Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 263−270
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Mechanism for thermite reactions of aluminum/iron-oxide nanocomposites based on residue analysis

Yi WANG[1,2], Xiao-lan SONG[3], Wei JIANG[1], Guo-dong DENG[1], Xiao-de GUO[1], Hong-ying LIU[1], Feng-sheng LI[1]

1. National Special Superfine Powder Engineering Research Center, Nanjing University of Science and Technology, Nanjing 210094, China;
2. School of Materials Science and Engineering, North University of China, Taiyuan 030051, China;
3. School of Chemical Engineering and Environment, North University of China, Taiyuan 030051, China

Received 16 October 2012; accepted 3 December 2012

Abstract: Sol−gel method was employed to combine Al and iron-oxide to form nanocomposites (nano-Al/xero-Fe_2O_3 and micro-Al/xero-Fe_2O_3). SEM, EDS and XRD analyses were used to characterize the nanocomposites and the results indicated that nano-Al and micro-Al were compactly wrapped by amorphous iron-oxide nanoparticles (about 20 nm), respectively. The iron-oxide showed the mass ratio of Fe to O as similar as that in Fe_2O_3. Thermal analyses were performed on two nanocomposites, and four simple mixtures (nano-Al+xero-Fe_2O_3, nano-Al+micro-Fe_2O_3, micro-Al+xero-Fe_2O_3, and micro-Al+micro-Fe_2O_3) were also analyzed. There were not apparent distinctions in the reactions of thermites fueled by nano-Al. For thermites fueled by micro-Al, the DSC peak temperatures of micro-Al/Xero-Fe_2O_3 were advanced by 68.1 °C and 76.8 °C compared with micro-Al+xero-Fe_2O_3 and micro-Al+micro-Fe_2O_3, respectively. Four thermites, namely, nano-Al/xero-Fe_2O_3, nano-Al+micro-Fe_2O_3, micro-Al/xero-Fe_2O_3, and micro-Al+micro-Fe_2O_3, were heated from ambient temperature to 1020 °C, during which the products at 660 °C and 1020 °C were collected and analyzed by XRD. Crystals of Fe, $FeAl_2O_4$, Fe_3O_4, α-Fe_2O_3, Al, γ-Fe_2O_3, $Al_{2.667}O_4$, FeO and α-Al_2O_3 were indexed in XRD patterns. For each thermite, according to the specific products, the possible equations were given. Based on the principle of the minimum free energy, the most reasonable equations were inferred from the possible reactions.
Key words: Al; nanocomposites; thermite reaction; reaction mechanism

1 Introduction

As a kind of energetic materials, thermites can release enormous heats during the combustion [1−3]. Certainly, thermite reaction is the chemical reaction that was discovered 200 yeas ago. They served as solder for rail and powders in combustion bomb because the high burning heats can make steel melt easy and burn down the hard targets. It should (or had) be a good proposal to use these little projectiles as impact initiated energetic materials (i.e. the reactive materials) that had become the focus in the studies about thermites [4,5]. This kind of materials will be ignited by impact action and show their excellent energy release characteristics during penetration process [6,7]. However, the energy release is not the dominating effect for target damage; it is only a complementary of penetration in that course. So, reaction performance of the projectiles becomes the most crucial factor (the poor performance cannot support the further damage to hard targets in such short time course, i.e. penetration course). In this case, seizing the mechanisms for the reactions of thermites consisting of nanoenergetic composites became very important. The known mechanisms can be used to guide the formulation selection and interpret the results of kinetic and thermodynamic studies.

For the reactions based on solid−solid reaction (in particular reactions between metallic particles and metal oxides), the performance is determined by thermal reactivity of fuel(s) and combination state between fuel(s) and oxidizer(s). For the former, two methods were employed to largely promote the thermal reactivity of aluminum, i.e. using nano-Al or Al-based alloy particles (with nanometer structures) as the fuel(s) [8−12]; for the later, fabricating nanocomposite composed of Al and metal-oxide(s) were investigated [13−15]. These researches employed many classic methods that hastened

Foundation item: Project (51206081) supported by the National Natural Science Foundation of China
Corresponding author: Feng-sheng LI; Tel: +86-25-84315942; E-mail: wangyi528528@yahoo.com.cn
DOI: 10.1016/S1003-6326(14)63056-9

