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Reaction path in the aluminothermic reduction nitridation reaction to synthesize $MgAl_2O_4$/TiN composite

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Abstract

X-ray diffraction (XRD), differential thermogravimetric analysis (DTA) and differential scanning calorimetric analysis (DSC) were performed on 8Al–TiO_2–xMgO mixtures and compacted sample treated in nitridation furnace, to foster an understanding of the reaction path involved in the $MgAl_2O_4$/TiN composite-forming aluminothermic reduction and nitridation. The results show that: (a) when N_2 gas is apt to diffuse in green body, first, aluminum powders react with N_2 to yield AlN, replacement reaction between AlN and TiO_2 occurs, and then TiN and Al_2O_3 are produced; (b) when N_2 gas diffusion is difficult, Ti element formed by Al reduction of TiO_2 reacts with N_2 to form TiN. The results also show that MgO facilitates TiN formation by removal of intermediates.

Keywords: Reaction path; $MgAl_2O_4$/TiN composite; Aluminothermic reduction

1. Introduction

TiN has a high melting point, high hardness (1800–2100 kg/mm^2) and good corrosion resistance to acidic slag and alkaline slag in CO and N_2 atmospheres. TiN based composite ceramics, such as Al_2O_3–TiN [1], TiN/Al–O–N [2,3], AlN–TiN [4], Si_3N_4–TiN [5], TiB_2–TiN [6], show excellent performances. Study on phase relationship of Ti–Al–O–N showed that the materials in the Ti–Al–O–N system would have good potential for use as high-temperature engineering ceramics [7]. As we all know, $MgAl_2O_4$, which has a high melting point, good chemical stability, and good resistance to alkaline slag and has better thermal shock resistance than Al_2O_3 and MgO, is a super-quality refractory. The $MgAl_2O_4$/TiN composites may have good properties and potential application. $MgAl_2O_4$/TiN composite ceramics were synthesized by aluminothermic reduction and nitridation [8]. But reaction path in the aluminothermic nitridation reduction reaction has not been apparently reported up to now. The present study deals primarily with reaction path in the synthesis of $MgAl_2O_4$/TiN composite ceramics from aluminothermic reduction.

2. Experimental procedure

Commercial aluminum powder (Al > 98%, <180 meshes), anatase-form TiO_2 (TiO_2 > 98.5%,) and MgO (chemical purity), were used for the preparation of $MgAl_2O_4$/TiN composite.

8Al–TiO_2–xMgO mixtures of were weighed according to the stoichiometry of reactants in Eq. (1), and then thoroughly dry-mixed in ball mill to ensure homogeneity. The mixtures were die-pressed at pressure of 200 MPa to form cylindrical green compacts 20 mm in diameter and 20 mm in thickness. The green compacts were treated in a nitridation furnace at 1000 °C for 3 h.

$$8Al + 6TiO_2 + xMgO + 3N_2 = xMgO \cdot Al_2O_3 + 6TiN + (4 - x)Al_2O_3 \quad (1)$$

The phases present in its composites were investigated by XRD with X'PERT MPD PRO attached by X'celerator (Philips) using Ni-filtered, Cu Kα under the following

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condition: scanning speed of 2°/min, temperature of 16 °C. DTG and DSC were also carried out on mixture 8Al–6TiO_2–xMgO mixtures at heating rate of 10 °C/min in N_2 atmosphere (TG-DSC from NETZSCH STA 409C, German and LABSYS TG-DSC1600 from France). Phase analysis of the 8Al–TiO_2–xMgO mixture after DTG and DSC at given temperature was examined by XRD.

