



Kinetic and thermodynamics studies on the decompositions of Ni₃C in different atmospheres

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ABSTRACT

The thermal decompositions (including TG and DSC) of nickel carbide were studied under different atmospheres of Ar, air and H₂. X-ray diffraction combined with element analysis indicated that nickel metal, together with solid amorphous carbon, was formed during Ni₃C decomposition in Ar atmosphere, accompanying mass invariant in this process. While in H₂ atmosphere nickel metal was the only residual from reactions. The carbon component of nickel carbide reacted with H₂ to form methane as the main volatile gases. Both the nickel and carbon components of Ni₃C reacted with O₂ in the air to form their corresponding oxides. Moreover, we calculated the activation energy for the decomposition process and the molar enthalpy of formation of Ni₃C based on the thermal analysis.

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1. Introduction

Ni₃C has a metastable phase at room temperature and decomposes at the temperatures above 430 °C in inert atmosphere, which make it hard to be synthesized [1]. Although many literatures have reported the formation of thin Ni₃C film [2,3], in the case of pure Ni₃C powder, only few groups succeeded to convert nickel metal fully into Ni₃C phase [4,5]. As a metastable phase resulted from the low solubility of carbon into nickel at high temperature and lack of ionic bonding [6], however, no detailed study has been reported on the decomposition of Ni₃C.

Synthesis of pure Ni₃C powder becomes the key to study the thermodynamics of Ni₃C and calculate its kinetic parameters. Recently, our group reported that pure Ni₃C powder could be transformed from Ni nanoparticles in organic solutions in the presence of surfactants [7], which provide us the possibility to study the thermal stability of Ni₃C phase. In addition, it is hard to distinguish hexagonal-close-packed Ni metal (JCPDS 45-1027) from Ni₃C phase (JCPDS 06-0697) according to their XRD patterns [8–10]. By analyzing the decomposition products, it may offer us an effective way

to distinguish these two materials. In this paper, we reported the decomposition of Ni₃C phase in different atmospheres, including the inert argon, the oxidative air and the reductive hydrogen. The activation energies and the molar enthalpy of formation of Ni₃C were also calculated based on the thermal analysis.

2. Experimental

Well-characterized Ni₃C nanoparticles were prepared in 1-octadecene by the decomposition of nickel formate, according to a slightly modified procedure reported by our group [7]. The nanoparticles were found to consist of pure Ni₃C phase, which was used for further decomposition in different atmospheres.

Thermogravimetric and differential scanning calorimetric (TG–DSC, NETZSCH STA 449 C) curves were recorded at 10 K/min in Ar (99.99%), H₂ (99.99%) and air atmospheres. Highly sintered α-Al₂O₃ was used as a reference material for the thermal measurements. This thermal analyzer is equipped with a mass spectrometer (MS) to detect the volatile components during the decomposition process. During the measurements, the sample mass was ca. 10 mg and all runs were conducted at a gas flow rate of 40 mL min⁻¹. In order to calculate the activation energy for the reaction of Ni₃C under different atmospheres, heating rates were varied 5, 10 and 20 K/min, respectively. X-ray diffraction (XRD, RIGAKU D/MAX-2400) was conducted using Cu Kα radiation to identify their structure of the decomposition solid products. 2θ scans were made from 30° to 80° at a rate of 4°/min with a step size of 0.02°. The

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measurements were conducted using a generator voltage of 40 kV and a current of 100 mA. Microscale elements analysis instrument (ELEMENTAR Vario EL) was adopted to detect the carbon content in the decomposed products using combustion analysis.

3. Results and discussion

3.1. Ni₃C decomposition in Ar atmosphere

Fig. 1 shows TG, DSC and MS curves of Ni₃C decomposition in Ar atmosphere at a heating rate of 10 K/min. The curves indicate that Ni₃C decomposes via a weight-loss step (process I) maximized at 540 K, ending up with solid products that produces an exothermic peak centered around 688.2 K (process II). In process I, the endothermic peak is attributed to the decomposition of the adsorbed surfactants on the surface of the Ni₃C particles. MS data identified the formation of small fractions of C, CO, CO₂, O, OH and H₂O during this process, corresponding to the mass loss by 2.9 wt% from 500 to 570 K in the TG curve. There is also an exothermic peak at 688.2 K in process II, which is associated to the decomposition of Ni₃C. The temperature for Ni₃C to decompose is slightly lower than that previously reported result, which is above 430 °C (703 K) [1]. Since no mass loss during process II is observed in the TG curve and no volatile gases are detected by MS, this process could be assigned to either a physical process, i.e. recrystallization of a solid product, or a decomposition process, during which all the decomposition products are solid matter. The decomposition products will be validated below in detail.

