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Electrochemical hydrogen storage in $TiC_{0.6}$, not in $TiC_{0.9}$

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ABSTRACT

We demonstrate that hydrogen can be electrochemically loaded, at room temperature, in the non-oxide ceramic $TiC_{0.6}$. A capacity of 2.9 wt.% is easily reached, corresponding to the formula $TiC_{0.6}H_{1.6}$. We also demonstrate that hydrogen absorption was not possible in $TiC_{0.9}$. This surprising result is interpreted in terms of absence of long-range ordered carbon vacancies, contrary to $TiC_{0.6}$. It seems that $TiC_{0.6}$ behaves like an intercalation compound for hydrogen.

1. Introduction

Titanium carbide, TiC, is a non-oxide ceramic possessing remarkable physico-chemical properties like exceptionally high melting point (3067 °C), high hardness ($H_V = 28$ GPa), excellent resistance to aqueous corrosion ($j_{corr} = 36$ nA/cm^2 in 1 M H_2SO_4), and good thermal conductivity (from 21 to 45 W m^{-1} K^{-1} between ambient and 2100 °C). Thus, it is largely used nowadays in numerous industrial applications such as cutting tools, wear-resistant coatings, heat exchangers, etc. Three other properties of TiC – that are of importance for the present study – are, first, its face-centered cubic (fcc) crystal structure, then, its wide range of substoichiometry, i.e., TiC_x, $0.5 < x < 1$, and finally, its good electronic conductivity ($\rho = 10^{-6}\ \Omega$ m) [1–4].

Titanium metal, Ti, is a well known material for absorbing large quantities of hydrogen, including by electrolysis of acidic water. It leads to the formation of titanium dihydride, TiH_2, and so to an hydrogen storage capacity of 4.0 wt.%, potentially. Although simple metal hydrides were almost abandoned in the past years as candidates for carrying hydrogen because of lacks of reliability, stability, rapid dehydriding, etc., they are regaining interest now that these materials can be synthesized at the nanometer scale. Nevertheless, the issue that remains is hydride embrittlement. Indeed, Ti having an hexagonal crystal structure, and TiH_2 an fcc one, decripitation occurs at room temperature after several hydriding–dehydriding cycles, causing ruin of the material [5–8].

Herein, we report on the synthesis of TiC_x ceramics, with $x = 0.6$, 0.7, 0.8, and 0.9, and want to provide the first insights into electrochemical hydrogen absorption in this type of material. To the best of our knowledge, this has not been previously reported, and shows very promising results concerning storage capacity and diffusion of hydrogen into the carbide, and also concerning stability, the reactant TiC_x and the product TiC_xH_y both having an fcc structure with close lattice parameters [9].

2. Experimental

2.1. Synthesis

TiC_x samples were prepared by reactive hot pressing, directly from powder mixtures of pure Ti and graphite, following the reaction

$$Ti + xC \rightarrow TiC_x \qquad (1)$$

Graphite powder (purity 99.5%, 325 mesh) was purchased from Cerac, USA, and titanium powder (purity 99.95%, <2 μm) from Neyco, France. Both were used as received, without further purification. Powders were mixed together in pure acetone. The stirring lasted for 24 h, to promote intimate mixing. True values of x at $\pm 10^{-3}$ were 0.599, 0.703, 0.807, and 0.896. The stoichiometric compound $TiC_{0.98\simeq 1}$ was purchased from Cerac (purity 99.5%).

Powders were sintered (La Physique Appliquée furnace, France) at 1815 °C at a pressure of 40 MPa, in a 15-mm graphite die, coated inside with boron nitride, BN. Pure argon atmosphere was used, to prevent oxidation. The temperature program was composed of a first segment from ambient temperature to 1600 °C at a rate of

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0.25 °C/s. Then, of a second segment from 1600 to 1700 °C at a rate of 0.016 °C/s in order to avoid melting of unreacted titanium metal. Subsequently, the sintering temperature was reached at a rate of 0.25 °C/s, and held for 3.5 h (12,600 s). To finish, the cooling from 1815 °C to ambient was done at a rate of 0.13 °C/s. The 40 MPa pressure was applied at 1100 °C, and released after the 3.5 h hold.

2.2. Characterization

Density of sintered samples was determined using Archimedes method. The obtained pellets were at least 99% dense. Scanning electron microscopy, SEM, was performed using a Philips XL 30 apparatus. Transmission electron microscopy, TEM, was carried out with a JEOL 2010 microscope operating at 200 kV, with in situ energy dispersive spectroscopy, EDS. X-ray diffraction, XRD, was done on a D8 Brüker diffractometer equipped with a copper anticathode and a backward monochromator. XRD patterns of TiC_x were obtained from pellets crushed into powder, using an agate mortar filled with liquid nitrogen.

2.3. Electrochemical apparatus

Electrochemical measurements were carried out at room temperature (25 °C) in a standard three-electrode cell configuration. An Autolab PGSTAT30 potentiostat was used, controlled by GPES 4.9 software (EcoChemie, The Netherlands). The reference electrode was a saturated calomel electrode, SCE, equipped with an extension of 1 M H_2SO_4. The counter-electrode was a platinum disk (10 mm in diameter) and the working electrode, WE, consisted in $TiC_{0.6}$ or $TiC_{0.9}$ pellets in a Teflon holder, with an effective surface area of 0.283 cm^2. The WE was mounted on a rotating disk electrode system EDI 101 (Radiometer-Analytical, France). Cyclic voltammograms were simulated with Comsol Multiphysics (Comsol AB, Sweden). File is available on demand.

3. Results and discussion

3.1. XRD and SEM

X-ray diffraction, XRD, was used to check the absence of impurities, mainly titanium oxides and unreacted reactants. As seen in Fig. 1A, the XRD pattern only shows peaks at $2\theta = 35.9°$, 41.7°, 60.5°, 72.4°, 76.1°, and 90.8°, due to diffraction of TiC fcc planes (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), and (4 0 0), respectively [9]. XRD was also used to determine lattice parameter, *a*, as a function of *x* (Le Bail method) [10,11]. The variation of *a* with *x* [1,12] is given in Fig. 1B, and its influence can be seen in the inset of Fig. 1A. Indeed, for the peak (4 0 0), a shift towards smaller values of 2θ is first observed as *x* increases from 0.6 to 0.9, and then towards higher values between 0.9 and 1. These XRD results show that pure TiC_x compounds have been obtained, with a controlled substoichiometry *x*. To finish, the SEM image of Fig. 2A shows a brittle fracture, typical of transition-metal non-oxide ceramics, and a grain size in the range 10–100 μm.

3.2. Electron diffraction

Electron diffraction, ED, was performed on samples at compositions $x = 0.6$, 0.7, and 0.9, using a TEM microscope. Fig. 2B, a–c shows the classical [1 1 0] zone axis of fcc-TiC (spots $1 1 \bar{1}$, 2 0 0, etc.), and Fig. 2B, d the EDS analysis, characteristic of all samples. This latter figure confirms the purity of TiC_x, i.e., the absence of oxides or oxycarbides. For $TiC_{0.6}$ (Fig. 2B, a), additional spots not belonging to the standard ED pattern of TiC, and not visible on Fig. 2B, c for $TiC_{0.9}$, can be observed at coordinates $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, $(\frac{3}{2}\frac{1}{2}\frac{1}{2})$, etc. This feature is reputed to be caused by layered and long-range ordered (LRO) carbon vacancies. Theoretically, at the composition $x = 0.67$, one third of {1 1 1} carbon planes is empty, the two other thirds being fully occupied, and at $x = 0.5$, {1 1 1} carbon planes are alternately full and empty [13–15]. For $TiC_{0.7}$ (Fig. 2B, b), periodic and diffuse streaks, with maxima centered at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, $(\frac{3}{2}\frac{1}{2}\frac{1}{2})$, etc., were observed and interpreted in terms of disappearance of long-range order, a short-range order (SRO) yet remaining [13–15].

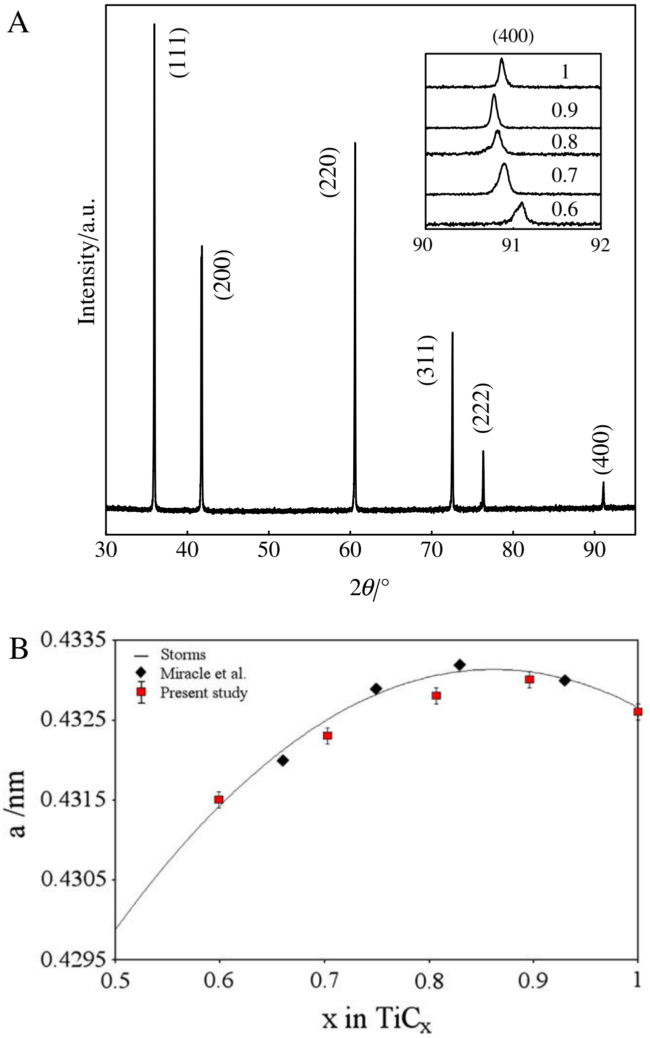

Fig. 1. (A) XRD pattern of the prepared $TiC_{x=0.6}$. Inset: peaks (4 0 0) for five different compositions, $x = 0.6$, 0.7, 0.8, 0.9, and 1. (B) Evolution of TiC_x lattice parameter with *x*. Line and squares, see Refs. [1,12].

3.3. Electrochemistry

Electrochemical measurements were carried out on $TiC_{0.6}$ and $TiC_{0.9}$, in order to test hydrogen absorption for these two different compositions.

3.3.1. $TiC_{0.6}$ electrode

Fig. 3a shows the initial cyclic voltammogram, CV, of $TiC_{0.6}$ in 1 M H_2SO_4. It was recorded in the range −0.5–0.5 V/SCE at a scan rate of 25 mV/s, before any electrochemical treatment. The initial zero-current potential, $E_{j=0}$, was around +0.2–0.3 V/SCE. The observed background current was low, i.e. ca. 1 $\mu A/cm^2$, and showed neither oxidation nor reduction waves, indicating stability of the electrode in this potential range. Then, the electrode was cathodi-