3. Results and discussion

DTG and DSC measurements were performed up to 1500 °C. The DTG and DSC results for the 8Al–TiO_2–xMgO mixtures are shown in Fig. 1. Each DSC curve of the 8Al–TiO_2–xMgO mixture ($x > 0$) shows two endothermic peaks at ~370 and ~657 °C, respectively. But DSC curve of the 8Al–TiO_2 mixture exhibits no endothermic peak at ~370 °C, weight gain or loss at the same temperature is little. The peak at ~370 °C may be attributed to decomposition of a small amount of $Mg(OH)_2$ presented in MgO powders and the peak at about 657 °C is due to the melting of aluminum. Below 1000 °C or so, no high peaks can be observed in DTG curve, which indicates that no weight gain occurred and no/or little N_2 gas reacts with aluminum, and titanium formation by reduction of TiO_2. Aluminothermic reduction and nitridation reaction can be responsible for the high and sharp DTG and DSC peaks at ~1000 and 1400 °C, except for those endothermic peaks at ~370 and ~657 °C, the slow DSC releasing heat and weight gain of DTG curves in the temperature range of 200–1000 °C indicate that aluminothermic reduction and nitridation did not happen in a magnificent manner. Up to about 1000 °C, the rapid DSC releasing heat and high weight gain of DTG curves prove that aluminothermic reaction and nitridation begin to happen quickly.

