

## Fabrication of (Al<sub>2</sub>O<sub>3</sub>-IMC)p/Al Composite Materials by In-situ Reaction Using MA Processed Al/MO Powders

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### Abstract

A planetary ball milling (PBM) technique was employed to fabricate mechanically alloyed (MA processed) Al-ZrO<sub>2</sub>, Al-Ta<sub>2</sub>O<sub>5</sub>, Al-Nb<sub>2</sub>O<sub>5</sub>, Al-WO<sub>3</sub> and Al-MoO<sub>3</sub> composite powders (Al/MO powders). Nano or sub-micron sized metal oxide particles were homogeneously embedded in the Al particles after milling for various periods. The milled Al-10, 15, 20wt%MoO<sub>3</sub> composite powders have a number of homogeneously embedded metal oxide particulates with a nano scale, respectively. The sequence of the in-situ reaction was confirmed by DTA, DSC, XRD measurements, optical microscopy and EPMA. Al-based metal matrix composites (MMC) reinforced with sub-sieve sized  $\theta$ -Al<sub>2</sub>O<sub>3</sub> particulates, Al<sub>3</sub>Zr, Al<sub>3</sub>Ta, Al<sub>3</sub>Nb, Al<sub>5</sub>W, Al<sub>12</sub>Mo intermetallic compounds formed by the in-situ reaction between Al and each of the metal oxides were homogeneously distributed in the Al matrix during sintering. Nano sized  $\theta$ -Al<sub>2</sub>O<sub>3</sub> particulates are preferentially distributed near the intermetallic compounds and their interfaces with the Al matrix contain no products. The manufactured ( $\theta$ -Al<sub>2</sub>O<sub>3</sub> + Al<sub>12</sub>Mo)p/Al composites have more refined products than the others.

**Keywords:** Metal matrix composite (MMC), Mechanical alloying (MA), In-situ reaction, Metal oxide (MO).

### 1. Introduction

Metal matrix composites (MMC) reinforced with ceramic particles, whiskers, or fibers have been commonly used in automobile, aircraft and space industries due to their high strength, superior wear resistance and other excellent mechanical properties [1,2]. There are a number of issues in the metal matrix composite research field. Bonding strength between the reinforcement and metal matrix, size of the reinforcements and big differences of the thermal expansion coefficients between reinforcement and metal matrix should be considered for the further applications of metal matrix composite materials. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> reinforced Al matrix composites fabricated by the in-situ reaction of Al and SiO<sub>2</sub> have a good wettability between the Al matrix and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles [3]. The intermetallic compounds of Al-Zr, Al-Ta, Al-Nb, Al-W and Al-Mo could decrease the difference of the thermal expansion coefficients between Al<sub>2</sub>O<sub>3</sub> and Al matrix. The composite structures of mechanically alloyed powders can be produced by planetary ball milling (PBM). The produced powders contain a number of diffusion couples composed of metal oxides and the Al matrix [4]. During heat treatment of composite powders at the in-situ reaction temperature, the solid-liquid reaction will occur. Direct bonds between ceramics and the metal matrix could be broken during temperature changes due to their large difference of the thermal expansion coefficients [5]. During cooling from the joining temperature, the contraction of the metal part is usually much larger than that of the ceramic part. The generated residual stress, which exceeds the strength of the ceramic parts, causes the breaking of the reaction products or the interface of the joints. It is well-known that reinforcement of metals, including intermetallic alloys, with ceramic phases to form a metal matrix composite can improve their high temperature strength [6,7]. When the reinforcement phase is mechanically milled into the matrix phase, it may not be in the thermodynamical equilibrium with the matrix at high temperatures and can thus degrade the properties. In-situ produced reinforcement

phases are more likely to be thermodynamically compatible with the matrix. By appropriately selecting the reactants and minimizing the volume changes resulting from the in-situ reaction, the near net-shape metal and intermetallic compounds-ceramic composite can be obtained. Therefore, the objective of this study is to fabricate the mechanically alloyed Al/ZrO<sub>2</sub>, Al/Ta<sub>2</sub>O<sub>5</sub>, Al/Nb<sub>2</sub>O<sub>5</sub>, Al/WO<sub>3</sub> and Al/MoO<sub>3</sub> composite powders using a planetary ball milling machine with different milling conditions and to examine the microstructural characteristics of the fabricated Al<sub>2</sub>O<sub>3</sub>-IMC reinforced aluminum matrix composites.

