Synthesis of alumina ceramic encapsulation for self-healing materials on thermal barrier coating

O P Golin\(^1\), N Prastomo\(^1\), H Izzudin\(^2\), S Hastuty\(^3\), R Sundawa\(^2\), E Sugiarti\(^2\) and K A Z Thosin\(^2\)

\(^1\)Engineering Physics Department, Surya University, Tangerang, Banten, 15810 Indonesia
\(^2\)Research Center for Physics, Indonesian Institute of Sciences, Komplek Puspiptek, Serpong, Tangerang Selatan 14314, Indonesia
\(^3\)Mechanical Engineering Department, Universitas Pertamina, South Jakarta, Jakarta, 12220 Indonesia

E-mail: obert.golim@gmail.com

Abstract. Durability of Thermal Barrier Coating or TBC can be optimized by inducing Self-Healing capabilities with intermetallic materials MoSi\(_2\). Nevertheless, high temperature operation causes the self-healing materials to become oxidized and lose its healing capabilities. Therefore, a method to introduce ceramic encapsulation for MoSi\(_2\) is needed to protect it from early oxidation. The encapsulation process is synthesized through a simple precipitation method with colloidal aluminum hydroxide as precursor and variations on calcination process. Semi-quantitative analysis on the synthesized sample is done by using X-ray diffraction (XRD) method. Meanwhile, qualitative analysis on the morphology of the encapsulation was carried out by using Scanning Electron Microscope (SEM) and Field Emission Scanning Electron Microscope (FESEM) equipped with dual Focus Ion Beam (FIB). The result of the experiment shows that calcination process significantly affects the final characteristic of encapsulation. The optimum encapsulation process was synthesized by colloidal aluminum hydroxide as a precursor, with a double step calcination process in low pressure until 900 °C.

1. Introduction

Thermal Barrier Coating or TBC is a type of coating that is commonly applied on substrate used on a high temperature, such as super alloys on turbine gas engine. It enables the substrate to work on a higher temperature [1]. The main structure of TBC is composed of two main parts, top coat and bond coat. The top coat is an oxide layer that has high temperature resistance and the bond coat connects the oxide layer to the substrate. During operation, oxygen may diffuse through the oxide layer and reacts with the bond coat to form another layer which was called the thermally grown oxide (TGO) layer, that has a very distinctive coefficient of thermal expansion with the oxide layer on top of it [2]. Extreme cyclic operating condition may cause stress to occur due to the difference in thermal expansion coefficient and induced crack on TBC which later would cause the coating to peel off, leaving the substrate to be unprotected [3].

Experiment had shown that self-healing properties induced on the TBC may help close up cracks appeared and extend its lifetime. The self-healing mechanisms proposed occurred whenever cracks formed on the TBC, causing the self-healing material to be exposed with oxygen and formed an oxide materials to heal the crack [4].
Due to its extreme operating conditions, there are several limitations for the healing material that can be used. First, the healing material must have a solid phase to prevent any significant difference on the coefficient of thermal expansion between the healing materials and the TBC. Second, it must be able to form a healing product that has similar properties to the TBC. Literature shows that materials composed of early transition metal and group A element exhibit properties that fulfill the criteria specified above. Materials used on past experiment, MoSi$_2$, was also included in this group. Nonetheless, materials from this group will undergo an oxidative decomposition on high temperature environment, thus reducing its healing capabilities [4-7].

Therefore, a specific method was needed to protect the self-healing materials from early oxidation. A study has shown that self-healing materials are isolated from the outside medium through an encapsulation process. These encapsulations prevent contained self-healing materials to undergo early reaction, and enables the healing process to occur when the capsule was ruptured [5]. However, there are several criteria that must be fulfilled for the encapsulation, which is to be oxygen impenetrable and have a similar coefficient of thermal expansion with the TBC. Literature has shown that alumina encapsulation was the best type of encapsulation that able to fulfill those criteria [4, 6].

Several researches have shown that alumina encapsulation can be synthesized through several methods. However, the simplest method to produce an alumina encapsulation was through the precipitation method [5, 6, 8]. This method consists of two main steps, the first one is the formation of simple coating through precipitation method. The second step is the formation of oxide encapsulation layer through calcination process [8, 9].

