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Thermochimica Acta 276 (1996) 123–129

thermochimica
acta

TG–DTA–MS study of self-ignition in self-propagating high-temperature synthesis of mechanically activated Al–C powder mixtures

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Received 12 July 1995; accepted 23 September 1995

Abstract

When mechanically activated Al–C powder mixtures were heated in flowing nitrogen containing a small amount of oxygen, or in static air, the exothermic reaction due to the oxidation of the disordered carbon, formed by grinding, was initiated at around 100°C, and was followed by the oxidation of Al metal. This result verified that the disordered carbon served as an igniter for the self-propagating high-temperature synthesis reaction induced by mechanical activation of Al–C powder mixtures.

Keywords: TG–DTA–MS; Self-propagating high-temperature synthesis (SHS); Mechanical activation; Grinding; Al–C mixtures

1. Introduction

Mechanical activation or mechanosynthesis is reported to be a potential process for the production of new materials, particularly advanced ceramics such as metal nitrides and carbides [1, 2]. In addition, self-propagating high-temperature synthesis (SHS) has been noted as a novel method for producing advanced inorganic materials [3]. In this process, the reaction is initiated by ignition and propagated spontaneously through reactant mixtures accompanied by high formation energies.

We have recently developed a unique technique combining mechanical activation by grinding and SHS. This technique has been successfully applied to the synthesis of

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aluminum nitride in air [4]. Powders of aluminum metal and natural graphite mixed in various molar ratios were ground in a planetary ball mill. When the mechanically activated mixtures were exposed to air, the exothermic reactions spontaneously occurred in two successive steps: first the exothermic reaction occurred at several points, evolving red heat (step 1) and propagated toward neighboring regions; second a violent second exothermic reaction occurred, evolving white heat (step 2). The temperature attained in steps 1 and 2 were estimated by measurement with an optical pyrometer to be about 800 and 1800 °C, respectively. The main product was aluminum carbide in step 1 and aluminum nitride and carbide in step 2. Mechanical grinding of the powder mixture of Al and C was found to lead to an activated state in the following manner: decrease in particle size of Al and C, coating of Al particles with disordered carbon; formation of new active surface; store of strain energy and increased temperature. On the basis of these results, a possible mechanism of the SHS reaction was proposed.

The purpose of the present study was to verify the self-ignition reaction in the SHS process by investigation of the thermal behavior of the mechanically activated Al–C powder mixtures using thermogravimetry (TG), differential thermal analysis (DTA), and mass spectrometry (MS).

2. Experimental procedures

The procedures of mechanical activation of Al–C powder mixtures are outlined only briefly, because the details have been described elsewhere [4]. The powders of aluminum metal (particle size varying between 61 and 104 μm) and natural graphite (mean flake size 5 μm) mixed in molar ratios of Al : C = 5.75 : 1.25 and 4 : 3 were ground in air for 90 min in a P-7 planetary ball mill (Fritsch). A 25 ml jar and four balls of 12 mm diameter of tungsten carbide were used. The temperature of the mixtures reached about 70 °C after grinding for 90 min. When the mechanically activated mixtures were exposed to air immediately after grinding, they ignited instantly. Therefore, in order to avoid ignition the ground mixtures were taken out of the jar after the temperature dropped to about room temperature; they were then submitted to TG–DTA–MS.

Simultaneous TG–DTA–MS measurements were performed with a Mac Science 2000 apparatus attached to a gas analysis system (VG QMS Thermolab) in a stream of nitrogen (20 ml min^{-1}) or in static air, at a heating rate of 10 °C min^{-1} . In the former case, before heating, a stream of nitrogen was passed through the TG–DTA–MS apparatus for more than 30 min to displace the air. The weight of samples used was 17.3–21.3 mg. The purity of nitrogen gas was 99.9%.

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku Denki RAD-B using Ni-filtered CuK_α radiation.

