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Review

Combustion synthesis of bulk nanocrystalline iron alloys

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Abstract

The controlled synthesis of large-scale nanocrystalline metals and alloys with predefined architecture is in general a big challenge, and making full use of these materials in applications still requires greatly effort. The combustion synthesis technique has been successfully extended to prepare large-scale nanocrystalline metals and alloys, especially iron alloy, such as FeC, FeNi, FeCu, FeSi, FeB, FeAl, FeSiAl, FeSiB, and the microstructure can be designed. In this issue, recent progress on the synthesis of nanocrystalline metals and alloys prepared by combustion synthesis technique are reviewed. Then, the mechanical and tribological properties of these materials with microstructure control are discussed.

Keywords: Combustion synthesis; Nanocrystalline; Mechanical behavior; Tribological properties

1. Background

The preparation and mechanical properties of bulk nanocrystalline metals and alloys have received much attention in two decades because of their unusual microstructures. Bulk nanocrystalline metals and alloys have been usually fabricated by consolidation of nano-powders, devitrification of amorphous materials and severe plastic deformation, but most of these techniques are limited to small-scale synthesis [1,2]. And this limits their extensive engineering application.

The combustion synthesis (CS, also known as self-propagating high temperature synthesis-SHS) is based on systems able to react exothermal when ignited and to sustain them by forming a combustion wave, which was founded by Merzhanov et al. in the 1960s [3]. This process evolves large sums of heat and forms a solid product in the chemically active systems, and shows some excellences such as self-sustaining reaction, high purity, high productivity and so on [4,5]. So it is used to prepare various types of advanced materials, such as metallic or ceramic powders, bulk materials. By using the high exothermic characterization, this technique has tried to be employed to prepare bulk nanocrystalline combined rapid cooling method by authors' group. Firstly, a bulk nanocrystalline Fe_3Al-based alloy has successfully been prepared via CS [6]. This technique is convenient, low-cost, and large-scale processing for preparing bulk nanocrystalline metals and alloys.

Inspired by the idea, we have prepared many bulk nanocomposite materials, such as FeC, FeNi, FeCu, FeSi, FeB, FeAl, FeSiAl, FeSiB, FeNiCu. Most of those metals and alloys have excellent thermal stability, high strength and ductility, good wear resistance and other properties. This review will discuss the combustion synthesis approach to achieve significant nano-equiaxial grain and other heterogeneous nanocomposite metals and alloys. Basically for the large-scale nanocrystalline alloys, the microstructure will be checked before the mechanical and tribological properties discussion. Finally, we will estimate the prospects of the combustion synthesis technique in large-scale preparing of the nanocomposite metals and alloys with excellent mechanical and tribological properties.

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2. Design and principle of combustion synthesis of bulk nanocrystalline alloys

2.1. Design of combustion synthesis large-scale metals and alloys

According to the depiction of self-sustaining, for preparing bulk metals and alloys, combustion synthesis is usually designed as a redox reaction:

$$(a+b)\mathrm{Me}+\mathrm{TM}_c\mathrm{O}_d=\mathrm{TM}_c\mathrm{Me}_a+\mathrm{Me}_b\mathrm{O}_d+Q \quad (1)$$

Me is metals such as Al, Fe, Mg, TM is metals (mainly transitional metals) such as Fe, Cu, W, Cr, Q is heat of reaction.

The experimental procedure has been designed as follows: Me and TM_cO_d mixture reactants were pressed into a steel jar on the copper or steel mold. The mold with the reactants was placed in a CS reactor (Fig. 1a). The reactor was purged with argon gas at room temperature (RT), heated to 420–490 K, and then purged for a second time. Heating of the reactor continued after the introduction of 4–8 MPa of argon gas. The reaction of the igniter was started when the temperature reached 500–550 K. The released heat ignited the redox reactants and the synthesis reaction was subsequently finished in a few seconds. The products were kept in the reactor under argon gas pressure to cool. After cooling to RT, the products were taken out from the reactor (Fig. 1b).

