

Preparation of ultrafine TiC, MgAl₂O₄ and AlON composite powder using chemical furnace

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AlON and TiC have good corrosion properties in special refractories such as for trough refractories, submerged nozzles and sliding gate nozzles, but the cost of producing these materials is still higher than oxide refractories. Combustion reactions are performed on samples composed of carbon black, titanium, titanium oxide, Al, MgAl and aluminum dross powders by use of a self propagation high temperature synthesis (SHS) process. A chemical furnace is employed for SHS reactions between substances with a high heat of formation of the final product such as in the titanium-carbon system. The TiC and MgAl₂O₄ composite particles are prepared by the thermite reaction of TiO₂, Al and MgAl alloy and carbon black. The phases are characterized by X-ray diffraction. The microstructure and chemical composition are studied by scanning electron microscopy and XRF, respectively.

Key words: Chemical furnace, SHS, Thermite reaction, TiC, MgAl₂O₄ and AlON composite particles.

Introduction

In every metallurgical situation where molten metal is covered by a silicate slag, there will be contact between the molten metal, or slag and the refractory process vessel lining. The contact will eventually lead to a corrosive reaction with the refractory. The alumina composition of a refractory nozzle is more easily corroded than that of non-oxide refractory materials such as borides, nitrides, carbides and silicides. In some cases, the combinations among oxide and non-oxide materials are suitable for high performance applications. Applications of feasibility demonstrations for high performance of non-oxide refractories have made considerable progress. TiC and aluminum oxinitride (AlON) have been attractive as high performance refractories because they show excellent properties such as high melting point, hardness values and excellent corrosion resistance against molten metal and slags.

Many researchers have tested these materials for use as lining materials in the iron and steel making process, and also as a trough refractory, [1] for submerged nozzles and sliding gate nozzles to improve their resistance to slag and steel corrosion. From this point-of-view, thermal spalling of refractories for continuous casting such as immersion nozzles must be an especially large problem from the view point of reliable operation. Some results show that refractories with AlON and TiC improve their resistance to slag and steel corrosion [2]. Thus AlON and TiC have good properties in special refractories, but the production cost of these materials is still higher than oxide refractories.

Therefore a very unique process must be invented to become cost effective.

The self propagation high temperature synthesis (SHS) process is a very promising method to cut down the cost for fabricating high temperature materials from the energy point-of-view. Once the materials are ignited, a combustion wave propagates itself from one side to the opposite one without any other supply of energy. Many research articles, related to this topic, are focused on the morphological and micro-structural control such as of the grain size and particle shape [3-5]. Among these studies, the synthesis of nanomaterials becomes a particularly promising center of interest [6-9]. Nevertheless, for SHS to be used safely in industry and to synthesize nanomaterials with controlled properties, the formation of nanostructures have to be precisely understood.

In this study, a chemical furnace is employed for self propagation high temperature synthesis (SHS) using Ti and C, and a nano-sized commercial TiO₂ powder, MgAl alloy, and carbon black are used to form a nano-sized TiC powder using the thermite reaction. The exothermic reaction will be described to find the optimum conditions for fabricating nano-sized TiC in a mixture of the thermite reaction and an AlON solid solution in a chemical furnace.

Experimental Procedures

Combustion reactions were performed on samples composed of carbon black (Korea carbon black), titanium (Aldrich), titanium oxide (Nano Co.), Al (Aldrich), MgAl and aluminum dross powders by use of a chemical furnace method. The commercial carbon black and titanium were used to supply the heat (the chemical furnace) to enhance the thermite reaction. The nano-sized commercial TiO₂