## 2. Experimental procedure

The materials used in the experiments were pure commercial Al (purity : 99.99%, mean size : 104 $\mu$ m), ZrO<sub>2</sub> (purity : 99.99%, mean size:147 $\mu$ m), Ta<sub>2</sub>O<sub>5</sub> (purity : 99.99%, mean size : 7 $\mu$ m), Nb<sub>2</sub>O<sub>5</sub> (purity : 99.99%, mean size : 3 $\mu$ m), WO<sub>3</sub> (purity : 99.99%, mean size : 10 $\mu$ m) and MoO<sub>3</sub> (purity : 99.99%, mean size : 10 $\mu$ m) powders produced by Soekawa Chemical Co in Japan, as shown in Fig.1. The Al-10, 20, 30wt%ZrO<sub>2</sub>, Al-10, 20, 30wt%Ta<sub>2</sub>O<sub>5</sub>, Al-10, 20, 30wt%Nb<sub>2</sub>O<sub>5</sub>, Al-10, 20, 30wt%WO<sub>3</sub> and Al-10, 15, 20wt%MoO<sub>3</sub> with Al/MO-1wt% stearic acid as a process control agent (PCA) that was used to protect the agglomeration among themselves during milling were located into stainless steel bowls of SUS316 with stainless steel ball of SUS316 under an argon atmosphere (Ar gas flows with 20ml/min for 1min) using an inlet-outlet device. The weight ratio of ball to powder was 8.1:1. The sealed vials were located into the planetary ball milling machine (pulverisette 7 planetary micro mill equipment made by FRITSCH Co). The powders were milled for 8h with interval time for 1h in every hour. All milled powders were measured by XRD and FE-SEM. The 8h-milled powders were examined by DSC measurements with the heating rate of 5°C/min to 700°C using DSC. For making the sintering samples, each of the 8h-milled Al/MO powders were cold pressed by cold presser using a cylinder type of stainless steel mold with a load of 0.5MPa. The shape of the preforms was  $\phi$ 10mm with 3.28mm height using 0.5g. The cylinder type of each preforms were sintered at 700°C for 12h in a tube furnace with an Ar atmosphere (Ar gas flow rate : 1 $\ell$ /min). The preforms were heated up to 700°C with the heating rate of 5°C/min and cooled down to room temperature with the cooling rate of 5°C/min. The sintered specimens that were carefully polished and etched by the Nital solution for 5min were measured by OM, XRD and FE-SEM.

