Scripta Materialia 132 (2017) 30–33

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular Article

Core-shell amorphous metal oxides/metallic glassy particles for absorbing application of toxic heavy metal and electromagnetic wave

DongJun Wang [a,c,*], Yongliang An [b], JianMing Qiang [a], Hao Yuan [a]

[a] National Key Laboratory for Precision Hot Processing of Metals, Harbin Institute of Technology, Harbin 150001, PR China
[b] School of Materials Science and Engineering, Heilongjiang University of Science and Technology, Harbin 150022, PR China
[c] Key Laboratory of Micro-systems and Micro-structures Manufacturing, Ministry of Education, Harbin 150001, PR China

ARTICLE INFO

Article history:
Received 8 January 2017
Received in revised form 24 January 2017
Accepted 25 January 2017
Available online xxxx

Keywords:
Titanium
Amorphous materials
Powder processing
Absorption property

ABSTRACT

Ti-based metallic glassy powders were utilized as dealloying precursors and core-shell structured absorbents with metallic glassy particles as core and amorphous metal oxides as shell were synthesized through hydrothermal method. The absorbents exhibited superior adsorption efficiency and capacity for removing toxic Cr^{6+} in aqueous solution. In addition, the electromagnetic wave absorption properties were investigated and the absorbents had considerable electromagnetic wave absorbing ability owing to its dielectric loss. This work provides a strategy for fabrication of core-shell particles using facile dealloying of multiple component alloys.

1. Introduction

In recent years, the presence of heavy metals in water has been a major environmental contamination concern owing to their extremely toxic towards aquatic life and human beings [1–3]. Among them, Cr^{6+} coming from industrial waste is a well-known highly toxic element and its concentration in aqueous system must be reduced to very low levels prior to release of wastewater throughout the world [4–5]. To address this problem, numerous treatment techniques have been employed to treat wastewater [6] including chemical precipitation, ion exchange and filtration, most of which suffer from drawbacks such as ineffective and expensive. For removing heavy metal pollutant from wastewater, absorption becomes an attractive process because it is inexpensive and there are various absorbent materials can be used [7]. Compared with conventional absorbents, nano-structured absorbents exhibit remarkable advantages due to their higher surface areas and more surface active sites than bulk materials [8], which in turn lead to higher removal efficiency. However, nano-structured absorbents, especially nanoparticles, are difficult to be separated and recovered from liquid system because of high surface energy and ultra small size, which may generate secondary pollution and seriously restrict their applications [8].

On the other hand, with the development of communication devices, such as mobile phones, networks, satellites and radar systems, serious electromagnetic (EM) interference as specific environmental pollution has drawn much attention recently [9–11]. To resolve the issue, the electromagnetic wave absorbents have been widely investigated to eliminate the above problems [12–13]. Up to date, most of the EM wave absorbents are usually ferrites, metal/alloy and their oxides [14–15]. In addition, preparation of traditional microwave absorption materials with a core/shell structure might be a promising way to improve their microwave absorption properties [16]. Nevertheless, ferromagnetic EM wave absorbent materials are commonly too heavy to be used in the case of light-weight required conditions [14]. Furthermore, nano-size/sub-micro-size metal oxide absorbents are easy to aggregate during the thin coating process, preventing their actual applications.

In this work, Ti-based metallic glassy particles are used as dealloying precursors and core-shell structured absorbents are synthesized. For the absorbents, the light metal based metallic glassy particles are the micro-sized cores and amorphous metal oxides form on the surfaces of the cores as the shells, which exhibit superior absorption capacity and efficiency for removing Cr^{6+} in aqueous solution, as well as considerable EM wave absorption properties. In particular, the novel absorbents have more widely application potential as they are convenient to be separated and renewed in liquid system. Furthermore, the novel absorbents may be utilized to fabricate uniform light-weight EM wave absorbent coatings compared with conventional absorbent materials due to their micro-scale size and low density. This work provides a new broad field to obtain novel core-shell metal/alloy based functional materials using facile and generic dealloying strategy and will help to open a new opportunity for further applications of metallic powders.

