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In situ formation of Fe–NbC/C composite powders from solution-derived precursors by a gas reduction–carburization process

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Abstract

The *in situ* formation of Fe–NbC/C composite powders was studied using solution-derived precursors and a gas reduction–carburization reaction at 1223 K. The effect of different $CH_4/H_2/Ar$ gas mixtures or a polymer (polyvinyl alcohol – PVA) combined with sucrose as carbon sources was analyzed. The results obtained were discussed in relation to the reduction–carburization sequence, microstructure and oxidation behavior of the composite powders. When the carbon was supplied by the gas phase (CH_4), the reaction mechanism proceeded *via* $FeNb_2O_6 \rightarrow Fe + NbO_2 \rightarrow Fe + NbC$. However, if the carbon was generated in the solid phase, from PVA–sucrose pyrolysis, the transformation to the compound powder was achieved faster by means of a carbothermal reduction reaction. The type of free carbon was characterized by a high degree of disorder and defined not only the powder microstructure but also the crystallite size of the reinforcement phase (NbC) and certain behavior features during oxidation. The carbon generated by PVA–sucrose pyrolysis (70 wt%) was the most adequate one to obtain a sponge-type morphology with nanocrystalline NbC (12 nm) and to protect the Fe particles from oxidation. Even so, all the composite powders prepared remained stable in air up to about 600 K.

Keywords: A. Powders: chemical preparation; B. Electron microscopy; C. Oxidation; D. Carbides

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1. Introduction

Composites with iron and ceramic particle reinforcements, such as NbC or TaC, play a key role in the production of relatively inexpensive and more environment-friendly wear-resistant materials. They are usually produced by powder metallurgy (P/M route, including high-energy milling-HEM, compacting and sintering) from iron and carbide powders prepared separately [1–3]. The typical advantages of this P/M route, referred to as *ex situ* processing, are raw-material savings and low energy costs. However, the composites thus obtained generally suffer from the problem of contaminated matrix–reinforcement interfaces with a weak bonding.

From this viewpoint, the techniques involving the *in situ* generation of the reinforcement phase have emerged as a preferred synthesis route for these materials. *In situ* techniques involve a chemical reaction resulting in the formation of a very fine and thermodinamically stable ceramic phase within a metal matrix. Consequently, the reinforcement surfaces are likely to be free from gas absorption, oxidation or other detrimental types of surface reaction contamination. Therefore, the interface between the matrix and the reinforcement bond tends to be stronger. Some of these technologies applied to synthesize Fe-NbC/TaC composites include the carbothermal reduction of columbite ores at 1673–1873 K [4,5], self-propagating high temperature (SHS) synthesis [6], infiltration casting process combined with heat treatment at 1445 K [7] and mechanical alloying of dry powder mixtures (FeNb + C, heated at 1073 K; Fe + Nb + C, followed by sintering at 1573 K) [8–10] or powder mixtures in organic media (Fe + Nb + toluene, including a method of magnetic pulse compaction) [11]. In most cases, while high-temperature ensures a fast, complete reaction, it also causes the coarsening of the carbide grains. For example, the particulate-reinforced composite produced by SHS cannot be directly used as structural material

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because of its porosity and looseness, making the intrinsic porosity in the reaction process difficult to handle.

It is well known that the reduction of the carbide size causes a significant improvement of the mechanical properties. The toughness of ceramics could be considerably increased by reducing grain size without sacrificing hardness. In this sense, alternative synthesis procedures of nanocrystalline composite powders, such as a gas reduction–carburization [12] and polymer-derived precursors [13], could be useful in assisting composite homogenization and densification and, therefore, in tailoring the final properties of the composite.

The present work proposes an alternative route to synthesize Fe–NbC/C composite powders, which combines the advantages of solution-derived precursors with a gas reduction–carburization reaction. This article pays particular attention to the effect of $CH_4/H_2/Ar$ gas mixtures or a polymer (polyvinyl alcohol – PVA) as carbon sources, on the *in situ* formation of the composite. Additionally, the microstructure and oxidation behavior of the composite powders are investigated and discussed in relation to the carbon supply from the solid or gas phase.

