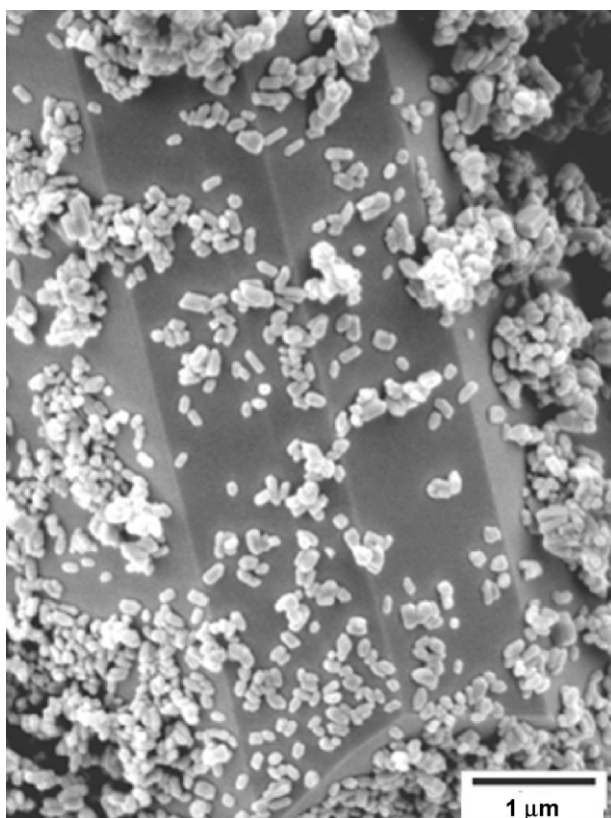
In this part we will write RW for the reaction of WC alone in the nitrates, RMW for the general reaction of a divalent metal and WC in nitrates and RNW, RCW and RZW to precise nickel, copper or zinc, respectively with WC in nitrates.

The evolution of the general properties of the three ions Ni^{2+} , Cu^{2+} , and Zn^{2+} are well-known. In contrast with Ae ions, they react with nitrate ions to produce the metal oxide, and we can ponder on the effect of this reaction on the formation of the metal tungstate.

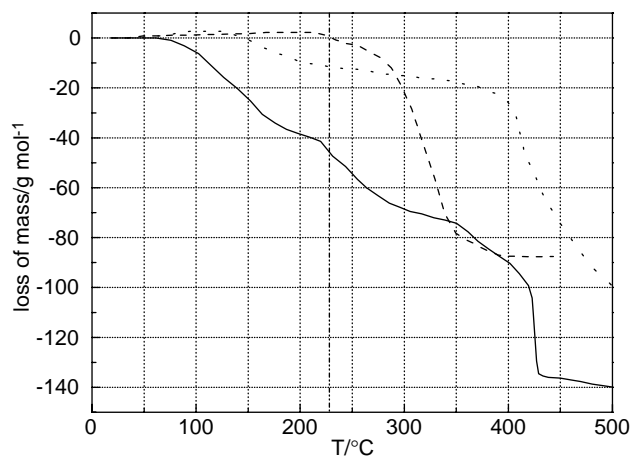
The XRD patterns (Fig. 7) of the powders correspond to the metal tungstates, ICDD n° 15-0755 for NiWO_4 ,

21-0307 for CuWO_{4-x} and 15-0774 for ZnWO_4 . They show a difference in the crystallinity of the powders. ZnWO_4 is as well crystallized as the alkaline-earth metal tungstate but the others are not. This difference in crystallinity is confirmed by SEM examinations. NiWO_4 (Fig. 8) presents small agglomerates with homogeneous sizes constituted from very small particles (about 50 nm, in good agreement with the size determined from line broadening using Scherrer formula: 38 nm). ZnWO_4 (Fig. 9) shows a mixture of very large single crystals (over $>2\ \mu\text{m}$) and small crystallites of 100 nm in size. The same repartition is found for CuWO_4 except that the crystals are smaller, about 500 nm.