3. Results and discussion

Figs. 1(a) and 1(b) show the TG–DTA and MS curves for the mechanically activated Al–C powder mixture (Al : C = 5.75 : 1.25) in nitrogen gas flowing at 20 ml min^{-1} . After

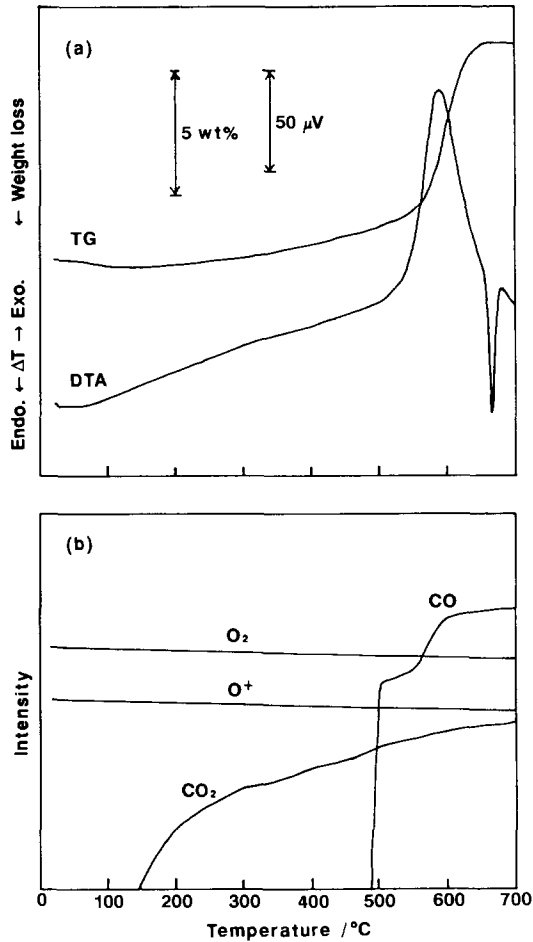


Fig. 1. (a) TG-DTA and (b) MS curves for the Al-C powder mixture (Al:C = 5.75:1.25) ground for 90 min; measurements were made in nitrogen flowing at 20 ml min^{-1} and at a heating rate of $10^\circ\text{C min}^{-1}$.

only 15 min grinding, the intensity of graphite 002 line ($2\theta = 26.3^\circ$) decreased markedly and disappeared completely after 45 min grinding, indicating the formation of disordered carbon caused by the disappearance of ordered stacking of the graphite layers. In contrast, no variation in Al metal lines was observed [4]. In Fig. 1(a), the DTA baseline began to shift to the exothermic side at about 100°C and then a large exothermic and a sharp endothermic peaks appeared at 585 and 665°C , respectively. The corresponding TG curve showed a slight weight decrease at the beginning; this turned to a gradual weight increase at about 300°C , followed by a marked weight gain at about 600°C . The weight gain at 700°C was 8.5 %w/w. X-ray diffraction patterns of

the products obtained at 700°C revealed the presence of unreacted Al metal and the formation of η -Al₂O₃ (Fig. 2(e)). Although all the runs were performed in flowing nitrogen, the presence of oxygen was detected by MS (Fig. 1(b)). Because of this, a stream of high-purity argon (99.9995%, less than 0.2 ppm oxygen), rather than nitrogen, was passed through the TG-DTA-MS apparatus at a rate of 100 ml min⁻¹ before and during heating. It was, however, difficult to replace completely the atmosphere in the apparatus with argon. It was, therefore, considered that the oxygen detected by MS came from the air remaining in the TG-DTA-MS apparatus and oxygen impurity in the nitrogen. The total oxygen content of the flowing nitrogen was estimated to be about 0.4% by calculation based on the weight gain in Fig. 1(a).