A study has shown that synthesis of alumina encapsulation for self-healing material MoSi$_2$ was possible using aluminium chloride as precursor. However, experiment results show the healing materials undergo premature oxidation that cause it to lose some of it healing properties during the encapsulation process [6].

This experiment was done to introduce a better method for synthesizing encapsulation for self-healing material MoSi$_2$ through the precipitation method with modification on the precursor used and the calcination method.

2. Methodology

2.1. Materials

The self-healing materials encapsulated on this experiment was molybdenum disilicide (Japan New Metals, Co. Ltd), and the materials used for the alumina encapsulation were aluminium hydroxide (Taimei Chemicals), nitric acid (65%, Merck), ammonium hydroxide (28%, Tedia), and locally produced distilled water.

2.2. Encapsulation procedure

The procedure of the encapsulation started with synthesizing the precursor by diluting aluminium hydroxide powder into nitric acid to form a colloid. Then the self-healing material was dispersed into the colloid with mol ratio of 1:10. On these experiment, a 5M precursor was used. The dispersion process was done with magnetic stirring and ultrasonication for 30 minutes. Next, the mixture was hydrolysed by addition of diluted ammonium hydroxide 25% slowly until the pH of mixture reach 9. While being titrated with ammonium hydroxide, the mixture was stirred with magnetic stirrer to prevent agglomeration of particles. The mixture was then aged for more than 15 hours at room temperature to settle the precipitate. After aging process, the sample was then filtrated with a filtration paper while being washed with distilled water at 80 °C to help clean the sample from salt residue from the hydrolyzation. Then, the sample was dried on low vacuum condition (10mbar) at 100 °C. Low vacuum condition was used to prevent premature oxidation of the self-healing material. The last step was calcining the pre-encapsulated MoSi$_2$ with a vacuum furnace. On this experiment, there are 4 types of calcination processed used: direct calcination process into 900 °C, step calcination process into 900 °C, direct calcination process into 1000 °C, and step calcination process into 1000 °C. Low-pressure condition was held at 15 Pa to prevent any premature oxidation of the self-healing material.
2.3. Characterization
The samples synthesized on this experiment were characterized with x-ray diffraction (XRD) and scanning electron microscope (SEM), before and after the calcination process. The XRD used to characterize crystalline structure of the sample using RIGAKU X-ray diffraction instrument in 2theta range 20° - 80° with a step size of 0.002°. The phase of sample obtained through Rietveld analysis profile fitting. SEM images were obtained on HITACHI SEM along with energy dispersive x-ray spectroscopy (EDS) to characterize the morphology of the encapsulated self-healing particle. The beam energy used was 20kV and the beam current was set into 86.1µA. EDS analysis was using the point analysis method with molybdenum, silicon, aluminium and oxygen element.

Sample with the best result was then characterized again using JEOL multi-beam field effect scanning electron microscope (FESEM) equipped with focus ion beam (FIB) to obtain the cross-section view of an encapsulated particle before and after the calcination process. The cross section of the sample was obtained by milling an encapsulated self-healing particle with Gallium ion beam under low vacuum condition. To gain the morphology of encapsulation, EDS mapping was used on molybdenum, silicon, aluminium, and oxygen element.

Prior to electron microscopy the samples were treated with thin carbon coating to prevent sample charging.

3. Results and discussions

3.1. Precursor synthesis
Aluminium hydroxide (Al(OH)₃) was diluted by nitric acid, considering its high solubility in strong acid or base solution [9]. However, some parts of the diluted aluminium hydroxide will react with nitric acid to form aluminium nitrate through equation 1 [10]. Therefore, the hydrolyzation process is needed for the formation of aluminium hydroxide precipitate that will encapsulate the self-healing particle. Hydrolyzation process will occur according to the chemical reaction on equation 2 [11].

\[ \text{Al(OH)}_3^{(s)} + 3\text{HNO}_3^{(aq)} \rightarrow \text{Al(NO}_3)_3^{(s)} + 3\text{H}_2\text{O}^{(aq)} \]  
(1)

\[ \text{Al(NO}_3)_3^{(l)} + 3\text{NH}_4\text{OH}^{(aq)} \rightarrow \text{Al(OH)}_3^{(s)} + 3\text{NH}_4\text{NO}_3^{(aq)} \]  
(2)

