ENCAPSULATION OF SACRIFICIAL SILICON CONTAINING PARTICLES FOR SH OXIDE CERAMICS VIA A BOEHMITE PRECURSOR ROUTE

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ABSTRACT

Easy crack propagation in oxide ceramic coatings limits their application in high temperature environment (e.g. such as engines and gas turbine components) [1]. In order to overcome this problem, incorporation of sacrificial particles into an oxide ceramic coating may be a viable option. Particles of silicon compounds, such as: Si_3N_4, SiC, $MoSi_2$, $TaSi_2$ and WSi_2 are attractive due to their unique features of producing a reaction product (i.e. SiO_2) which fills the crack and bonds well to the surrounding matrix and exhibit, a relatively low density and melting point above that of the matrix [2]. To achieve a better control of the self-healing process with silicon compound particles a gas tight encapsulation procedure of these particles is a crucial prerequisite in order to avoid premature oxidation in the absence of a local crack. One possible route is the encapsulation of these particles by a sol-gel method [3, 4]. The dispersed healing particles were coated by Al_2O_3 layer prepared from boehmite sols, using two different alumina precursors (salt and alkoxide precursors). The resulted embedded sols were annealed in reducing atmosphere at temperatures above 1200 °C in order to achieve a dense α-Al_2O_3 microcapsule shell wall. The morphology, structure and composition of the encapsulation are determined with advanced analysis techniques. The thermal stability of the encapsulated healing particles is studied by high temperature exposure in air.

1. INTRODUCTION

Oxide ceramic coatings are promising materials for technological applications which require high temperatures, oxidation resistance and long term stability. The most important factor in the development of these types of materials is the improvement of their mechanical behaviour. The lifetime of oxide ceramic coatings is strongly affected by the crack propagation which limits their application in high-temperature environments (e.g. furnace heating elements, engines and gas turbine components) [1]. A possible route to overcome this critical issue is the incorporation of sacrificial particles into an oxide ceramic coating. Intermetallic particles based on silicon compounds, such as Si_3N_4, SiC, $MoSi_2$, $TaSi_2$ and WSi_2 are attractive due to their unique features of forming a reaction product, mainly SiO_2, which fills the crack and bonds well with the surrounding matrix [2].
To have a better control of the self-healing process with silicon based intermetallic compounds an encapsulation process is prerequisite in order to avoid the premature oxidation in the absence of any local crack. One possible way to achieve this is via

inorganic encapsulation of these particles using soft-chemical methods (precipitation or sol-gel).

In this work, an encapsulation process of $MoSi_2$ particles via boehmite precursor route has been developed.

2. MATERIALS AND METHODS

Aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, 99% purity, Sigma Aldrich), ammonium hydroxide (NH_4OH, aqueous solution 25%, J.T. Baker Chemical Co) and molybdenum disilicide ($MoSi_2$ 99.5% purity, average particle size 20 μm, ChemPur) were used as starting materials.

The encapsulation process was performed at room temperature. $MoSi_2$ particles were firstly dispersed in $AlCl_3 \cdot 6H_2O$ aqueous solution. The obtained suspensions were stirred and ultrasonicated for 30 minutes to break up the agglomerates and to avoid the particles sedimentation. Subsequently, the mixture was hydrolysed by slow addition of NH_4OH under continuous stirring, at room temperature, until the reaction mixture attained a pH value between 5.0 – 6.0. The concentration of $AlCl_3 \cdot 6H_2O$ varied from 0.5 M, 2 M, 3.5 M to 5 M and the molar ratio $AlOOH/MoSi_2$ was fixed at 10 : 1. The obtained precipitates were separated by filtration, washed of free chloride and ammonium ions with hot bi-distilled water and dried at 100 °C for 2h. The as synthesized samples were then annealed at 1300 °C for 2 hours, in a reducing atmosphere (10% H_2 and 90% N_2). The flowchart of the encapsulation process of $MoSi_2$ particles is shown in Figure 1.
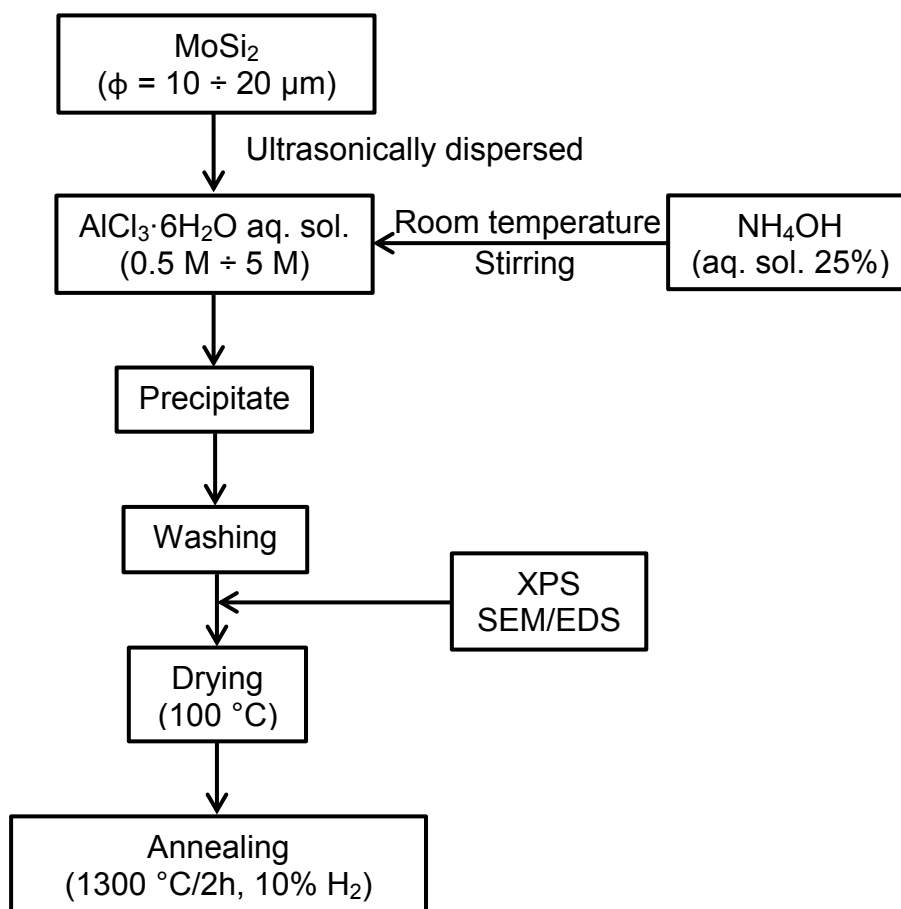

Figure 1: Flowchart of $MoSi_2$ encapsulation with $AlOOH$.

3. RESULTS AND DISCUSSION

The morphology of the $MoSi_2$ healing particles before and after encapsulation was observed by means of scanning electron microscopy (SEM); see Figure 2. The $MoSi_2$ particles are of irregular shape with sizes in the range of 10 to 20 µm; see Figure 2a. The precipitation of boehmite in a $AlCl_3·6H_2O$ 0.5 M aqueous solution completely covered the surface of $MoSi_2$ particles; see Figure 2b. Similar observations were made for the other suspensions prepared by using more concentrated solutions of $AlCl_3·6H_2O$ (2 M, 3.5 M and 5 M, respectively).

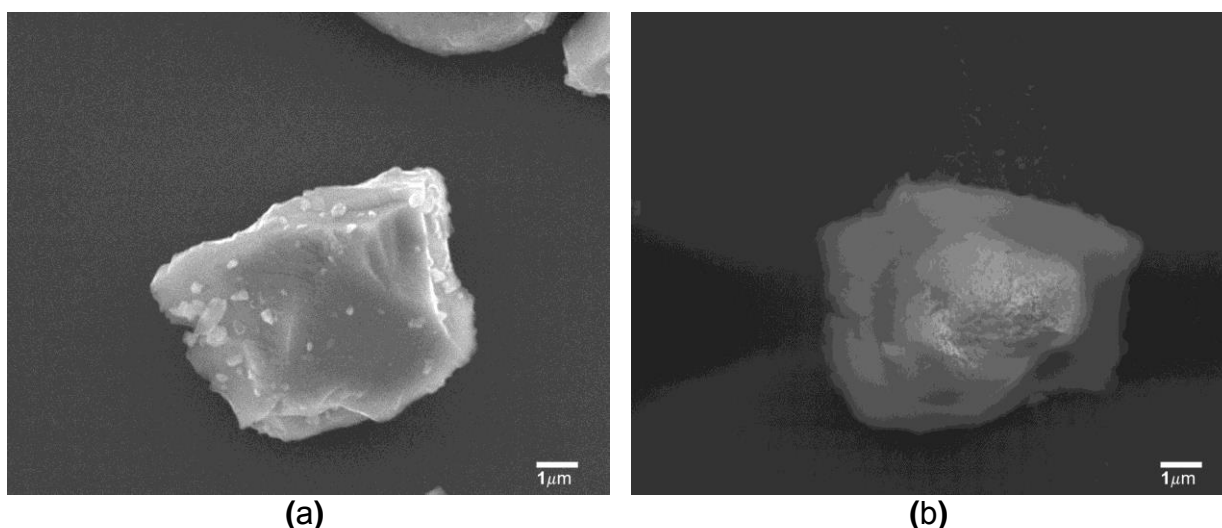(a)   (b)

Figure 2: SEM images of uncoated and coated $MoSi_2$ particles: (a) as received $MoSi_2$ particles and (b) boehmite coated $MoSi_2$ particles prepared by using $AlCl_3·6H_2O$ 0.5 M aqueous solution.

Another evidence of boehmite shell formation on the surface of $MoSi_2$ particles is given by X-ray Photoelectron Spectroscopy (XPS). For all the layers deposited onto the $MoSi_2$ particles, the O 1s peaks can be described precisely by two components corresponding to OH^- and O^{2-}, respectively. The curve fitting of the O 1s photoelectron peak was performed using a Gaussian-Lorentzian fitting curve in the binding energy region of 526–538 eV after subtraction of the Shirley type background. The binding energies corresponding to the resolved OH^-, O^{2-} components of O 1s and Al 2p are summarized in Table 1.

Table 1: Binding energies corresponding to O^{2-}, OH^- and Al 2p components of the Boehmite shells obtained from the curve fitting of the XPS spectra.

Concentration AlCl₃ solution	O^{2-} BE (eV)	OH^- BE (eV)	Al 2p BE (eV)
0.5 M	531.0	532.6	74.0
2.0 M	530.9	532.9	74.0
3.5 M	530.8	532.2	73.9
5.0 M	530.8	532.1	74.0

The binding energies of both components, O^2 and OH^- present narrow ranges: 530.8 – 531.0 eV and 532.1 – 532.9 eV, respectively. These values for O 1s components are in agreement with the results presented in the literature [5].

As already observed with SEM and confirmed with XPS, the MoSi$_2$ healing particles are fully covered with boehmite, since no photoelectron peaks corresponding to Mo or Si were detected.

The MoSi$_2$ particles remained intact during the encapsulation process, as evidenced by X-ray diffraction patterns of the particles before and after encapsulation.

After annealing the boehmite encapsulated MoSi$_2$ particles in reducing atmosphere (10% H$_2$ and 90% N$_2$) at 1300 °C analysis suggests that the boehmite is transformed to the desired α-Al$_2$O$_3$ phase.

4. CONCLUSION

MoSi$_2$ healing particles were successfully encapsulated with boehmite using a soft-chemical method. A closed shell of aluminium oxyhydroxide layer was formed on the surface of MoSi$_2$ particles after the precipitation process. Annealing the encapsulated particles in a gas mixture of 10% H$_2$ and 90% N$_2$ at 1300 °C transformed the boehmite into α-Al$_2$O$_3$, while the MoSi$_2$ core remained intact.

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