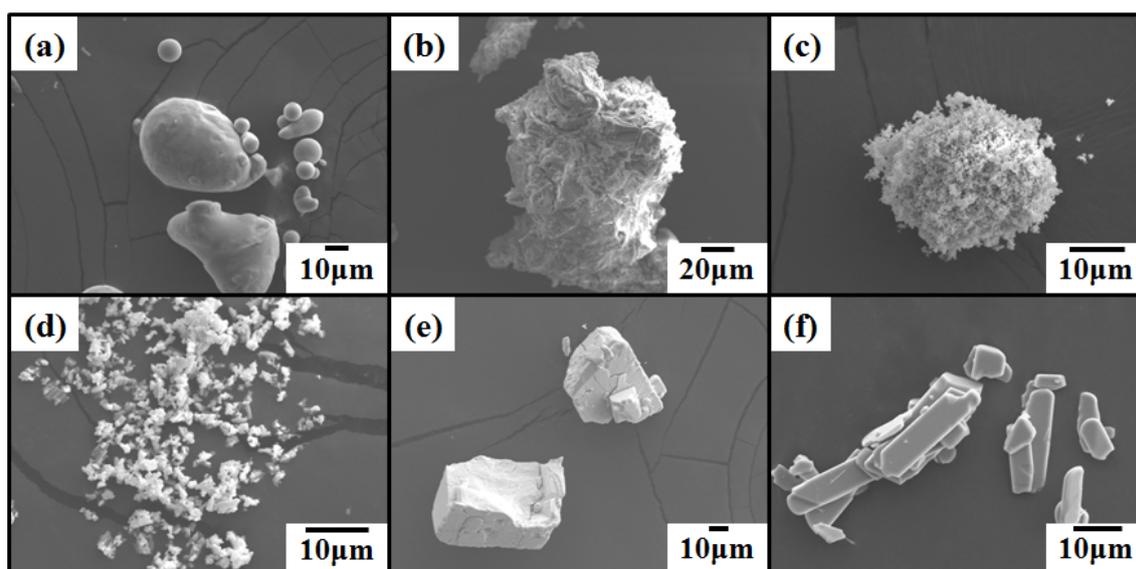


Fig.1. EPMA images of the (a) Al, (b) ZrO<sub>2</sub>, (c) Ta<sub>2</sub>O<sub>5</sub>, (d) Nb<sub>2</sub>O<sub>5</sub>, (e) WO<sub>3</sub> and (f) MoO<sub>3</sub> powders as a starting material.

### 3. Results and Discussion

The milling system in this study is the ductile-brittle system because Al is ductile and MOs are brittle as shown in Fig.1. Fig.2 shows FE-SEM images of the cross sections of the each 8h-milled powders. The embedded MOs particles with various sizes are homogeneously distributed on the Al matrix particles. The particle size of the embedded  $Ta_2O_5$  and  $Nb_2O_5$  particulates are larger than the others. However, the embedded  $MoO_3$  particulates with nano size are smaller than the others as shown in Fig.3. It seems that the size and morphology of the embedded MOs are depend on the shape and their properties of the MOs as a starting materials. The bar shapes of  $MoO_3$  as a starting material have more easily cracked and trapped on the ductile Al matrix powder during milling because the milling system is the ductile-brittle system. A number of diffusion couples between Al and MO particles having no pores, cracks and by-products on their interfaces are observed. It is more benefit to form resultants without unreacted parts because there are no mixed parts after milling. The temperature of the container could be increased due to the impact energy during milling. But, all of the milled powders have no XRD peaks of transformed phases, indicating that no in-situ reaction between Al and MOs occurs during milling. Therefore, the in-situ reaction will occur only when the sintering is performed at specific temperatures.

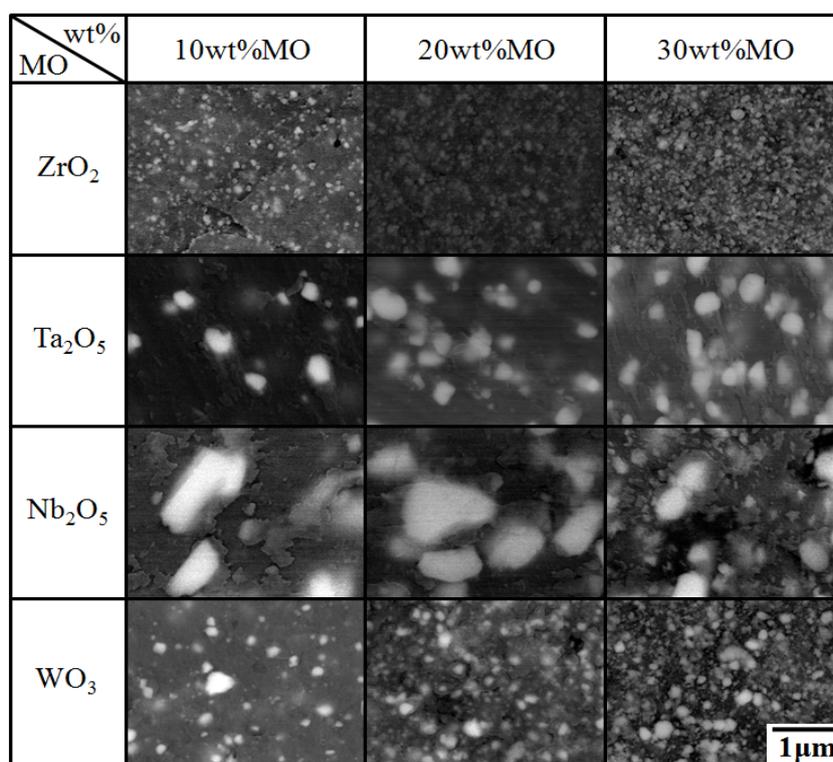


Fig.2. FE-SEM BSE images of 8h-milled Al/MO powders observed on the cross sections.