the reaction performance, in which the DSC data and burning rates served as the criterion to judge whether reactions were promoted or not. In fact, as known, a thermite reaction that illustrated only one heat release course in a DSC trace may consist of many specific chemical reactions. In particular, when the metal element can bond with other elements at different valence states, thermite reaction becomes rather complex. There were many reports about the reaction mechanisms of Al−Fe_2O_3 systems, but the results were different. MEI et al [16] compressed Al and Fe_2O_3 powders into a slice and heated it to different temperatures. The residues were analyzed by XRD and the products of Al, Fe, Fe_2O_3, Al_2O_3, Fe_3O_4, and $FeAl_2O_4$ were detected. Accordingly, they inferred that the whole reaction comprised two steps: Above 960 °C, the main reaction was $Fe_2O_3 \rightarrow 2FeO+0.5O_2$; at 960−1060 °C, three reactions (i.e. $FeO+Al_2O_3 \rightarrow FeAl_2O_4$, $Fe_2O_3+2Al \rightarrow Al_2O_3+2Fe$, and $9Fe_2O_3+2Al \rightarrow 6Fe_3O_4+Al_2O_3$) took place. GOYA and RECHENBERG [17] also investigated the Al−Fe_2O_3 systems. However, they used mechanical milling to intrigue the thermite reaction and the equation ($Al+Fe_2O_3 \rightarrow 3Fe_{0.67}Al_{0.33}+1.5O_2$) was suggested. CUADRODO also milled the Al−Fe_2O_3 and obtained the products of α-Fe, α-Al_2O_3, Fe−Al, and $FeAl_2O_4$. The result accorded with that of MATTEAZZI and CAER [18] who considered that the $FeAl_2O_4$ is the intermediate of the thermite reaction. DURAES et al [19] proposed that the producing of $FeAl_2O_4$ became more thermodynamically preferential when the mass ratio of Fe_2O_3 to Al was beyond the stoichiometric ratio in the theoretical equation ($Fe_2O_3+2Al \rightarrow Al_2O_3+2Fe$).

The abovementioned mechanism researches did not suggest an absolute right result because the mechanism was largely affected by internal or external factors such as ignition, formulation, combination, crystal properties of fuel(s) and oxidizers(s). Hence, the relationship between the reaction performance and reaction mechanism was proposed to take the comparison with the results that are obtained under the same condition. In this work, using 1,2-epoxypropane derived sol−gel method, we combined the fuel (metallic Al) and the oxidizer (iron-oxide) as nanocomposites to improve the thermite reactions. Reaction performance of nanocomposites and simple mixtures was studied by thermal analyses. The reaction products were analyzed and the most proper reaction equations were inferred.

2 Experimental

2.1 Fabrication of Al/iron-oxide nanocomposites

Nanometer and micron Al were respectively used to fabricate nano-Al/xero-Fe_2O_3 and micro-Al/xero-Fe_2O_3 nanocomposites, and the two nanocomposites were prepared by the same sol−gel process. Before fabrication, the aluminum particles were immerged in hot ethanol with agitating. Then the Al particles were added into ethanol solution of $Fe(NO_3)_3 \cdot 9H_2O$. The suspension was ultrasonic dispersed for several minutes, then 1,2-epoxypropane was introduced to make it gel. After being aged for 3−5 d, the wet gel was dried in vacuum and the xerogel contained Al particles. The xerogel was washed in ethanol at 45 °C and dried to Al/iron-oxide nanocomposites. In sol−gel process, the 1,2-epoxypropane was very important as an proton scavenger to consume H_3O^+ and make the solution gel. The gelled medium sustained the suspending Al particles and then the coated structure was formed after being dried. The process is sketchily depicted in Fig. 1.

2.2 Sample characterization

The morphology and surface elements of the samples were examined by S−4800 field-emission scanning electron microscope (SEM) coupled with energy dispersive spectroscopy (EDS). The phase of aluminum/iron-oxide nanocomposites and residues were investigated by a Bruker Advance D8 X-ray diffractometer, using Cu K_α radiation at 40 kV and 30 mA. Differential scanning calorimetry of the thermites was performed on a TA Model Q600 differential scanning calorimeter.

3 Results and discussion

3.1 Morphology and structure analyses

The micron morphologies of Al particles before and after coating are shown in Fig. 2. Raw Al particles showed their diameters of 30−90 nm (for nano-Al) and 1−3 μm (for micro-Al). After sol−gel process, both Al particles were densely wrapped by thick layers that were composed of nanoparticles (about 20 nm). The images roughly consisted with the designed results illustrated in Fig. 1. In our previous work, ammonium perchlorate (AP)/Fe_2O_3 nanocomposites were prepared by the method like this. The TEM images also confirmed the nanosize (about 20 nm) of Fe_2O_3 [20]. The EDS spectra of two nanocomposites were manifested in Fig. 3. It shows that the surface of nanocomposite contains Al, Fe, O and C. The mass ratios of Fe to O in nano-Al/iron-oxide and micro-Al/iron-oxide are 45.89%/22.96% and 43.11%/21.28% respectively, which roughly match with the mass ratio of Fe to O in Fe_2O_3. Accordingly, the iron-oxide coated Al was termed xero-Fe_2O_3 in this work. Figure 4 reveals that the iron-oxide coating on surface of Al is amorphous because all four diffraction peaks at 2θ of 38.47°, 44.90°, 65.09°, and 78.22° respectively refer to the (111), (200), (220), and (311) faces of metallic Al.