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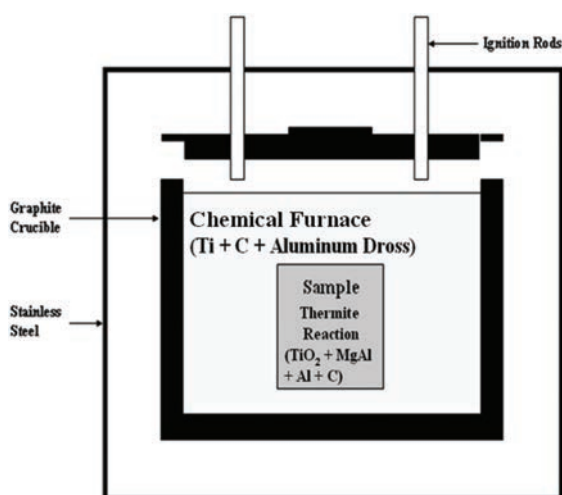


Fig. 1. Schematic view of the chemical furnace.

powder, MgAl, Al and carbon black were used to synthesis ultrafine TiC. The aluminum dross contains alumina, aluminum nitride and a small amount of aluminum. The raw materials were mixed according to the formulations in a ball mill for 24 hours and then dried at room temperature. The mole ratio of Ti and C for the chemical furnace was 1 : 1, and MgAl, aluminum, TiO₂ and C were 1 : 1 : 2 : 1 for the thermite reaction.

The particle size of titanium was changed from 10 to 100 μm to investigate the temperature in the chemical furnace. The mixture for the thermite reaction was uniaxially pressed to form a compact with a relative density of 47% under a pressure of 100 MPa. The green compact was then embedded in the chemical furnace as shown in Fig. 1. The aluminum dross with a diameter of 0.5 μm was used as a dilution agent. The graphite electrodes were connected to a welding transformer which can supply 50-150A current at 100 V. The vessel was safety grounded. The combustion-synthesized products were characterized by X-ray diffraction. The microstructures were studied by scanning electron microscopy. Elements in the aluminum dross were, before and after the treatment in the chemical furnace, analyzed by XRF.

Results and Discussion

Chemical furnace

The method of preheating and creating a thermite reaction involves the use of a chemical furnace releasing energy due to a thermal explosion or an SHS reaction between substances with a high heat of formation of the final product such as in the titanium-carbon system. The heating temperature may be determined by the thermo-physical properties of materials [10]. In this study, the chemical furnace was prepared by self propagation high temperature synthesis (SHS) using Ti and C. In SHS the high exothermicity of the reaction between Ti and C

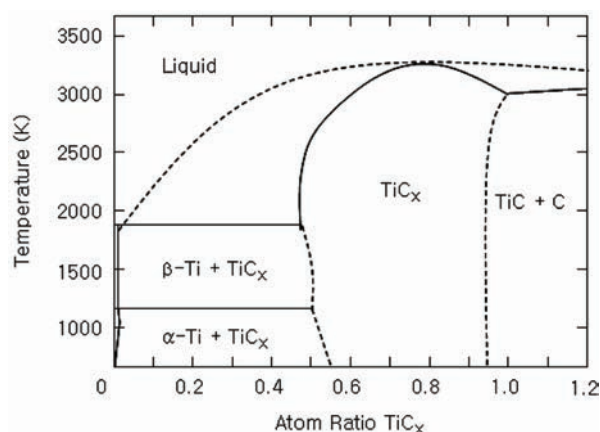
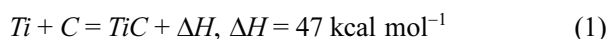


Fig. 2. The titanium and carbon phase diagram.

is exploited to our advantage. The adiabatic temperature T_{ad} of equation (1) has been calculated to be 3,210 K and the melting point of TiC may be considered as the same temperature. Titanium carbide, TiC_x, exists as a homogeneous phase within the limits $0.47 < x < 1.0$. There is some uncertainty concerning the existence of a two-phase mixture of titanium and TiC [11] as shown in Fig. 2. Depending on the composition, titanium carbide melts over a range 1,918 to 3,210 K, the highest temperature corresponding to the composition with $x = 1.0$. Therefore the value of $x = 1.0$ in this experiment is employed to support the maximum heat for the chemical furnace.