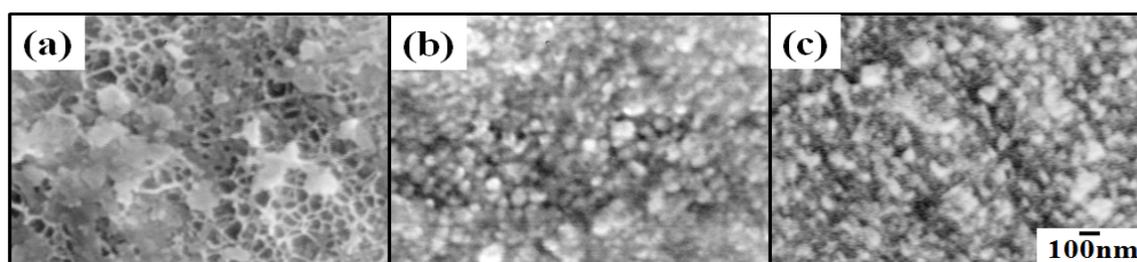


Fig.3. FE-SEM BSE images of 8h-milled (a) Al-10wt%MoO<sub>3</sub>, (b) Al-15wt%MoO<sub>3</sub> and (c) Al-20wt%MoO<sub>3</sub> powders observed on the cross sections.

Fig.4 shows the DSC results of the 8h-milled Al/MO powders. The exothermic peaks at around 680°C indicate that the main in-situ reaction occurs between the liquid state of Al and solid state of MO particles. Moreover, the in-situ reaction is almost completed at around 700°C. Therefore, the 8h-milled Al/MO samples should be sintered at around 700°C for the full of in-situ reaction. The in-situ reaction rate is significantly influenced by the size of the embedded MO particles. Therefore, the 8h-milled Al/MoO<sub>3</sub> powder needs not only small amount of heat absorption but also the heat evolution to complete the in-situ reaction as shown in Fig.4. However, the 8h-milled Al-Ta<sub>2</sub>O<sub>5</sub> and Al/Nb<sub>2</sub>O<sub>5</sub> powders having bigger sizes of the embedded MOs than the others need a long period to complete the in-situ reaction relatively.

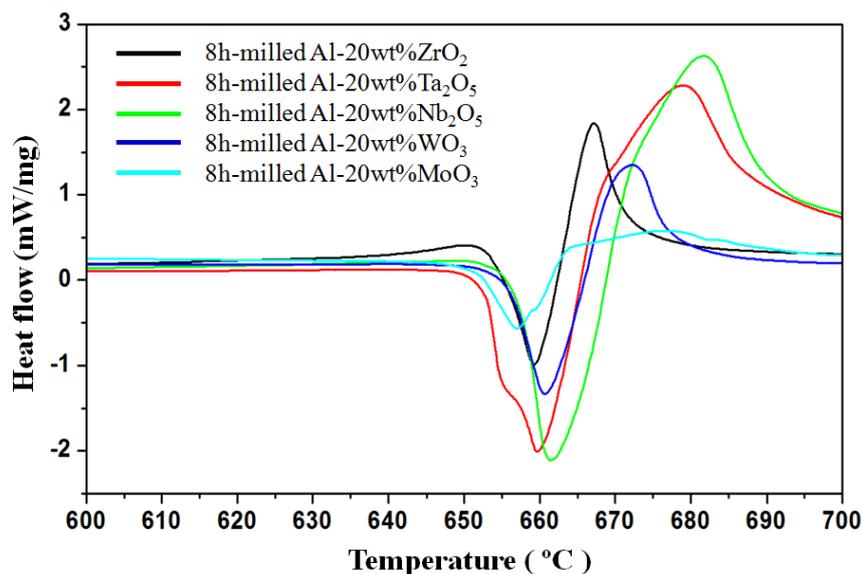


Fig.4. DSC curves of 8h-milled Al/MO powders.

