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Original Research Paper

Microstructure and thermal decomposition property of Ni-P/Cr_2N composite powder by electroless plating

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ABSTRACT

Cr_2N is the most promising blowing agent for the preparation of steel foam using melt foaming method. In this work, to obtain a blowing agent with suitable density and gas decomposition characteristics for steel melt foaming, Ni-P/Cr_2N composite powder was prepared by electroless plating. The surface morphology, phase, coating thickness, density and decomposition characteristics of Ni-P/Cr_2N composite powder were analyzed. The results indicate that the surface of Ni-P/Cr_2N composite coating powder is covered by the high nickel and low phosphorus layer which has a dense and uniform cell structure. The decomposition rate of the Ni-P/Cr_2N composite powder is 7.46 mW/mg slower than that of the uncoated Cr_2N powder at 1107.4 °C. When the plating time is 30 min, the thickness of Ni-P layer reaches 2.86 µm, the density of the Ni-P/Cr_2N composite powder is 7.45 g/cm^3, and maximal decomposition rate temperature reaches 1500 °C. These findings suggested that Ni-P/Cr_2N composite powder meets the requirements of decomposition temperature and density of the blowing agent used to produce steel foam with a uniform pore structure by the melt foaming method.

1. Introduction

With many superior properties such as low cost, high energy absorption, high heat resistance, and good weldability, steel foam has many potential applications in transportation including cores for beams and sandwich panels of weight-critical components, and energy absorbing components and structures [1–4]. At present, various methods have been used to prepare steel foams, such as powder metallurgy (PM), hollow spheres, and Gasar [1,4–6]. However, all these techniques have shortages: the size of PM metal foam is limited; the preparation process of hollow spheres is complex and costly; and the isotropic cell morphologies of the pore structure of Gasar metal foam are impossible to be obtained because of its highly anisotropic and aligned cell shapes [1].

Some studies suggest that melt foaming method is the best way to make metal foam at low cost and in large-scale production systems, and is widely used in the preparation of low melting point metal foam (typically aluminum foam) [7–10]. In the melt foaming process, gas bubbles are usually made by using a blowing agent as an additive which is the key to the melt foaming process [11–13]. The gas decomposition temperature range of the blowing agent has to be coordinated with the melting point of the metal to ensure satisfactory foaming results [14]. If the temperature of the blowing agent releasing gas is far below the metal melting point, the blowing agent will decompose quickly when it is added to the molten metal, which makes it difficult to control the cell structure and the gas retention amount in molten metal.

The studies on blowing agent have mainly concentrated on the preparation of low melting point metal foams, especially TiH_2 for aluminum foams [15–18]. To produce steel foam using the melt foaming method, a blowing agent with a higher decomposition temperature that close to the steel melting point ($T_m \sim 1350$ °C) is required. Nitride, for example Cr_2N, is considered as such a potential blowing agent [14]. However, the starting decomposition temperature and the maximal decomposition temperature of Cr_2N particle are about 700 °C and 1055 °C, respectively, which are significantly lower than the melting point of steel. In addition, the density of Cr_2N (6.8 g/cm^3) is lower than that of steel melt (about 7.4 g/cm^3 at 1350 °C). The mismatch between the decomposition temperature of Cr_2N and the melting temperature of steel makes Cr_2N particles release nitrogen immediately when Cr_2N particles are added into molten steel. Furthermore, Cr_2N's lower density makes it difficult to disperse quickly in molten steel. All of these

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factors make it too difficult to obtain steel foams with a uniform pore structure and a high-performance by melt foaming method. Therefore, decreasing Cr_2N decomposition rate of nitrogen release and increasing Cr_2N density are essential in improving the melting foaming method for steel foam production.

For decreasing the decomposition rate of the blowing agent, studies have been carried out on surface modifications of TiH_2 by the electroless plating method focusing on Al_2O_3, SiO_2, Ni or Ni-P coatings of TiH_2, and by pre-heating treatment of TiH_2 [19–23]. These studies showed that surface modification can act as a barrier layer to hinder the gas evolution process of blowing agent, and make the blowing agent insensitive to the outside high temperature [24].

In this paper, the Ni-P/Cr_2N composite powder was prepared by electroless plating method that uses nickel sulfate as the main salt, sodium hypophosphite as a reductive agent, sodium citrate as a complexing agent, and controls pH levels of the bath at 8.0–11.0 during the plating process. The morphology, phase, coating thickness, density and decomposition property of Ni-P/Cr_2N composite powder were investigated. We hope this exploratory study can play an important role in promoting the development of steel foam by metal foaming processing.

2. Experimental procedure

2.1. Pretreatment of Cr_2N powder

The average size of Cr_2N powder was about 20–40 μm. To get a complete and continuous coating of film, Cr_2N powder were pretreated before electroless plating, aiming at forming an activity surface on the Cr_2N powder [22]. Table 1 describes the steps of the pretreatment process.

