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Corrosion behavior of porous Ti_3SiC_2 in nitric acid and aqua regia

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Abstract: Porous Ti_3SiC_2 with high purity was synthesized using TiH_2, Si and C powders with mole ratio of Ti to Si to C being 3:1.2:2 by reactive synthesis method. The corrosion behaviors of porous Ti_3SiC_2 in nitric acid and aqua regia were investigated by immersing test. Scanning electron microscope (SEM), X-ray diffractometer (XRD), energy dispersive spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS) were used to analyze the morphology, compositions and element contents of the samples before and after corrosion to determine the corrosion product and corrosion mechanism. The mass loss values of porous Ti_3SiC_2 are 26.9 and 132.5 μg/cm^2, respectively after immersing in nitric acid and aqua regia for 600 h. The results indicate that Ti_3SiC_2 transforms to Ti_5Si_3 which has better corrosion resistance in nitric acid and aqua regia with mass loss values of 9.34 and 7.06 μg/cm^2 under the same immersing time, respectively. The dramatic dissolution of porous Ti_3SiC_2 in the acids is due to its special microstructure.
Key words: porous Ti_3SiC_2; Ti_5Si_3; nitric acid; aqua regia; reactive synthesis; corrosion behavior; mass loss

1 Introduction

In recent years, a family of layered ternary metal ceramics called MAX phases (where M is transition metal; A is an A-group element, mostly IIIA and VIA; X is C or N element) have attracted much attention due to their unique physical and chemical properties [1,2]. In this family, the representative is Ti_3SiC_2. There has been a great interest in the synthesis and characterization of this material after being discovered by JEITSCHKO et al [3]. Ti_3SiC_2 has a hexagonal crystalline lattice with parameters a=0.3068 nm and c=1.7669 nm [3], and the crystalline structure shows a typical laminate characteristic [4]. The special crystal lattice and bond structures make the material combine prominent properties of both ceramics and metals [5]. Up to now, the methods mainly including chemical vapor deposition (CVD) [6,7], self-propagating high-temperature synthesis (SHS) [8,9], reactive sintering [10,11], hot isocratic pressing (HIP) [12,13], hot pressing (HP) [14,15], spark plasma sintering (SPS) [16,17] and mechanical alloying (MA) [18,19] have been used to synthesize Ti_3SiC_2. However, high-purity Ti_3SiC_2 is difficult to be synthesized, and the purity depends on the processing parameters [5]. Besides, various properties of the synthesized Ti_3SiC_2 have also been studied systematically. Corrosion resistance is a key factor that must be considered in the application of chemical industry and metallurgy. The corrosion behavior of Ti_3SiC_2 in various acids, alkali and salt has been extensively studied [20,21]. JOVIC et al [20] discovered that Ti_3SiC_2 was quite stable and passivated in HCl, H_2SO_4 and NaOH solutions. TRAVAGLINI et al [21] studied the corrosion behavior of Ti_3SiC_2 in various acids and NaOH, and concluded that Ti atoms dissolved and Si atoms were in-situ oxidized to form a SiO_2-based layer on the surface, resulting in good corrosion resistance in acids. However, all the Ti_3SiC_2 reported is bulk material and the corrosion behavior in the strong oxidizing acids HNO_3 and aqua regia is not clear.

The corrosion behavior of porous materials in general, differed from that of the bulk materials of the same composition. Moreover, the pore morphology, porosity, pore size and pore surface condition also affect the corrosion process. A porous material was attacked not only on its surface but also from inside [22]. Although the excellent corrosion resistance of bulk Ti_3SiC_2 has

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been reported in Refs. [20,21], the corrosion behavior of porous Ti_3SiC_2 is necessary to be studied, and the variation of the pore structure should be considered, which is very important for the application of the porous material as a filter [23].

In this study, the corrosion behavior of porous Ti_3SiC_2 with high purity in HNO_3 solution and aqua regia was evaluated by immersing test. The microstructures and compositions before and after immersing in the solutions were characterized by SEM, EDS, XRD and XPS. The possible corrosion mechanism was proposed.