2. Materials and methods

2.1. Preparation

The synthesis of Fe–NbC/C composite powders was performed in four sequential steps, as shown in Fig. 1. The materials used as reagents were $Fe(NO_3)_3 \cdot 9H_2O$ (Merck, 99.9%) and $Nb(NH_4)[NbO(C_2O_4)_2(H_2O)_2](H_2O)_n$ (CBMM, Companhia Brasileira de Metalurgia e Mineração). Starting Fe ($0.1\ mol\ L^{-1}$) or Nb ($0.1\ mol\ L^{-1}$) containing solutions were prepared by dissolving their respective salts in distilled water and analyzed by complexometric and gravimetric analysis, respectively. $FeC_2O_4 \cdot 2H_2O$ and the $Fe_2(C_2O_4)_3$ aqueous solution were prepared and analyzed as reference 14 (step 1: individual solutions). Then, they were combined to obtain Fe:Nb = 1:1 source solutions with and without NO_3^- ions. The mixed-metal solution with nitrates was stable only in the presence of oxalic acid necessary to form an iron-oxalate complex (step 2: mixed-metal solutions). This solution was hydrolyzed by adding NH_3 $2\ mol\ L^{-1}$ up to pH = 10. The precipitate formed was filtered, washed and dried at 353 K for 24 h. On the other hand, the mixed-metal solution without nitrates was evaporated to dryness using a Büchi R-124 Rotavap at 333 K or a stirring hot plate at ~353 K. In the latter case, the mixed-metal solution was prepared by adding polyvinyl alcohol (Merck, PVA 72,000) $1\ mol\ L^{-1}$ and sucrose $2\ mol\ L^{-1}$ in the M: PVA = 2:1 (M: total metals) and sucrose:PVA = 4:1 M relations. In this way, dried solid precursors were obtained as amorphous (X-ray diffraction) loose powders, being brown, green or black according to the composition and experimental set-up preparation conditions (step 3: precursors).

Finally, the precursors were reduced–carburized by temperature-programmed reaction (TPRe) in different $CH_4/H_2/Ar$ mixtures (0/4/96 vol%, 16/4/80 vol% and 4/16/80 vol%, > 99.99% purity). The TPRe experiments were performed using an Ohkura TP2002S analyzer equipped with a thermal conductivity detector (TCD). Between 150 and 200 mg of each precursor were loaded into an 8 mm (o.d.) quartz tube stuffed with quartz wool at the bottom to hold the powders. The powders were heated at $10\ K\ min^{-1}$ up to 1223 K during variable times and, then, they were cooled by quenching at room temperature. This cooling process to room temperature was performed in the reactor under flowing gas-mixture $50\ cm^3\ min^{-1}$ (step 4: composite powders).

2.2. Characterization

The structure of precursors and composite powders was examined at room temperature by X-ray diffraction (XRD). Routine patterns were obtained from a Shimadzu XD-D1 automated diffractometer using graphite-monochromated Cu K_α

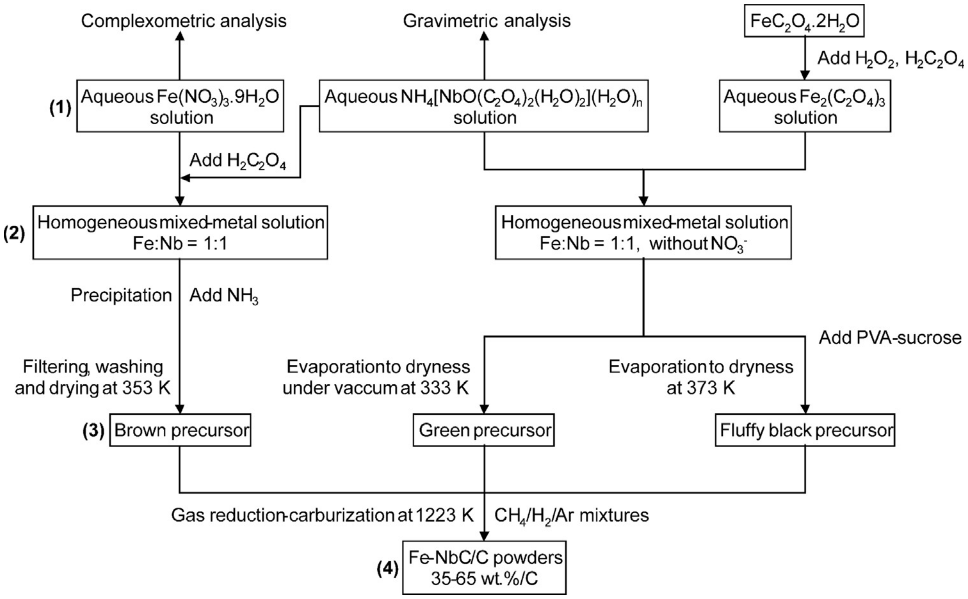

Fig. 1. Synthesis scheme for Fe–NbC/C composite powders.