The as-synthesized Ni₃C nanoparticles was heated to 600 K at a heating rate of 10 K/min and then cooled to room temperature, that is, after the endothermic peak is completed (process I), but before the emergence of the exothermic peak (process II), the decomposed product was measured with XRD. As shown in Fig. 2(b), no structural change was observed compared with the XRD pattern of the as-synthesized Ni₃C (Fig. 2(a)), which confirms that the endothermic peak belongs to the decomposition and desorption of the adsorbed surfactants. This result agrees well with the MS data by detecting the small molecules coming from the surfactants (process I). According to the Scherrer equation, the average crystallite size of Ni₃C was estimated to be 40 nm, which was slight smaller than that calculated from the TEM image (supporting information). Microscale element analysis by combustion experiment confirms

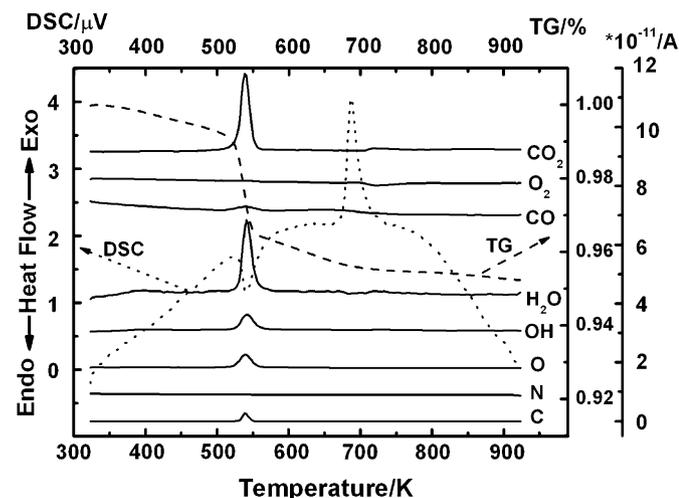


Fig. 1. TG, DSC and MS curves recorded for Ni₃C at 10 K/min in a dynamic atmosphere of Ar (the dash line denotes the TG curve, the short-dash line denotes the DSC curve and the solid lines denote the MS data).

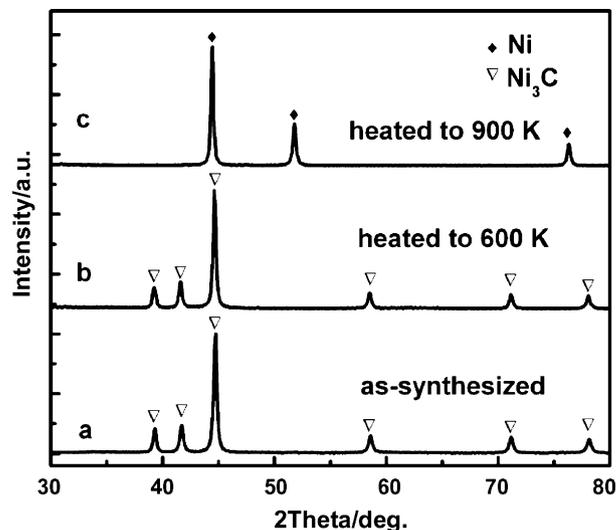
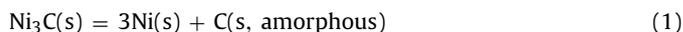


Fig. 2. XRD patterns for: (a) the as-synthesized Ni₃C nanoparticles, (b) the powders obtained after heating to 600 K in Ar and (c) the powders obtained after heating to 900 K in Ar.

that the carbon content is 6.42 wt% in the product after heating to 600 K, which accords well with the value of 6.38 wt% for pure Ni₃C phase. This result implies that after heating to 600 K, the product changes to pure Ni₃C with clean surfaces. After heating to 900 K, Ni₃C nanoparticles decompose to produce nickel metal (JCPDS 04-0850), as shown in Fig. 2(c), indicating that the exothermic peak was owing to the Ni₃C decomposition. Because no mass loss was observed in TG curves, no volatile carbon detected by MS and no crystalline carbon observed from XRD pattern during process II, microscale element analysis was performed to validate the presence of carbon in the decomposition products. It indicates that 6.39 wt% of carbon in the decomposed product after heating to 900 K, agreeing well with the carbon content in Ni₃C. This result confirms that the hcp phase should be Ni₃C rather than hcp Ni metal. Though such a large quantity of solid carbon was formed in this process, no crystalline carbon was detected by XRD, suggesting the carbon coexists with nickel metal in an amorphous state. The decomposition equation for Ni₃C in Ar atmosphere should be



The decomposition of Ni₃C in Ar was identified to be a single step reaction. In this case, the activation energy ΔE could be calculated for the decomposition process using Kissinger method based on the following equation [11]:

$$\ln \left(\frac{C}{T_p^2} \right) = - \left(\frac{\Delta E}{K_B T_p} \right) + A \quad (2)$$

where C is the heating rate, ΔE the activation energy, T_p the peak temperature, K_B Boltzmann constant, and A is a constant. With increasing heating rate, the peaks shift to higher temperatures. From the peak shift, ΔE could be calculated. As shown in Fig. 3, when the heating rates increase from 5 to 10 K/min and 20 K/min in Ar atmosphere, the peak temperature is 673.3, 688.2 and 698.0 K, respectively. According to Eq. (2), the calculated ΔE for Eq. (1) is 204 kJ mol⁻¹, with a correlation coefficient r to be 0.991.

DSC measurements are also used to calculate some thermodynamics parameters. The enthalpy (ΔH , Jg⁻¹) of the thermal events could be directly determined from the DSC data (recorded at 10 K/min) according to the peak area. The determined ΔH is used to calculate the specific heat capacity (C_p , J K⁻¹ g⁻¹) using the equation of $C_p = \Delta H / \Delta T$, where $\Delta T = T_2 - T_1$, and T_1 is the temperature from

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