Solid-liquid reactions are common in the SHS of several silicides, carbides and borides. In the case of carbides and borides, the metallic element is in the molten condition at T_{ad} , while the formation of carbide, titanium is in the molten condition. The mechanism for the formation of TiC, which is typical of a solid-liquid reaction, has been extensively studied [12-17] and then established by considering that the melting of titanium must precede the combustion reaction. In recent articles by Khina et al. [18] and Locci et al. [19], the validity of theoretical models of TiC nucleation and TiC growth mechanisms have been checked. The real temperature can be varied by control of the processing parameters such as stoichiometric ratio, sample diameter, green density and particle size even though the adiabatic temperature is calculated to be 3,210 K.

The ignition propagation will be very restricted when the particle size of titanium is above 100 μm in the solid and liquid system [20]. This is the reason why the particle size was changed from 10 to 100 μm at the same relative green density of 47%. The temperature profile of this experiment was now changed by the variation of particle size of the titanium as shown in Fig. 3. The measured temperature in the system decreased from 2,650 $^{\circ}\text{C}$ to 2,360 $^{\circ}\text{C}$.

The temperature at a size of 50 μm is so high enough to enhance the activity of the thermite reaction of equation (1). Therefore the combustion temperature must be lowered by adding a dilution agent to the mixture of Ti and C.

The temperature is also decreased by increasing the

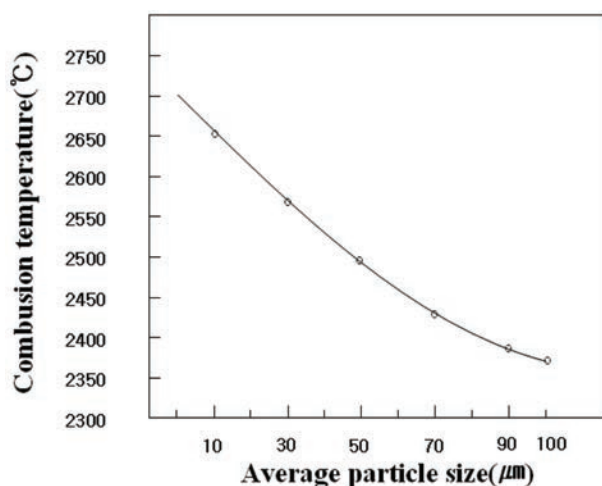


Fig. 3. The titanium particle size effect on the combustion temperature of the Ti and C system.

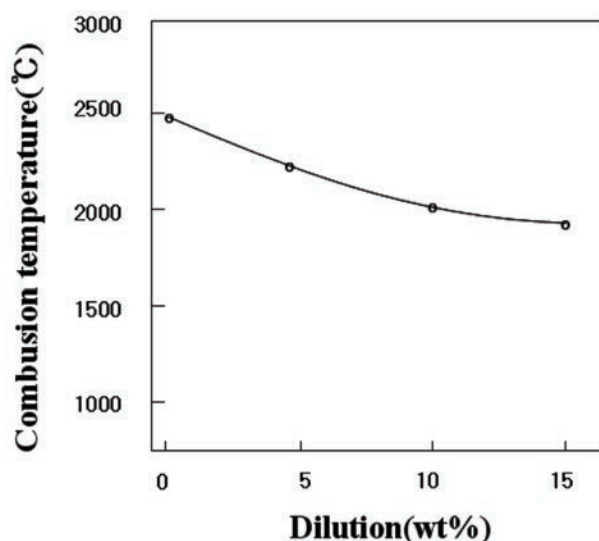


Fig. 4. The dilution effect on the combustion temperature of the Ti and C system.

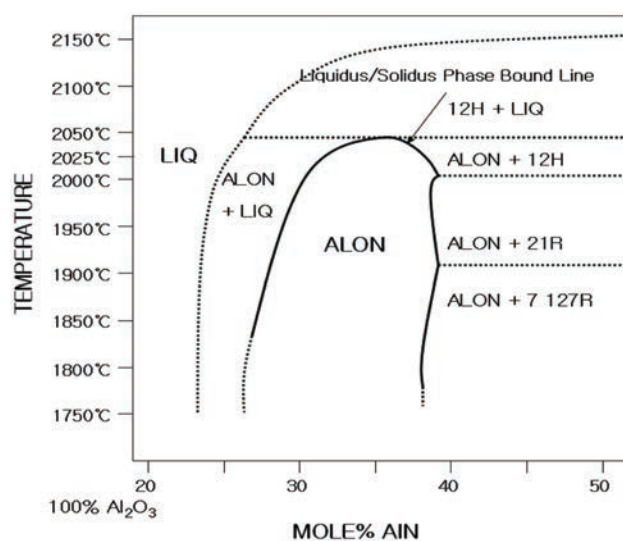


Fig. 5. The Al_2O_3 and AlN phase diagram.

aluminum dross content with a diameter of $0.5\ \mu\text{m}$ as the dilution agent as shown Fig. 4. The temperature now reached is $2,000\ ^\circ\text{C}$ when 10% aluminum dross is added. This temperature is also enough to change the phase of the aluminum dross into ALON in the mixture of Ti and C, and also initiate ignition of the mixture of TiO_2 and MgAl and Al for the thermite reaction. The ALON phase appeared in this condition but there AlN and alumina were still present after the heat treatment. ALON is a solid solution of alumina and aluminum nitride as known and many researchers have found a synthesis method. ALON solid solution can exist by adding more than 25% of AlN to Al_2O_3 at around $2,000\ ^\circ\text{C}$ as shown Fig. 5. The partial pressure of oxygen in equilibrium with ALON at $1,800\ ^\circ\text{C}$ is very low according to thermodynamic calculations [21, 22]. This means that the thermite reaction may not have sufficient time to form the ALON solid solution because combustion proceeds very rapidly.

The combustion reactions of metallic aluminum and corundum powder mixtures from 15% Al-85% Al_2O_3 to 50% Al-50% Al_2O_3 were performed in a nitrogen atmosphere by Zientara et al. [23]. It was observed that pre-heating of the Al- Al_2O_3 mixtures containing more than 15 wt.% Al in a nitrogen atmosphere involved a strong exothermic SHS reaction accompanied by bright radiation and rapid increase of temperature. This means that aluminum dross in this experiment can be regarded as a dilution agent because aluminum dross contains 7% aluminum. With this content, it was expected that the exothermic SHS reaction can not occur spontaneously in the Ti and C mixture.

From these considerations, ALON can be produced by controlling the temperature in the chemical furnace using aluminum dross as a dilution agent.

Thermite reaction

The thermite reaction was first described by Goldschmid as an exothermic reaction involving reduction of iron oxides with aluminum. The thermite reaction is used to describe a much broader class of reactions and can be defined as an exothermic reaction which involves a metal reacting with a metallic or a non-metallic oxide to form a more stable oxide and the corresponding metal or non-metal of the reactant oxide [24]. Most metals have a higher reducing tendency than the non-metal reducing agents considering thermodynamics. Aluminum is more commonly used because it has a comparable reducing agency. The heat released from the reaction heats up the product to the adiabatic temperature which can be calculated from the enthalpy of the reaction and the heat capacity of the product phases with the assumption of adiabatic conditions. A large number of oxides can be reduced by aluminum, which may cause an increase in the temperature up to $2,200\ ^\circ\text{C}$. In many cases, the adiabatic temperature exceeds the melting points of both the product phases. In the case of a TiO_2 and aluminum mixture, the adiabatic temperature of their reaction can not reach the melting point of the phases. This is reason why magnesium was first considered as

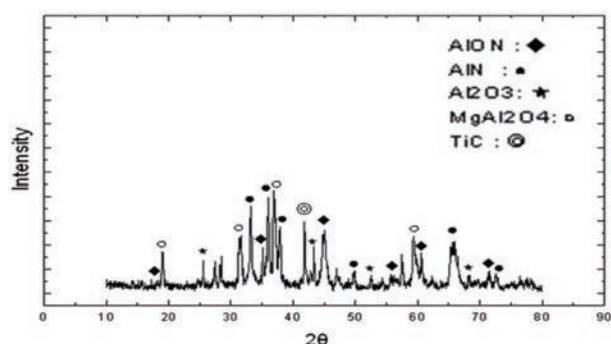
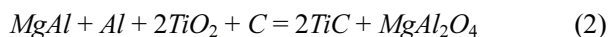