* Corresponding author at: National Key Laboratory for Precision Hot Processing of Metals, Harbin Institute of Technology, Harbin 150001, PR China.
E-mail address: dongjunwang@hit.edu.cn (D. Wang).

http://dx.doi.org/10.1016/j.scriptamat.2017.01.027
1359-6462/

2. Experimental and computational section

The Ti-based metallic powders with the nominal composition of $Ti_{42.5}Cu_{40}Zr_{10}Ni_5Sn_{2.5}$ (at.%) are fabricated by widely employed gas-atomization method in an argon atmosphere [17]. For the hydrothermal-dealloying process, the metallic glassy powders are chosen as the precursors and 5 M NaOH aqueous solution is used as the common solvent. 0.3 g powders are dispersed in 20 mL solution in a Teflon vessel placed into an autoclave and then heated in a furnace at 140 °C for 60 min and 120 min, respectively. After cooling, the product is washed with deionized water and dried. For convenience, we use the notations, D-powders-60 and D-powders-120, to describe the products dealloyed for 60 min and 120 min, respectively.

The structural characteristics of samples are investigated by scanning electron microscopy (SEM, Quanta 200F operated at 20 keV) and transmission electron microscopy (TEM, Tecnai G2 F30 operated at 300 keV equipped with energy dispersive spectroscopy (EDS)). The powder samples are tested as absorbents for removing Cr^{6+} from $K_2Cr_2O_7$ aqueous solutions under dark conditions. The absorption capacity is determined as C/C_0 at pH ~ 2.0 (adding dilute H_2SO_4 solutions) and 300 K, where C is the concentration of Cr^{6+} in the solution (mg/L) at time t and C_0 is the initial concentration of Cr^{6+}. An amount of 0.25 g of absorbent is added to 25 mL solutions for each test, and the C values are determined by analyzing the aqueous solution at different time intervals. To determine the maximal absorption capacities, 0.15 g absorbents are suspended in 75 mL solutions. The maximal absorption capacity is calculated by the following equation: $Q_m = (C_0 - C_t)(V / W)$, where Q_m is the maximal absorption capacity (mg/g), C_t is the concentration of Cr^{6+} in the solution after absorption (mg/L, $C_t \neq 0$), V is the solution volume (L), and W is the mass of the absorbent (g). The electromagnetic parameters and EM wave absorption properties of the synthesized samples are measured on a vector network analyzer (VNA; Agilent N5230A) and the details are described previously [11].

3. Results and discussions

Fig. 1a shows the SEM image of gas-atomized Ti-based metallic glassy powders. As shown, the alloy powders are spherical particles with smooth surfaces and diameters around 5–35 μm. Fig. 1b shows the morphology of D-powders-120 particles. As can be seen, network-like belts with the width of about 0.1 μm are grown on the surfaces of the Ti-based metallic glassy powders, forming a core-shell structure. By separating of the shell from the metallic powder matrix, the bright field (BF)-TEM image of the belt is shown in Fig. 1c. One can see that the network-like morphology of the shell is destroyed during magnetic stirring separation and these belts exhibit nano-sized cluster feature. According to the EDS analysis, the grown belts exhibit an average composition of $Ti_{17.44}Cu_{13.13}Zr_{4.25}Ni_{0.59}O_{64.59}$ (at.%), revealing that they are composed of different metal oxides. In order to determine the microstructure of this dealloyed product, the high resolution (HR) TEM investigation and corresponding selected area electron diffraction (SAED) analysis are performed, as shown in Fig. 1d. The HR-TEM image shows disordered microstructural characteristic, which suggests that the grown shell of network belts is amorphous. In addition, the SAED pattern displaying broad diffused diffraction ring also confirms the amorphous structure of these metal oxides, similar to that of D-powders-60 sample (not shown here). Based on the above results, it can be concluded that the dealloyed core-shell composite consists of metallic glassy micro-particles as the core and amorphous metal oxide nanostructures as the shell.