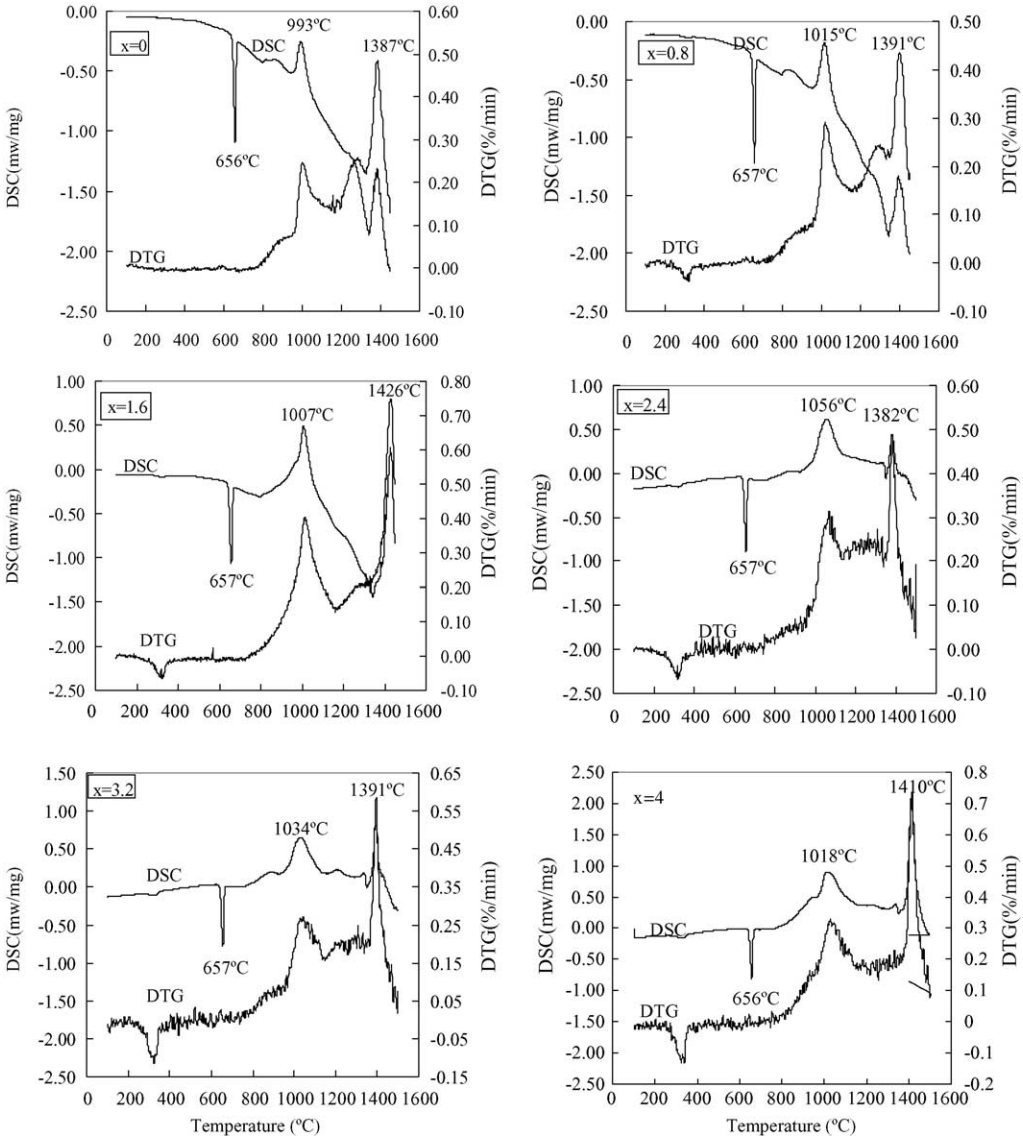

Fig. 1. DSC and DTG patterns of mixture 8Al–6TiO_2–xMgO with different MgO content, where x is 0; 0.8; 1.6; 2.4; 3.2; 4.0, respectively.

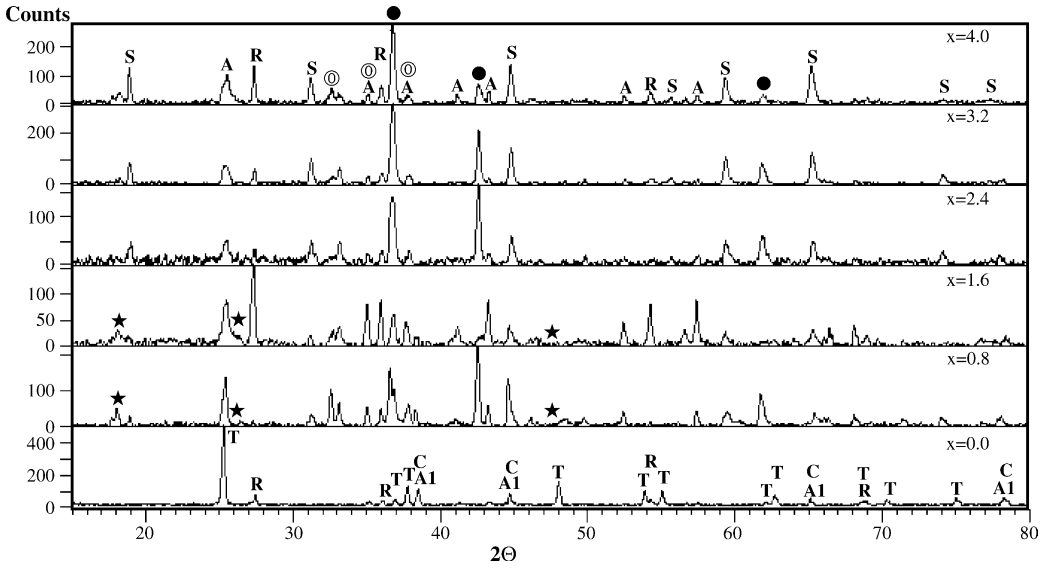

Fig. 2. XRD patterns of 8Al–6TiO_2–*x*MgO mixtures with different MgO/Al after DTG and DSC. A: α-Al_2O_3, S: $MgAl_2O_4$, ◎: H-AlN, •: TiN, T: $Ti_{0.72}O_2$, C: C-AlN, Al: alumimun, ★: Ti_3O_5.

XRD results for the 8Al–TiO_2–*x*MgO mixtures after DSC and DTG at 1500 °C are shown in Fig. 2. $Ti_{0.72}O_2$ (anatase-form), cubic AlN (C-AlN) or remnant Al and rutile can be observed in XRD pattern for the 8Al–TiO_2 mixtures, but α-Al_2O_3 and TiN cannot be detected, because the diffraction peaks of C-AlN and aluminum are too similar to be distinguished from each other, C-AlN and remnant Al can not be identified in XRD pattern. When $x = 0.8$ or 1.6, α-Al_2O_3, TiN, $MgAl_2O_4$ and a small amount of hexagonal AlN (H-AlN) and Ti_3O_5 were found in XRD pattern. When $x = 2.4$–4.0, $MgAl_2O_4$, TiN, α-Al_2O_3, rutile and a little H-AlN are identified (shown in Fig. 2). The presence of α-Al_2O_3, TiN and $MgAl_2O_4$ reveals that aluminothermic reduction and nitridation reaction occur, this also indicates that MgO can improve aluminothermic reduction and nitridation reaction.

In order to investigate reaction path further, XRD analysis was performed on the 8Al–6TiO_2–2.4MgO mixtures after DTG and DSC at 1056 and 1382 °C (weight gain and exothermic peak at DTG and DSC curve) (shown in Fig. 3). At 1056 °C, anatase, rutile, $MgTi_2O_5$, MgO, $MgTiO_3$ and C-AlN and/or aluminum were found in XRD pattern, weight gain peaks on DTG curve indicate that nitridation reaction has happened, nitridation reaction products should be TiN,

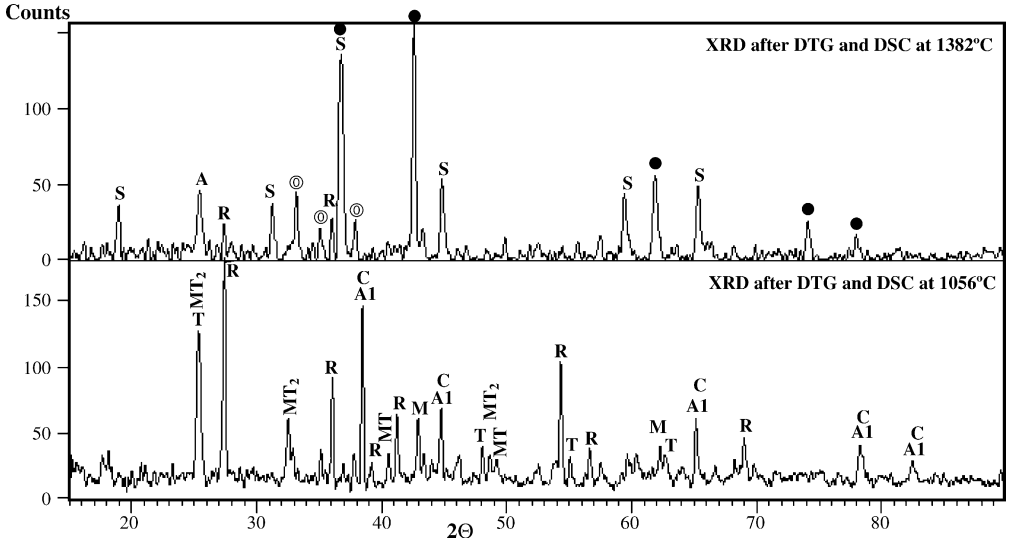

Fig. 3. XRD patterns of 8Al–6TiO_2–2.4MgO mixtures after DSC and DTG at 1382 and 1056 °C, respectively. A: α-Al_2O_3, S: $MgAl_2O_4$, ◎: H-AlN, •: TiN, MT_2: $MgTi_2O_5$, R: rutile, T: anatase, Al: aluminium, MT: $MgTiO_3$, C: C-AlN.