The purity of these compounds needs to be tested since the XRD pattern of NiWO_4 (Fig. 7) showed a weak line corresponding to the main line of NiO . Chemical analyses were performed and results are presented in Table 3: in each case, the amount of carbon is low or very low, the oxidation of WC has been achieved.

Fig. 8. Scanning electron micrograph of NiWO₄.Fig. 9. Scanning electron micrograph of ZnWO₄.Table 3
Chemical analysis of divalent transition metal tungstates

	%w.	M	W	C	M/W at.
NiWO ₄	Theor.	21.5	67.4		
	Exp.	20.1	57.6	0.05	1.09
CuWO ₄	Theor.	20.4	59.0		
	Exp.	24.5	52.3	0.2	1.35
ZnWO ₄	Theor.	20.9	58.7		
	Exp.	21.4	58.3	0.01	1.03

Fig. 10. TG curves of the reaction in nitrates of ZnCl₂(dotted line), WC (broken line) and their mixture (solid line). Dash-dot dotted line shows the melting point of the eutectic.

These results show that the reaction does not lead, under these experimental conditions, to pure metal tungstate. For copper the proportion (M/W) is the same as for magnesium, it is somewhat smaller for nickel. The composition obtained with ZnCl₂ is close to that of the pure compound and it must be possible to optimize the experimental conditions to achieve this aim. The determination of some reaction pathways will indicate what parameter could be modified to improve the preparation of the metal tungstates.

In each case, TG analyses of the RMW reactions, exemplified by RZW in Fig. 10, show that both the single reactions of WC and of the metal precursor are modified when the precursor salts react together, particularly the whole reaction shifts towards the lowest temperatures. The differences are the rate at low temperature (faster for RZW) and the definition of the three or four steps (sharper for RZW). For RCW the TG reaction curve (Fig. 11) is roughly parallel to that of WC (Fig. 1). The reaction of RCW begins before the melting of the medium and is quite instantaneous as the medium turns into liquid. A marked level appears as the loss of mass corresponding to the WC reaction (88 g mol⁻¹) is reached, then a “second” reaction starts and continues to completion. Due to the high rate of

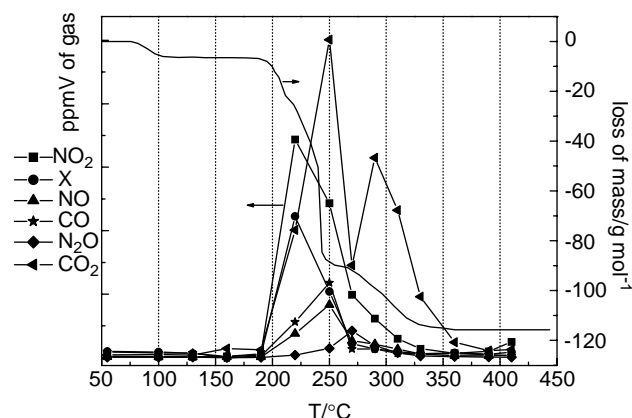


Fig. 11. TGA of the reaction of WC and CuCl_2 with nitrates and the respective compositions at given temperatures of the gas phase determined by IR spectroscopy.

Table 4

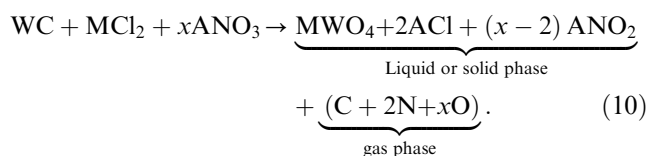
Determination of the coefficient of the alkali metal nitrate involved in the reaction with WC and divalent metal precursor

Reaction in ANO_3	Loss of mass (g mol^{-1})	x
CuCl_2/WC	110	4.4
NiCl_2/WC	136	6
ZnCl_2/WC	135	6

reaction the steps are not easy to determine but we will say that three steps are involved in the reaction.

As illustrated by Fig. 10, the whole loss of mass at 450°C of RMW is intermediate between the loss of RW (88 g mol^{-1}) and the sum of the individual losses (108 according to Eq. (4) + $88 = 196 \text{ g mol}^{-1}$).