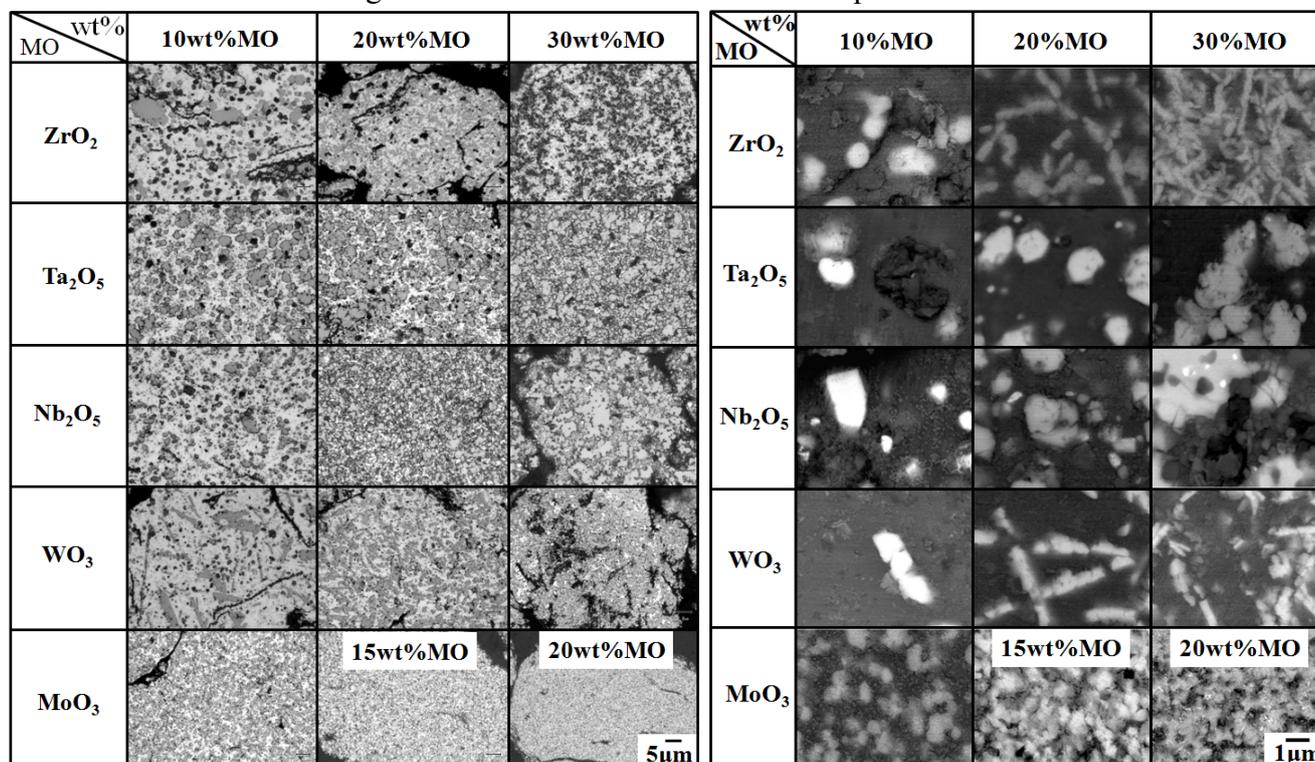
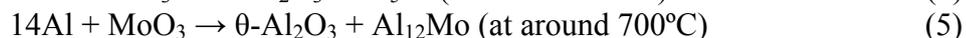
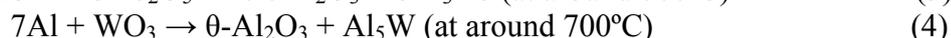
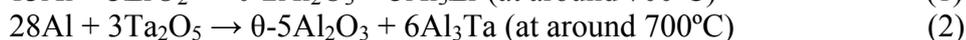
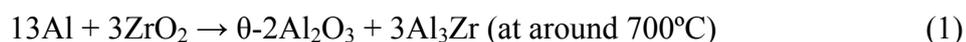


Fig.5. OM(left) and FE-SEM dark field images(right) of the sintered specimens using 8h-milled Al/MO preforms at 700°C for 12h in a tube furnace.

The microstructures of sintered specimens were measured by OM and FE-SEM and are shown in Fig.5. The resultants of the Al/MoO<sub>3</sub> specimens were homogeneously distributed on the Al matrix even when it sintered at 700°C for a long period. However, the others are coarsening during sintering and have irregular shapes of the resultants. The white part on the FE-SEM dark field images representing the intermetallic compounds have irregular shapes due to the different structures of the each intermetallic compounds.