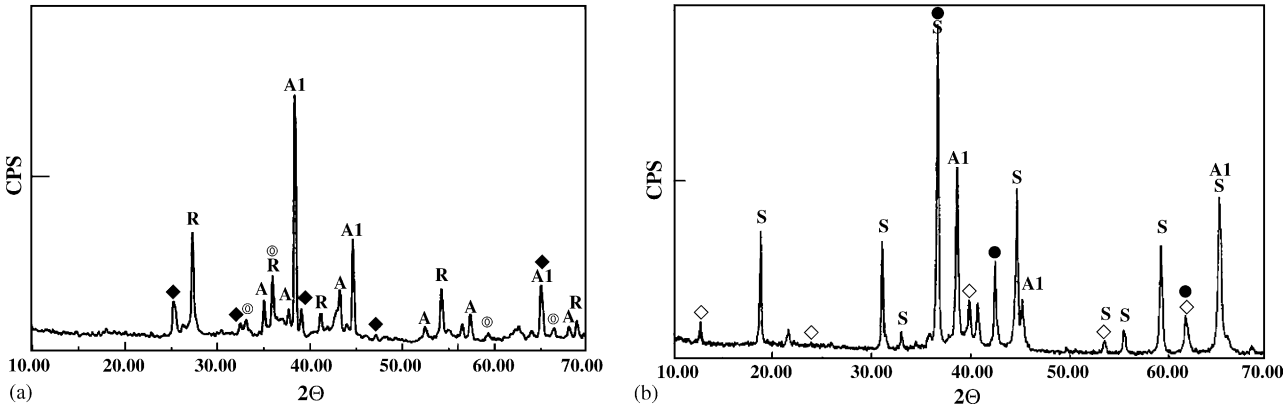

Fig. 4. XRD patterns of compacted sample treated in nitrogen at 1000 °C for 3 h. (a) Compacted sample from 8Al–6TiO_2 mixtures; (b) compacted sample from 8Al–6TiO_2–4MgO mixtures. Al: aluminum, R: rutile, S: $MgAl_2O_4$, •: TiN, A: α-Al_2O_3, ◎: H-AlN, ◆: Al_3Ti, ◇: Ti_2AlN.

AlN or Mg_3N_2, but TiN and Mg_3N_2 were not detected by XRD, so we conclude that C-AlN forms in nitridation reaction process. At this temperature, main possible reaction is written as follows:

$$2Al_{(l)} + N_{2(g)} = 2AlN_{(s)} \quad (2)$$

At 1382 °C, TiN, $MgAl_2O_4$, α-Al_2O_3, rutile and H-AlN were identified by XRD (shown in Fig. 3). Nitridation reactions determined by weight gain peaks at this temperature are listed below:

$$2Ti_{(s)} + N_{2(g)} = 2TiN_{(s)} \quad (3)$$

$$4AlN_{(s)} + 4TiO_{2(s)} = 4TiN_{(s)} + 2Al_2O_{3(s)} + O_{2(g)} \quad (4)$$

$$4AlN_{(s)} + 3TiO_{2(s)} = 3TiN_{(s)} + 2Al_2O_{3(s)} + 1/2N_{2(g)} \quad (5)$$

TiN are possible to be produced by two main reactions, one reaction is that element Ti reduced by Al from TiO_2 reacts with nitrogen to produce TiN (shown in Eq. (3)); the other reaction is replacement reaction between AlN and TiO_2 (shown in Eqs. (4) and (5)), this is consistent with the former researches [9].

Compared with phase analysis of the 8Al–6TiO_2–xMgO mixtures, XRD were performed on compacted sample obtained from 8Al–6TiO_2 and 8Al–6TiO_2–4MgO mixtures respectively (shown in Fig. 4a and b). Al, H-AlN, rutile, corundum and Al_3Ti alloy were found in XRD pattern of sample obtained from the 8Al–6TiO_2 mixtures at 1000 °C for 3 h in N_2 gas (shown in Fig. 4a). Al_3Ti alloy was formed between Al and Ti element formed by Al reduction of TiO_2. The occurrence of Al and Al_3Ti residue in the presence of N_2 gas at 1000 °C indicates that nitridation reaction was carried out incompletely due to inadequate N_2 gas diffusion in the compacted sample, in comparison with N_2 gas diffusion in the mixtures.

As for compacted 8Al–6TiO_2–4MgO samples, $MgAl_2O_4$, TiN, Al and Ti_2AlN were detected by XRD, as shown in Fig. 4b. The XRD result also shows that MgO can improve aluminothermic reduction nitridation reaction and accelerate formation of TiN. The overall reaction process can be divided into two stages: the first stage is formation of intermediate species, such as AlN, Ti_2AlN, Al_xTi_y alloy; AlN is formed in the presence of enough N_2 gas, Al_xTi_y alloy or Ti_2AlN was produced under inadequate N_2 condition. The second stage is formation of TiN, TiN can be obtained from replacement reaction between AlN and TiO_2 or from direct nitridation of Ti element

4. Conclusions

The investigation has shown that: (a) when N_2 gas can diffuse easily in green body, first, aluminum powders react with N_2 to yield AlN, replacement reaction between AlN and TiO_2 occurs, and then TiN and Al_2O_3 are produced; (b) when N_2 gas diffusion is difficult, Ti element formed by Al reduction of TiO_2 reacts with N_2 to form TiN. Addition of MgO facilitates TiN formation by removal of intermediate species.

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