Fig. 6. X-ray diffraction pattern of AlON, MgAl₂O₄, TiC by SHS.

a strong reducing agent because the reaction temperature is higher than that of aluminum. In some cases, where safety is a consideration case needs to be taken because the reaction with magnesium is very explosive compared with that with aluminum additions. This is the reason why this experiment employs a magnesium aluminum alloy to reduce the TiO₂. In this study, the nano-sized commercial TiO₂ powder and carbon black were used to form a nano-scaled TiC powder by use of a thermite reaction. The thermite reaction of these experiments is described by the equation (2):



To form the TiC in this reaction, the reaction temperature does not exceed the melting temperature of Ti. Therefore some extra energy must be supplied to enhance the reaction temperature. That is the reason why the concept of a chemical furnace is now employed for this system. The chemical furnace is prepared by self propagation high temperature synthesis (SHS) using Ti and C. The adiabatic temperature T_{ad} of equation (1) has been calculated to be 3210 K [25]. The phases of TiC and MgAl₂O₄ are created by the thermite reaction of the TiO₂, MgAl, Al, and C mixture as shown Fig. 6. As in the SHS process, melting point of Ti precedes the combustion reaction as required by this mechanism. But this melting may be confined to only a limited thickness on the particle surfaces when the particle size is increased, due to the high thermal mass of larger particles. This leads to a reduction in the combustion reaction, resulting in a lower combustion temperature. This is why nano-sized TiO₂ and C were selected to enhance the activity of the thermite ignition. The nano-scaled particles in the final products of the thermite reaction are shown as Fig. 7. Owing to the availability of additional heat from the chemical furnace, reactants may be in the molten state during combustion. It is expected that the final particles will be larger with aggregates at this high temperature. But the particles in the agglomerates are very small and easily ground into nano-sized range because the carbon black separates the particles such as TiC and MgAl₂O₄ during the thermite reaction. From these results, it is expected that many nano-sized carbides, borides and silicides may be synthesized by this cost effective way.

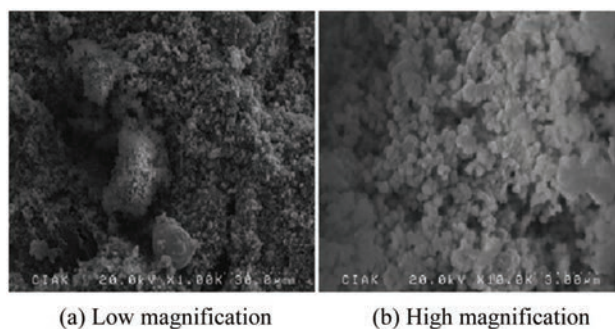


Fig. 7. Scanning electron micrographs of AlON, MgAl₂O₄, TiC composite powder.

Aluminum dross always contains many elements including the alkali metal in forms such as K₂O, Na₂O. The alkali metal oxides are very corrosive to refractories. These elements were, before and after the heat treatment, analyzed to investigate possibility of lowering the contamination level because they can be easily eliminated at a high temperature. The results show that the contaminate levels in aluminum dross were reduced markedly.

Conclusions

1. The temperature profile in this experiment was changed from 2,650 °C to 2,360 °C by a variation of the particle size of the titanium.
2. The temperature was changed to 2,000 °C by increasing the aluminum dross content with 0.5 μm diameter as the dilution agent up to 10%.
3. AlON can be produced by controlling the temperature in the chemical furnace using aluminum dross as a dilution agent.
4. The phases of TiC and MgAl₂O₄ appeared by the thermite reaction of TiO₂, MgAl and Al, and C mixture.

Acknowledgement

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