Merzhanov indicated that CS can be considered as an extreme chemical process [3]. It contains two main characters of the maximum combustion temperature T_m, and the velocity of front propagation U. T_m is highest temperature of combustion synthesis process. U presents the time of combustion synthesis, which is usually below 10 s. The maximum combustion temperature T_m in the CS can be measured by the adiabatic temperature (T_{ad}). The T_{ad} of combustion synthesis at initiated temperature T_0 can be calculated by using Eqs. (2) and (3) [5].

$$\Delta H_{r,T_0}=\int_{298\ \mathrm{K}}^{T_0}\Delta C_P dT+\Delta H_{r,\ 298\ \mathrm{K}}{}^{\circ} \quad (2)$$

$$\Delta H_{r,\ T_0}{}^{\circ}=\int_{T_0}^{T_m}C_{Ps}dT+\int_{T_m}^{T_{ad}}C_{Pl}dT+\Delta H_m \quad (3)$$

In the equations, C_{ps} and C_{pl} are solid and liquid state heat capacities of the products respectively, $\Delta H_r{}^{\circ}$ is enthalpy of the reaction (1), which is the difference between formation enthalpy ($\Delta H_f{}^{\circ}$) of the products and the reactants, ΔH_m is melting enthalpy of the products, ΔC_P is the difference between the heat capacity of the products and the reactants. In these calculations, it is assumed that there is no loss of heat to the surroundings, meaning that it is a 'closed system'. Thus T_{ad} is only a measure of the exothermicity of the reaction and defines the upper limit for any combustion system. Table 1 presents T_{ad} of some combustion synthesis reactions when the T_0 is about 530 K. Different redox presents different T_{ad}, depending on the reactants and products thermal physical properties. From Eqs. (2) and (3), the initiated temperature also affects the T_{ad}. Fig. 2 shows the T_{ad} of $Fe_{88}Si_{12}$ alloy prepared by CS as function of initiated temperature T_0. When T_0 is about 410 K, the T_{ad} rapidly decreases to zero. This adiabatic temperature observably does not happen during CS. So the initiated temperature should be in the proper range.

First, T_{ad} would be lower than boiling point of the reactants and products to maintain tailored composition of products. Second, the product would go through solidification to form nanocrystalline, so the T_{ad} would be larger than melt point of the products. The boiling points of products increase with the applied pressure according to the "Clausius–Clapeyron equation" and "Trouton's rule" [7,8].

$$\left(\ln\frac{P_2}{P_1}\right)=\left(\frac{\Delta_{vap}H_m}{R}\right)\times\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \quad (4)$$

$$\left(\Delta_{vap}H_m\right)\approx 88\times T_b\ \left(\mathrm{Jmol}^{-1}\right) \quad (5)$$

$\Delta_{vap}H_m$ is the vaporization enthalpy of the products, R is the mol gas constant, T_1 and T_2 are the boiling points of liquid at pressures P_1 and P_2 respectively. T_b is the boiling point at atmosphere pressure. When $P_1=0.1$ MPa, P_2 is the experimental pressure. Here taking the example of $Fe_{88}Si_{12}$ alloy prepared by CS, the boiling point of the product at the experimental condition is shown as inset of Fig. 3. The boiling point of Al_2O_3 and $Fe_{88}Si_{12}$ alloy are the range from 3800 K to 4200 K when the applied argon pressure is in the range from 4 to 8 MPa. To ensure the target products compositions, the highest temperature T_{ad} would be lower than the T_{bp}.

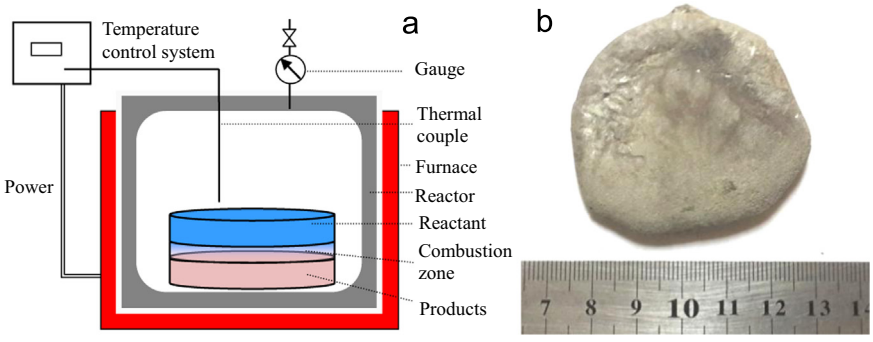

Fig. 1. Sketch of the combustion synthesis apparatus (a) and sample (b).