During the hydrolyzation process, the precipitates interacts with the self-healing material to form an encapsulation. This interaction mainly caused by the difference in surface potential of MoSi₂ and aluminum hydroxide. Past studies have shown that the zeta potential of MoSi₂ at pH 9 was around -80 mV, while the zeta potential of aluminum hydroxide under the same conditions are around -35 mV [12, 13]. Even though both particle has a negative surface charge, the difference in the magnitude of the potential itself cause an interaction between both particles. It is stated that particle with charge that is more positive are attracted to particle with negative charges. Therefore, it can be assumed that aluminum hydroxide particle will be attracted to MoSi₂ particle to form an encapsulation.

3.2. Encapsulation result before calcination process
Alumina encapsulation will form through the calcination process of boehmite. Boehmite itself will form on the drying process that evaporates water according to this below reaction [14].

\[ \text{Al(OH)}_3^{(l)} \rightarrow \text{AlOOH}^{(s)} + \text{H}_2\text{O}^{(g)} \]  
(3)

Figure 1a shows the boehmite encapsulated MoSi₂ after the drying process. Aside from the coated material, there could be observed some agglomerates of the boehmites particle that forms on the surface of the self-healing material. These agglomerates of boehmite particle formed when the precipitates failed to form encapsulation and agglomerates with other precipitates.

The XRD result on figure 2 shows that phase diagram of the coated self-healing material is dominated by boehmite. It is caused by the large number of the aluminium hydroxide precipitate which later formed the boehmites particles according to equation 3.
3.3. Encapsulation result after calcination process

After the calcination process, the boehmite encapsulation of MoSi$_2$ particle undergo a significant change that can be shown from the SEM and XRD results. The surface morphology of encapsulated MoSi$_2$ particle can be shown through the SEM images on figure 1b. Through the EDS point analysis, it is known that particle surfaces contain aluminium element, which means that the encapsulation was still intact. The effect of calcination process variations to the encapsulation can be seen from the XRD result in figure 2. Boehmite encapsulation undergo a change into alumina encapsulation according to equation 4 [15]. However, it is also shown that when the calcination temperature increased from the 900 °C to 1000 °C, Mullite and Mo$_5$Si$_3$ are formed, which means that the self-healing material undergo a premature oxidation according to equation 5 and 6 [6, 16]. The premature oxidations are caused by the rapid crystallization of alumina on higher temperature, which later caused the encapsulation to peel off from the surface and fail to protect the self-healing materials.

\[
\text{AlOOH} \xrightarrow{500-700^\circ C} \gamma-\text{alumina} \xrightarrow{>900^\circ C} \theta-\text{alumina} \xrightarrow{>1100^\circ C} \alpha-\text{alumina} \quad (4)
\]

\[
\frac{7}{5} \text{MoSi}_2(s) + \frac{7}{5} x \text{O}_2 \xrightarrow{800-1000^\circ C} \frac{7}{5} \text{MoSi}_3(s) + \frac{7}{5} x \text{SiO}_2(s) + (1-x) \text{MoSi}_2(s) \quad (5)
\]

\[
\frac{7}{5} x \text{SiO}_2(s) + \frac{21}{10} x \gamma, \eta, \delta \text{Al}_2 \text{O}_3(s) \xrightarrow{1000^\circ C} \frac{7}{5} x (3\text{Al}_2\text{O}_3 + 2\text{SiO}_2)(s) \quad (6)
\]

Figure 1. SEM images of coated MoSi$_2$ particle (a) before calcination (b) after step calcination to 900 °C.

The XRD results contradicts the result of an experiment, where calcination up to 1000 °C are proven to better [6]. On this experiment, it can be observed that calcination process up to 900 °C does not...
not produce a significant amount of Mullite through the XRD analysis even though there are faint peaks of Molybdenum Silicide (Mo$_5$Si$_3$), which proves MoSi$_2$ does not undergo a lot of premature oxidation. Apparently, this result could be achieved while doing the calcination process under low pressure condition. Medium vacuum condition of 15 Pa has enabled oxygen from ambient air to be limited, therefore oxidations of self-healing materials may be prevented [17]. The large alumina phases on XRD result was caused by the large amount of boehmite particle from the drying process. Boehmite that does not form an encapsulation still undergo phase change due to the heat treatment process to form alumina crystal as shown in figure 1b.