The in-situ reaction equations derived from XRD are as follows.



The  $\theta\text{-Al}_2\text{O}_3$  particulates and IMC are coexisted in the Al matrix with the different shape and different size. Moreover, the distribution of  $\theta\text{-Al}_2\text{O}_3$  and IMC are irregular. The shape of resultants is influenced by the state of the embedded MOs. The sintered specimens using a milled Al/MoO<sub>3</sub> powders that have a lot of embedded MoO<sub>3</sub> with nano level have more refined IMC than the others. The refined MOs embedded in the Al matrix can be easily reacted with Al during sintering. It is also easy to make resultants more refined.

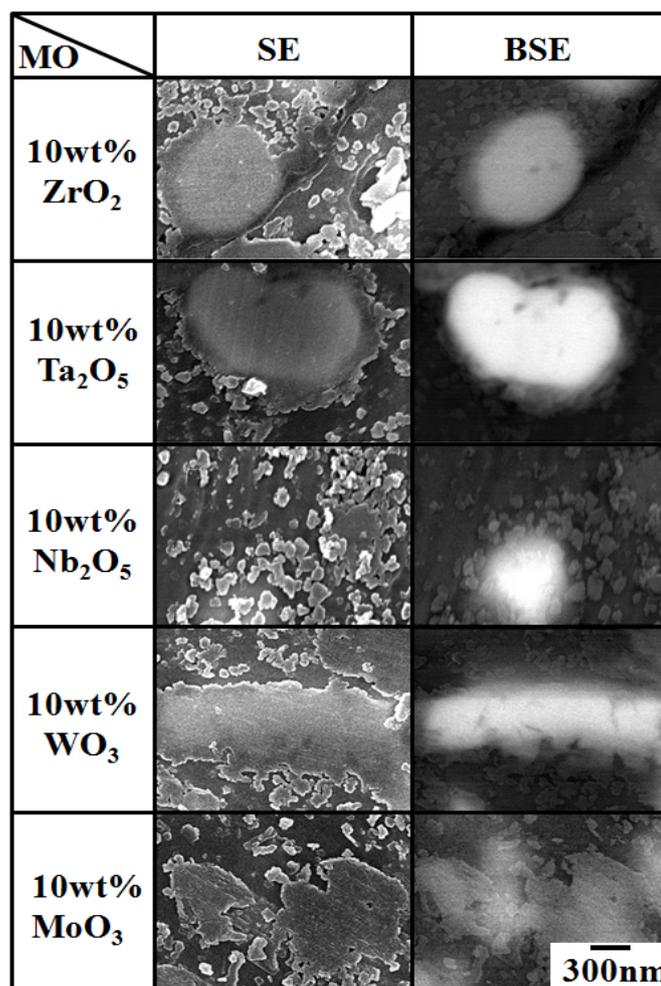


Fig.6. FE-SEM images of the sintered specimens with high magnification at 700°C for 12h.

Fig.6 shows the magnified FE-SEM images of the sintered preforms at 700°C for 12h. Nano sized  $\theta$ -Al<sub>2</sub>O<sub>3</sub> particles were preferentially located near the intermetallic compounds. It seems that the nano sized  $\theta$ -Al<sub>2</sub>O<sub>3</sub> particles were spontaneously departing from the interpenetrated microstructure of the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> during sintering. The in-situ reaction is almost completed by the sintering at 700°C for 12h. But, the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> could transform into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with nano or submicron size when it is exposed over 700°C for a long period.

#### 4. Conclusion

The fully embedded MO particles in the Al matrix powder have been successfully fabricated using planetary ball milling. The milled Al/MO powders have a number of diffusion couples without pores, cracks and by-products in the interface between the Al matrix powder and embedded MO particles after milling. The in-situ reaction does not occur during milling. The in-situ reaction mainly occurs between the liquid state of Al and the solid state of the embedded MO particles at around 700°C. The reaction rate is mainly influenced by the size of the embedded MO particles. The  $\theta$ -Al<sub>2</sub>O<sub>3</sub> and IMCs were successfully formed by the in-situ reaction. Nano sized  $\theta$ -Al<sub>2</sub>O<sub>3</sub> particles and interpenetrated microstructure of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> were located near the IMC.

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