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THE SOLVOTHERMAL SYNTHESIS OF A NEW CLASS OF MATERIALS : THE PHYLLOSILOXIDES

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ABSTRACT

The thermal stability of natural phyllosilicates is strongly limited by the presence of hydroxyl groups (OH) in the lattice ($2\text{OH}^- \rightarrow \text{O}^{2-} + \text{H}_2\text{O}$). On the basis of the structure of mica-phlogopite [$\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$] and using cationic substitutions on both Oh and Td sites a new composition can be set up : $\text{K}(\text{Mg}_2\text{Al})\text{Si}_4\text{O}_{12}$.

Using combined two steps-process - (i) an all alkoxide sol-gel conversion and (ii) a solvothermal treatment (in supercritical conditions of the residual solvent $50 \leq P \leq 100$ MPa ; $700 \leq T \leq 800^\circ\text{C}$; $48 \leq t \leq 72$ h) - this new layered oxide was prepared and characterized.

This axis of research open a route to a new class of layered oxides isostructural of phyllosilicates and called : PHYLLOSILOXIDES.

1. Introduction

In a composite material with a ceramic (or a vitreous) matrix (CMC or CMV), an interphase is used for controlling the fiber-matrix bonding. The role of such an interphase is : (i) to act as a fuse in order to deflect the propagation of the microcracks in the matrix from perpendicularly to the fibers (mode I) to parallelly to the fibers (mode II) when the composite is loaded along the fiber axis, (ii) to allow enough load transfer from the matrix to the fiber, (iii) to release part of the residual stresses due to processing and (iv) to act as a diffusion barrier.

From the present state of knowledge, compliant materials with a layered crystal structure or a layered microstructure have been shown to be the best interphase materials [1].

The choice of the interphase material depends on three main criteria :

- the first is structural, a layered structure or microstructure being preferred.

- a good resistance to oxidation in particular for composites used in oxidizing atmospheres,

- a high thermal stability.

Through the first criteria, three types of materials can be selected : pyracarbon (PyC), boron nitride with turbostratic structures (hex-BN) and phyllosilicates. Table I gives a comparison of the main properties of these three materials with a view to their use as interphase in CMC's.

It appears that none of these materials fulfilled perfectly all the required properties.

The resistance to oxidation cannot be improved very significantly for graphite and BN. Consequently the objective of our research-work was to improve the thermal stability of phyllosilicates. Such a challenge required to eliminate the hydroxyl groups [2].

The substitution of F^- for OH^- has been tested and fluoro-micas (which exist in nature) have been tentatively used as interphase in CMV [3].

TABLE I - Some properties required for interphase use in CMCs.

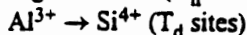
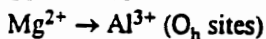
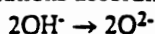
Material	PyC	hex-BN	Phyllosilicates
Criteria			
Cleavage (fuse function)	Yes	Yes	Yes
Resistance to oxidation	No	limited	Yes
High thermal stability	Yes	Yes	No

We have developed another route involving the anionic substitution $\text{OH}^- \rightarrow \text{O}^{2-}$ in order to prepare new layered oxides. Such a route required in parallel cationic substitutions, e.g. $\text{M}^{2+} \rightarrow \text{M}^{3+}$ into the (T) or (O) layers of the phyllosilicate lattice. The corresponding oxides, free of hydroxyl groups, has been called the "phyllosiloxides".

2. Preparation of the "phyllosiloxide" derived from mica-phlogopite

Mica-phlogopite has been selected as starting model. With a general formula $[\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2]$, where Mg^{2+} are located in octahedral sites (O_h), Al^{3+} and Si^{4+} being in the tetrahedral ones (T_d).

The selected compensated ionic and cationic substitutions according to the following equations :



lead to the theoretical formula : $\text{KMg}_2\text{AlSi}_4\text{O}_{12}$.

The first step was an all alkoxide sol-gel process in order to achieve a great homogeneity of the final product. The starting compounds were $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_2\text{H}_5)_3$, $\text{Mg}(\text{OC}_2\text{H}_5)_2$ and KOCH_3 . The sol-gel transformation was induced by a thermal treatment at 150°C during 1 hour.

All the conventional thermal treatment tested as second step for transforming the resulting gel to a layered oxide have led to three dimensional materials as MgSiO_3 , Mg_2SiO_4 and Al_2SiO_5 [4]. Consequently, we have developed a solvothermal treatment of the

gel issued from the first step. A solvothermal treatment can be described as a chemical reaction into a solvent in supercritical conditions using high temperatures and high pressures condition [5]. This type of process, using the specific physico-chemical properties of the solvents in supercritical conditions can help the synthesis of materials [6].

In our case, the solvent was the glycol monoethyl ether used in the first step and adsorbed on the resulting gel. The experimental conditions were $50 \leq P \leq 100 \text{ MPa}$, $700 \leq T \leq 800^\circ\text{C}$, $48 \leq t \leq 72 \text{ h}$.

3. Physico-chemical characterizations of the phyllosiloxide $\text{K}(\text{Mg}_2\text{Al})\text{Si}_4\text{O}_{12}$

3.1 X-ray diffraction

The X-ray pattern is isotypic of the mica-phlogopite used as starting model. A HR-TEM image starting underlines the layered structure of this new oxide.

3.2 SEM characterization of the microcrystallites

SEM images were used to determine the average size (close to $1 \mu\text{m}$) and the morphology (hexagonal platelets) of the phyllosiloxide microcrystallites.

3.3 I.R. spectroscopy

The domain of investigation was limited to $400\text{--}3800 \text{ cm}^{-1}$. The powder samples were in suspension in nujol or mixed with KBr. The observed IR-spectrum is given on the figure.

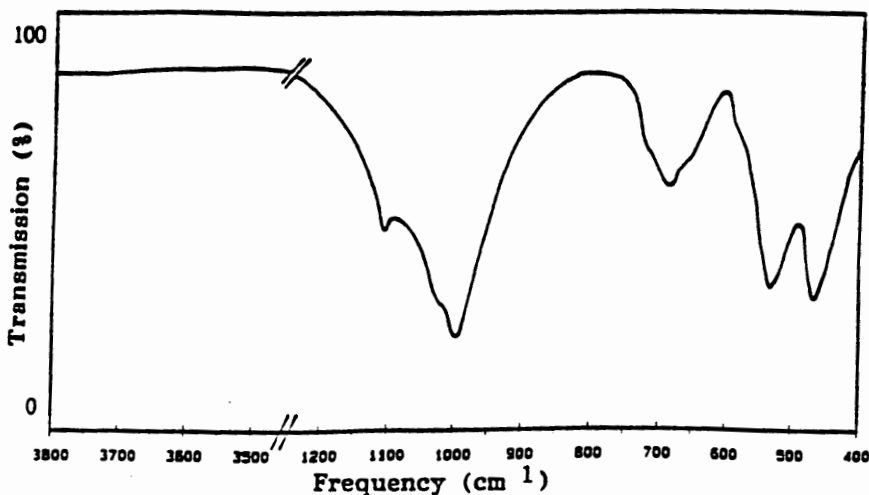


Figure - IR spectrum of the $\text{KMg}_2\text{AlSi}_4\text{O}_{12}$ "phyllosiloxide".

The absence of adsorption bands in the 3500-3800 cm^{-1} domain corresponding to the vibration of elongation $\nu(\text{OH}^-)$ or in that attributed to the OH^- deformation $\delta(\text{OH}^-)$, $\gamma(\text{OH}^-)$ (600-900 cm^{-1}) [7] confirms clearly the absence of hydroxyl groups in the mica-phlogopite lattice and thus the preparation of a new layered oxide : the phyllosiloxide.

3.4 Thermal stability of the $\text{KMg}_2\text{AlSi}_4\text{O}_{12}$ phyllosiloxide

XRD experiments have been performed between 25 and 1000°C. No change (after an isothermal-plateau of 1 hour) is observed between 25 and 800°C. Beyond 900°C, the intensity of the (002) diffraction line decreases. The phyllosiloxide tends to become amorphous at a temperature close to 950°C. At 1000°C tridimensional structures (i.e. SiO_2 , Mg_2SiO_4 ...) resulting from a thermal decomposition are observed. Consequently, it appears clearly that the $\text{KMg}_2\text{AlSi}_4\text{O}_{12}$ phyllosiloxide is thermally more stable ($T \approx 950^\circ\text{C}$) than the corresponding mica-phlogopite (500-700°C).

4. Conclusions

On the basis of the phyllosilicate lattices, in particular the mica-phlogopite ones, and using associated anionic and cationic substitutions, the preparation of a new class of layered oxides : the phyllosiloxides can be possible through a high pressure solvothermal process [6].

Acknowledgements

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