If the experimental loss was 88 g mol^{-1} , this would prove that the metal ion was a spectator in the redox reaction of WC and did not react itself with the medium. In this case, WC reacts as in Eq. (8) and the divalent metal ion progressively forms the metal tungstate insoluble in the molten medium. On the contrary, if the experimental mass loss was the sum of the individual ones (196 g mol^{-1}) we should obtain in the medium, a mixture of alkali metal tungstate and of divalent metal oxide. On washing, the alkali metal tungstate would dissolve as previously and the solid product would be the pure divalent metal oxide. The TG curves, the XRD and the chemical analysis show, especially for RZW, that the reaction involves strong interactions between the two reactants. The same equation as for RW (Eq. (7)) can be written as



The losses of mass $(40 + 16x) \text{ g mol}^{-1}$ allow the calculation of x; the values are given in Table 4. Whole

values obtained for RNW and RZW show that the process can be described by this formalism. The compounds prepared would have the same level of purity within the limits of accuracy. The value 4.4 obtained for RCW, because of its significant decimal figure, improves the chemical analysis result and lets assume a different mechanism of reaction. It can be shown by the composition of the evolved gases.

The infrared studies of the gases released during the reactions can be helpful in determining the steps corresponding to a redox process (production of carbon oxides and the related nitrogen oxides) and those corresponding to an acido-basic process (production of nitrogen oxides, mainly NO_2 , Eq. (4), without carbon oxides).

Qualitatively, the IR spectra of RMW compare with those obtained in the WC reaction, the same gases are evolved. However, the proportions of the different gases released during the reactions RCW and RZW reveal marked differences, whatever could be the accuracy of the IR determination.

For RCW, the TG curve (Fig. 11) reveals three steps corresponding to the temperature domains: $200\text{--}240^\circ\text{C}$, step 1, $240\text{--}250^\circ\text{C}$, step 2 and $260\text{--}350^\circ\text{C}$, step 3. The first one corresponds to the simultaneous emission of all the gaseous compounds with a predominance of NO_2 . This phenomenon, not observed in RW, shows that reactions (Eqs. 4 and 7) occur at the same time and consequently CuO is formed to some extent. The release of carbon dioxide presents two maxima related to the last two steps of the TG curve. The maximum of the carbon monoxide evolution corresponds only to the first dioxide peak. The lack of CO in the third step shows that it is different from the previous one. Moreover, the nitrogen oxides can be considered as absent in this step. It does not correspond to a redox reaction but to the decomposition of intermediate carbonate compounds. These compounds would be formed during the very fast second step. In this step, according to Eq. (10), nitrite ions form that render the medium around WC particles more basic in a very short time so that CO_2 cannot be released as fast as it forms. This carbon dioxide is able to react with CuO produced in the previous step to give oxocarbonate such as $\text{CuO} \cdot \text{CuCO}_3$. The corresponding hydroxocarbonates and their decomposition at low temperature are well-known [13]. After the plateau corresponding to the quasi-completion of the redox reaction and to the formation of the oxocarbonates, both of them cause the pressure of CO_2 to decrease. A further mass loss occurs as $\text{CuO} \cdot \text{CuCO}_3$ begins to decompose to copper oxide. At the end of the process, because of the formation of copper oxide, some tungstate ions must be balanced by alkali metal ions. Alkali metal tungstate dissolves on washing, and the powder obtained contains an excess of CuO .

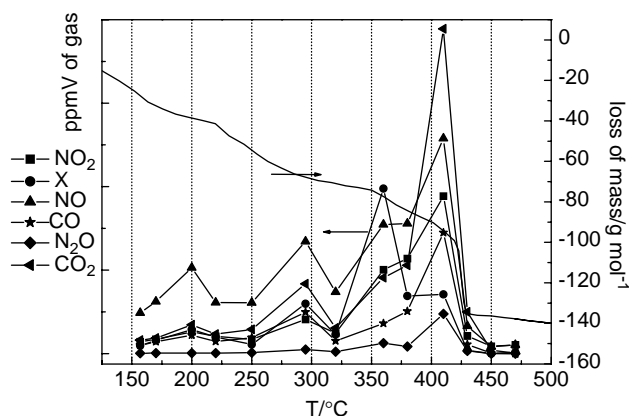


Fig. 12. TGA of the reaction of WC and ZnCl_2 with nitrates and the respective compositions at given temperatures of the gas phase determined by IR spectroscopy.