2 Experimental

2.1 Material synthesis

Porous Ti_3SiC_2 was prepared using commercially pure TiH_2, silicon and graphite powders as the starting materials. The purity of raw powders is 99.9% and their nominal composition is 72.1%TiH_2−16.3%Si−11.6%C with the mole ratio of Ti to Si to C being 3:1.2:2. Excessive silicon addition can make up for the evaporation loss of Si at high temperatures and ensure the purity of the samples. The powders were gently ball-mixed for 10 h using a powder rotator mixer, and then the mixed powders were formed into compact discs with dimensions of 30 mm × 3 mm under a pressure of 200 MPa at room temperature. The as-pressed compact discs were then sintered in a vacuum furnace with a pressure of 1×10^{-3} Pa using a step sintering method. During the heating process, the heating rate is 5 °C/min. The compacts were then initially sintered at 600 °C for 60 min to remove H from TiH_2. Then, the compact discs were held at 1350 °C for 3 h. The sintered discs were then cooled inside the vacuum furnace to the room temperature. Porous Ti_5Si_3 samples were also prepared by powder metallurgy method using TiH_2 and Si powders as the raw materials and finally sintered at 1200 °C for 2 h in the vacuum furnace.

2.2 Characterization

The macroscopic morphology of porous Ti_3SiC_2 was revealed by 3D X-ray microscope (Xradia VersaXRM−500−3D X-ray microscope). The specimens before and after immersing were characterized by field-emission scanning microscopy (Nova Nano SEM 230) equipped with an energy dispersive spectroscopy (EDS) system to study the morphology and compositions. The phase compositions of porous samples were analyzed by X-ray diffraction (XRD Dmax 2500VB) using a Cu K_α source. The open porosity of Ti_3SiC_2 was measured using Archimedes method and the pore size was determined on a porous material test instrument based on the bubble point method with N_2 as the fluid medium. The surface area of the porous Ti_3SiC_2 was measured using Brunauer–Emmett–Teller (BET) method (Monosorb, Quatachrome). The surface compositions of the samples were detected by X-ray photoelectron spectroscopy (XPS K-ALPHA)

2.3 Immersing test

The immersing tests were conducted at room temperature for 600 h. Five parallel samples were immersed in enough concentrated nitric acid (HNO_3, 68%, mass fraction), dilute nitric acid (HNO_3, 11%) and aqua regia to make sure the ratios for solutions and samples are larger than 20 mL/cm^2 according to standard ASTM NACE/ASTM G31−2012a [24]. The samples were periodically removed from solutions, rinsed in ultrasonic cleaner with deionized water and acetone 5 times respectively, and then dried in vacuum drying oven. Mass changes were measured on an analytical balance with a resolution of 0.1 mg for every cycle over a whole period.

3 Results and discussion

3.1 Characterization of synthesized porous Ti_3SiC_2

Figure 1(a) shows the macrograph of the synthesized porous specimen obtained layer by layer scanning with 3D X-ray microscope. From the edge of the image, it can be seen clearly that the pores are uniformly distributed in the whole body, and the overall and open porosities are 54.3% and 48.6% measured according to the Archimedes method, respectively. Figure 1(b) shows the SEM image of the porous sample, indicating that the pores are abundant. Figure 1(c) shows the pore diameter distribution of the porous sample, demonstrating that the average pore diameter is 6.2 μm, which is significantly narrower compared with most conventional porous metals, proving that the pore size of porous Ti_3SiC_2 is uniform. The specific surface area was measured to be 0.53 m^2/g by BET method. Figure 1(d) shows the corresponding EDS spectrum, indicating that there are three elements Ti, Si and C, and the mass ratio of Ti to Si to C nearly the same as the element compositions of Ti_3SiC_2. Figure 2 shows the XRD patterns of the compacts before and after sintering. From the XRD patterns, we can find that after sintering, the raw materials of TiH_2, Si and C (Fig. 2(a)) have completely transferred to Ti_3SiC_2 (JCPDS No. 74−0310). The purity of Ti_3SiC_2 calculated using the calibrated standard addition method [25] is 99.4%, much higher than the value reported previously [5].

3.2 Immersion test results

Mass loss curves from immersion testing in HNO_3 and aqua regia are plotted in Fig. 3. It is obvious that the mass of Ti_3SiC_2 is nearly constant in concentrated HNO_3