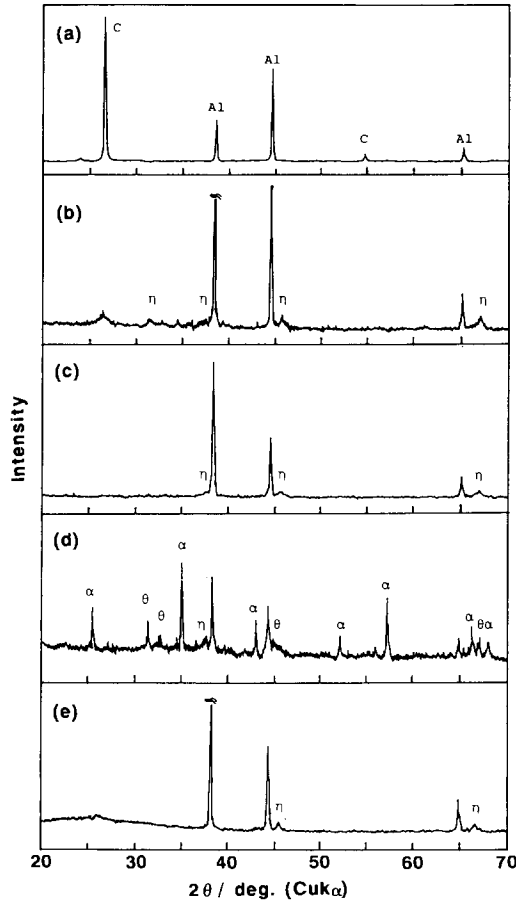


Fig. 2. XRD patterns of the final products obtained in the TG-DTA runs shown in Figs. 1 and 3. (a) the unground Al-C powder mixture (Al:C = 4:3) heated to 900°C (Fig. 3(a)); (b) the ground mixture heated to 800°C (Fig. 3(b)); (c, d) ground mixtures heated to 800 and 1000°C (Fig. 3(c)); (e) the ground mixture (Al:C = 5.75:1.25) heated to 700°C (Fig. 1(a)). Al, Al metal; C, graphite; η , η -Al₂O₃; θ , θ -Al₂O₃; α , α -Al₂O₃.

Furthermore, in the MS curve the release of carbon dioxide and monoxide was observed at temperatures greater than 150 and 480°C, respectively. From the results of Figs. 1(a) and 1(b), it was found that the early exothermic reaction occurring at about 100°C is the formation of carbon dioxide by the oxidation of the disordered carbon formed on the surface of Al particles by grinding, followed by the oxidation of the Al particles revealed after combustion of the carbon covering them. The latter oxidation reaction is reflected in the weight increase in the TG curve at 300°C or above. On further heating, remarkable oxidation of C and Al metal yielded a large exothermic peak and weight increase at 550–650°C, and the unreacted Al metal melted at 665°C. The formation of carbon monoxide at 480°C or above may be attributable