The powder samples are tested as adsorbents for the removal of Cr^{6+} in aqueous solution and the adsorption capacities of the samples are shown in Fig. 2. As shown, with the increasing of time to 60 min, the value of C/C_0 nearly maintains constant of 1.0 for the gas atomized powders, indicating that there is no adsorption effect

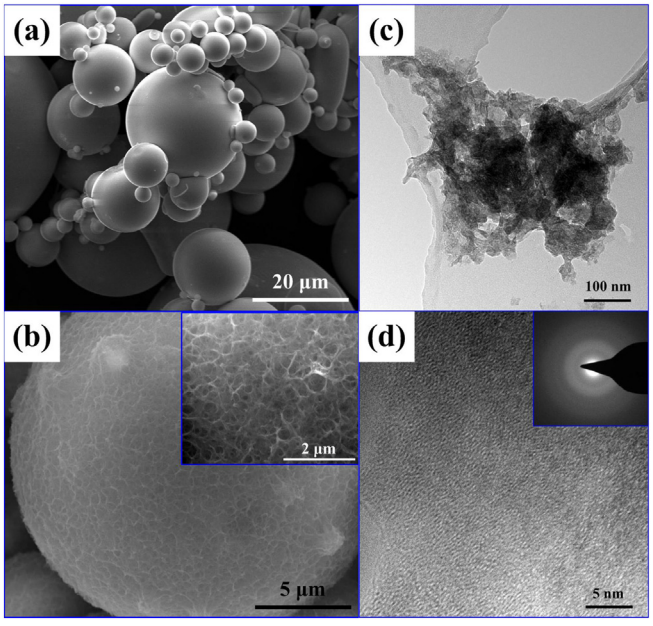

Fig. 1. SEM images of gas-atomized Ti-based metallic glassy powders (a) and core-shell D-powders-120 (b) BF-TEM morphology (c) and HR-TEM image (d) of D-powders-120 sample. Inset of (d) shows corresponding SAED pattern.

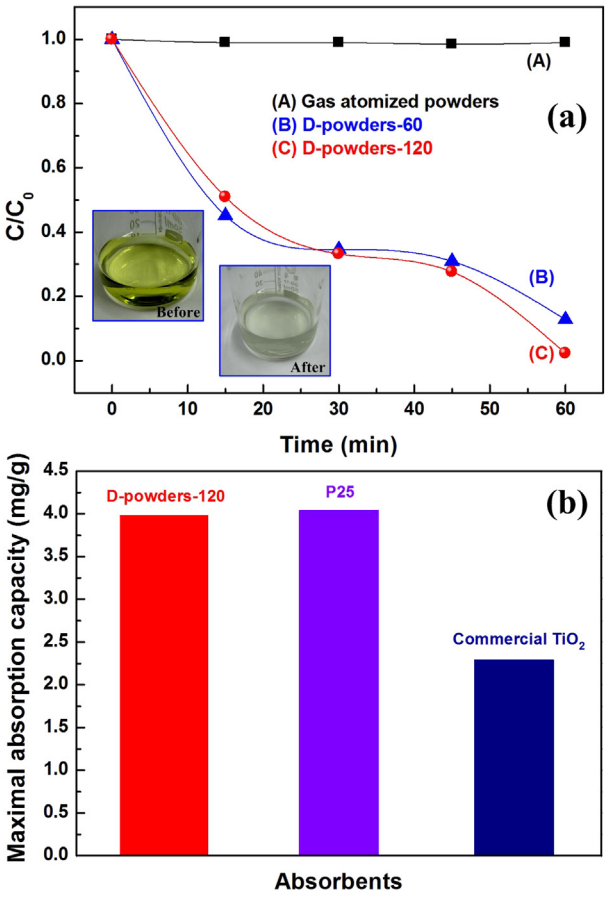

Fig. 2. Removal of Cr^{6+} solution as a function of time (a) and maximal absorption capacity (b) over different powder samples. Inset of (a) show the appearances and colors of Cr^{6+} solution before and after the removal by D-powders-120 sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)