3.4. Morphology of encapsulation by FESEM

The best encapsulated self-healing materials obtained through calcination up to 900 °C with step process, was characterized again using FESEM. Figure 3a and b shows characterization result of encapsulated MoSi$_2$ before calcination process. According to the observation, previous statement on the existence of aluminium hydroxide precipitate on the surface of encapsulated particle can be proven. It is shown through the mapping of aluminium in figure 3b that some of the boehmites that does not form encapsulation, agglomerated and some others form encapsulation on the surface of the material. While on figure 3c it can be observed that oxygen is also located on the aluminium position. Both mapping image shows that there is a thin encapsulation that covers the self-healing material composed of aluminium and oxygen. However, due to the thickness of the encapsulation is lesser than the depth of penetration of EDS analysis, the mapping is dominated by molybdenum element on top of the material surfaces (red-coloured).

Figure 4 shows the result of characterization of encapsulated MoSi$_2$ after calcination process. According to the mapping, the surfaces are still covered with a faint of aluminium and oxygen element, which correlates with previous statement that after the calcination process alumina coating was still intact with the self-healing particle. It can also be observed that minimum number of oxygen is located on the materials, which proves that premature oxidation of the self-healing material is reduced. The cracks observed in SEM images from figure 4a were formed when the cross-section process using destructive ion gallium beam was done.

Figure 3. (a) SEM images of cross sectioned coated MoSi$_2$ particle, (b) EDS mapping of aluminum (blue) and molybdenum (red), and (c) EDS mapping of oxygen (green) and molybdenum (red) before calcination.
4. Conclusions

Encapsulation of self-healing material MoSi$_2$ was successfully synthesized through the proposed precipitation method with colloidal aluminium hydroxide as precursor. Through the experiments, it is shown calcination processes are proven to affect the final properties of encapsulation greatly. Step calcination until 900 °C under low pressure condition proved to be the most effective calcination processes in forming the alumina encapsulation with reduction in premature oxidation of the self-healing material.

References

[1] Sampath S, Schulz U, Jarligo M O and Kuroda S 2012 MRS Bull. 37 903
[2] Clarke D R, Oechsner M and Padture N P 2012 MRS Bull. 37 891
[3] van der Zwaag S 2010 Bull. Pol. Ac.: Tech. 58 227
[4] Sloof W G, Turteltaub S, Carabat A L, Derelioglu Z, Ponnusami S and Song G M 2015 Self-healing materials - pioneering research in the Netherlands Crack healing in yttria stabilized zirconia thermal barrier coatings (Netherlands: Delft University Press) pp 219-227
[5] Ollier R, Rodriguez E and Alvarez V 2013 Compos. Part A: Appl. Sci. Manuf. 48 137
[6] Carabat A L, van der Zwaag S and Sloof W G 2015 J. Am. Ceram. Soc. 98 2609
[7] Kötteritzsch J, Schubert U S and Hager M D 2013 Nanotechnol. Rev. 2 699
[8] Chavda V P, Soniwala M M and Chavda J R 2012 Crit. Rev. Pharm. Sci. 1 15
[9] Tregubenko V Yu, Udras I E, Drozdov V A and Belyi A S 2011 Russ. J. Appl. Chem. 84 9
[10] Levin O V, Sidel'kovskaya V G, Aliev R R and Leshcheva E A 1997 Chem. Technol. Fuels Oils 33 97
[11] Morgado E Jr, Lam Y L and Nazar L F 1997 J. Colloid Interface Sci. 188 257
[12] Yan Y, Li W, Yang J, Zheng A, Liu F, Feng X and Sparks D L 2014 Environ. Sci. Technol. 48 6735
[13] Sandlin M S, Butt D P, Taylor T N and Petrovic J J 1997 J. Mater. Sci. Lett. 16 1336
[14] Chiou Y H, Tsai M T and Shih H C 1994 J. Mater. Sci. 29 2378
[15] Santos P S, Santos H S and Toledo S P 2000 Mat. Res. 3 104
[16] Zhang H A and Gu S Y 2011 Advanced Material Research 284-286 1630
[17] Shigematsu T and Nakanishi N 1990 Solid State Ion. 40 799