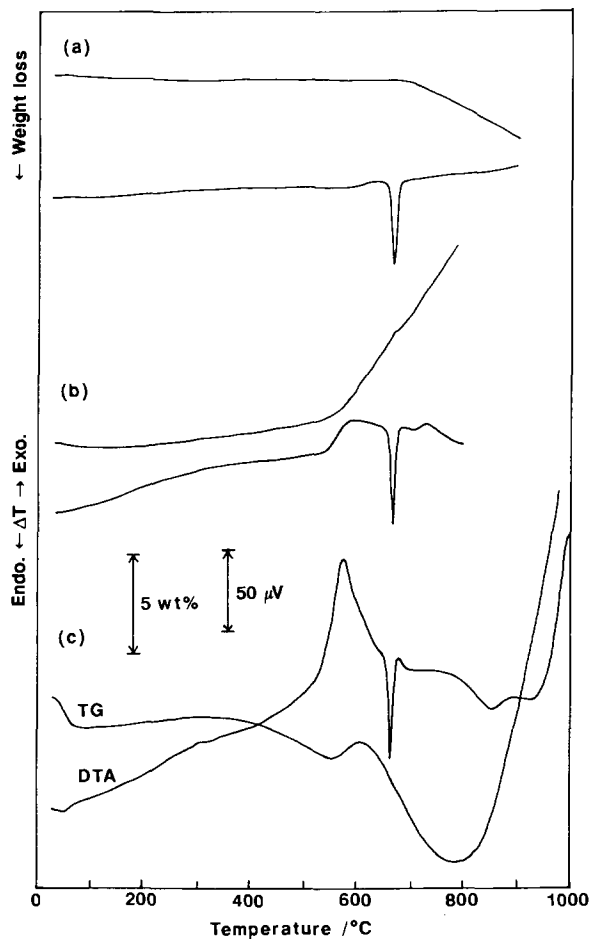


Fig. 3. TG-DTA curves for Al-C powder mixtures (Al:C = 4:3) (a) unground and (b, c) ground for 90 min; measurements were made in flowing nitrogen (a, b) or static air (c).

to an abrupt shortage of oxygen content in the surrounding gas as a result of oxidation of Al metal.

Figs. 3(a)–3(c) show TG–DTA curves for the unground and ground Al–C powder mixtures (Al:C = 4:3) in flowing nitrogen or a static air. The X-ray diffraction patterns of the final products obtained in TG–DTA runs are shown in Fig. 2. In the TG–DTA curves of the unground mixture in flowing nitrogen (Fig. 3(a)), no reaction was observed before the melting of Al metal at 666°C, but a weight decrease of ca. 3 %w/w as a result of the oxidation of the unground graphite was observed between 700 and 900°C. Sharp diffraction lines of Al and C were still apparent from the sample heated to 900°C (Fig. 2(a)). In contrast with this, a marked increase in the reactivity of the ground Al–C powder mixture can be seen in Fig. 3(b). That is, the beginning of an exothermic reaction at 100°C and a weight increase at 300°C is highly analogous to that for the ground Al–C powder mixture (Al:C = 5.75:1.25) shown in Fig. 1(a), though the magnitude of the exothermic peak at around 600°C is different. This indicates that the same reactions occurred in both mixtures. In fact, the X-ray diffraction pattern of the sample heated to 800°C (Fig. 2(b)) showed the presence of unreacted Al metal and η -Al₂O₃, similar to Fig. 2(e). The reason why the exothermic peak at 600°C in Fig. 3(b) is smaller than that in Fig. 1(a) is believed to be because of the smaller Al metal content of the mixture and its less activated state. The minimum grinding time for ignition was 105 min for Al:C = 4:3 and 75 min for Al:C = 5.75:1.25 [4]. On the other hand, TG–DTA curves of the ground mixture in static air showed a drastic change (Fig. 3(c)). The disordered carbon formed by grinding began to oxidize immediately upon heating. Apparent cessation of the weight loss observed between 100 and 350°C may be because of balancing with the weight increase resulting from oxidation of Al metal. On further heating, intense oxidation of C and Al metal occurred at around 600°C. After that, the unreacted Al metal melted at 663°C and was then rapidly oxidized at temperatures greater than 800°C accompanied by a very large weight increase. The X-ray diffraction patterns of the samples obtained at 800 and 1000°C showed the formation of η -Al₂O₃ (Fig. 2(c)), and θ - and α -Al₂O₃ (Fig. 2(d)).

From the above results, it was found that when the mechanically activated Al–C powder mixtures were heated in flowing nitrogen containing a small amount of oxygen or in a static air, the oxidation of the disordered carbon formed by grinding occurred first, followed by oxidation of Al metal. Although oxidation of Al metal in the presence of oxygen is expected, on the basis of thermodynamic data, to occur preferentially, the particles of Al metal are covered by fine particles of the disordered carbon, and hence oxidation is inhibited [4]. The results obtained in the present TG–DTA–MS runs have supported the mechanism in which SHS of mechanically activated Al–C powder mixture was initiated by self-ignition of disordered carbon formed by grinding, as previously discussed [4]. In the TG–DTA–MS runs aluminum oxide was mainly formed, although aluminum carbide was formed in the SHS runs. This difference may be ascribed to the sample mass used, that is, about 20 mg was used for the TG–DTA–MS runs and 8–10 g for the SHS runs. In the former, easy diffusion of oxygen into the bulk of the sample would lead to favorable conditions for the formation of aluminum oxide.

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