The optimization of the formation of pure CuWO_4 , if possible, would require the reaction of CuCl_2 with the nitrate to be delayed. Also required, would be the slowing of the redox reaction, by a decrease of the heating rate and a greater dilution of the reactants in the molten salts, to avoid the formation of the intermediate compounds.

By considering the composition of the gases (Fig. 12), the reaction RZW progresses more regularly in three or four steps revealed by relative maxima of given compounds. These maxima are related to the steps of the TG curve (the difference between the temperatures of the last step is not significant).

The first maximum at 200°C is difficult to use because all the gases, except NO, are in low concentration; however, NO is the main gas evolved as in RW. At 295°C, the second maximum, the gases appear in the same order as in RW, and the ratio NO/CO₂ is the same (1.6 and 1.5 resp.). At 360°C, disregarding the X compound, the ratio NO/CO₂ seems to increase (1.7). At higher temperatures a fast redox reaction occurs producing all the products at the same time. CO₂ is the main gas in this step, it is worth noting that this predominance does not exist in RW (Fig. 1). Then the reaction goes to completion, the ratios between the gases remain constant; it ends at 450°C.

As a difference with RCW, NO₂ is never the main gas or even the main nitrogen oxide released showing that the formation of the metal oxide does not take place. As another difference, the last step in RZW is a redox reaction which is not in RCW, this indicates that the formation and the decomposition of carbonate compounds do not occur with Zn ions.

The results could be explained as follows. The Zn precursor alone reacts only at high temperature (Fig. 10) with the nitrates; in this respect it is similar to the alkaline earth metals. We can assume that in the first low-temperature steps, the similarity of the composi-

tions of the gas phases in RZW and RW shows also the absence of reaction of the Zn precursor in RZW. So, during the first steps WC reacts with the nitrates, even in the solid state at low temperature. The reason why the presence of ZnCl_2 (and more generally MCl_2) lowers the temperature of reaction of WC is difficult to explain; a possibility could be that the divalent metal ions polarize more efficiently the nitrate ions than alkali metal ions do. Once the medium is liquid, the precipitation of ZnWO_4 is easier and, as W(VI) disappears, this favors the oxidation of W(IV) to the detriment of C, whose oxidation could stop at elemental carbon (250–375°C). Then, the major part of W being oxidized and precipitated as ZnWO_4 , the oxidation of C(s) by the nitrates takes place, typically producing CO and CO₂. The very small amount (Table 3) of C(s) which has not been oxidized gives the grayish color to the solid.

The synthesis of pure ZnWO_4 is feasible. The low content of ZnO which was formed in these experiments arose from last fast step, a decrease of the temperature level can probably slow it down. The most recent results on the reactivity of ZnCl_2 indicate that the reaction performed in KNO_3 , rather than in the KNO_3 – NaNO_3 mixture, could give pure zinc tungstate because the basicity of KNO_3 is lower than that of the mixture.

5. Conclusion

This study shows that WC can readily be oxidized completely in molten nitrates and that metal tungstates can be precipitated. The presence of a transition metal ion in the medium decreases the temperature of the onset of the reaction and of the main step. Without any optimization, the process allows CaWO_4 and ZnWO_4 to be prepared with a good yield (90%). The syntheses realized in molten salts do not involve hydroxo species as do aqueous processes, the water used to dissolve the cake affects only the surface of the crystals. The temperature used in this work is relatively high for this kind of syntheses. It can be lowered close to the melting point of the system in order to decrease the crystals growth and so as to obtain crystals on the nanoscale.

Acknowledgments

We are indebted to Région Rhône-Alpes for financial support from the program “Powders and multi-components materials”.

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