2.2. Preparation of Ni-P/Cr_2N composite powder by electroless plating and testing methods

A solution of nickel ion was prepared by dissolving an analytical grade $NiSO_4{\cdot}6H_2O$ in de-ionized water. The pH value of the solution was adjusted to 8.0–11.0, using ammonium hydroxide ($NH_3{\cdot}H_2O$), and the solution was heated to 60–80±5°C. Sodium dodecyl sulfate was chosen as the surfactant, sodium citrate as the complex agent, and sodium hypophosphite as the reducing agent. The pretreated Cr_2N powder was added into the plating solution, and reacted for approximately 15–60 min. Then the treated powder was separated from the solution by filtration, and washed three times with de-ionized water. Finally, the Ni-P/Cr_2N composite powder was obtained after drying at 60 °C for 3 h. The components of the electroless nickel plating solution are shown in Table 2.

The surface morphology, coating thickness and the phase composition of coated Cr_2N powder were characterized by scanning electron microscopy (SEM, XL30ESEM-TMP, Philips-FEI™), energy dispersive spectrometers (EDS, NSS, Thermal Scientific™), X-ray diffraction (XRD, D8 Advance, Bruker™), and X-ray photoelectron spectroscopy (XPS, PHI5000 Versaprobe-II, ULVAC-PHI™). The density was measured using a drainage method. The decomposition characteristics of Ni-P/Cr_2N composite powder were studied by differential scanning calorimetry (DSC, STA 449F3, NETZSCH™) that was performed in an Ar atmosphere with a heating rate of 20 °C/min from room temperature to 1500 °C.

3. Results and discussion

3.1. Surface morphology and phase composition of Ni-P/Cr_2N composite powder

The surface morphologies of raw Cr_2N particle, and microetching treated Cr_2N particle are shown in Fig. 1. Fig. 1(a) shows that the surface of raw Cr_2N particle has a multilateral shape and a smooth surface, but microetching treated Cr_2N particle (Fig. 1(b)) has many tiny microetching stripes on the surface. For solid materials, the surface catalytic activity is positively correlated to the surface defects per unit area (such as the surface of the adsorbent islands, steps, dislocations), therefore, the more the surface defects, the higher the surface catalytic activity. It is expected that the striped defects produced on the surface of the microetching treated Cr_2N particles are beneficial to the adsorption, nucleation, and growth of the Ni-P layer during the electroless plating process [25].

The XRD patterns of the Cr_2N powder and the Ni-P/Cr_2N composite powder are shown in Fig. 2. It can be seen that the Ni-P/Cr_2N composite powder has a typical semi-crystalline structure, that is, a mixture of a broad peak amorphous structure and a crystallized structure. The broadening of the peak is mainly attributed to both microstress and the microcrystalline structure or amorphous structure of Ni-P films supersaturated with phosphorus [26,27]. Besides Cr_2N, CrN that comes from raw material is found in the XRD patterns, but with very small amount of content.

Table 2
Composition of electroless nickel-phosphorus plating.

Chemical	Formula	Concentration (g/L)
Nickel sulfate	$NiSO_4{\cdot}6H_2O$	25–50
Sodium hypophosphite	$NaH_2PO_2{\cdot}H_2O$	30–40
Sodium citrate	$Na_3C_6H_5O_7{\cdot}2H_2O$	23–35
Boric acid	H_3BO_3	28–38
Sodium dodecyl sulfate	$C_{12}H_{25}NaO_4S$	0.02–0.06

Table 1
Stages of Cr_2N powder pretreatment process.

Stage	Purpose	Description
Cleaning	• To clean the remnant grime on the surface of the Cr_2N particles	• The Cr_2N powder was cleaned in carbinol, NaOH solution and HCl solution for 10 min by magnetic stirring.
Microetching	• To make the Cr_2N particles surface rougher by chemical attack. The uneven surface allowed more bonding sites and good coating adhesion	• The Cr_2N powder was microetched in an aqueous solution of 50 mL/L hydrofluoric acid (HF), 80 mL/L nitric acid (HNO_3) and 2 g/L ammonium fluoride (NH_4F) for 25 min by magnetic stirring.
Sensitization	• To sensitize the surfaces of the Cr_2N particles for the subsequent activation stage	• The Cr_2N powder was sensitized in a solution of 10 g/L $SnCl_2$ and 40 mL/L HCl (36 wt%) for 20 min by magnetic stirring. • Tin ion Sn^{2+} was absorbed at the bonding site created on the substrate surface, acting as a new nucleation site for Ni-P compound
Activation	• To increase the surface fraction of the catalytic sites serving as preferred heterogeneous nucleation	• The Cr_2N powder was activated in a solution of 0.5 g/L $PdCl_2$ and 10 mL/L HCl (36 wt%) for 20 min by magnetic stirring • The palladium ion reacted with the previously deposited tin ion and is converted to elemental palladium by the following reaction: $Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd$