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Valence states, impurities and electrocrystallization behaviors during molten salt electrorefining for preparation of high-purity titanium powder from sponge titanium

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Abstract: High-purity titanium powder was prepared by molten salt electrorefining from sponge titanium in NaCl−KCl−$TiCl_x$ salts. The titanium valence, purity and electrocrystallization during electrolysis process were studied. The XPS analysis showed that the titanium valences are mainly +4, +3 and +2 at the earlier, medium and later stages of electrolysis, respectively. During the electrolysis process, the contents of impurities Si, Cr, Mn, Al vary little, and the contents of impurities Fe, Cu, Ni decrease markedly, while the contents of impurities O, N, H increase obviously. The residual impurities are usually distributed in small tunnel of dendritic crystals. Enhancing the electrolysis temperature and prolonging the electrolysis time can increase the titanium particle size. The TEM analysis showed that the electrodeposited titanium is not a single crystal, but contains many nanostructured grains and subgrains, with grain size of 100−500 nm. The electrolysis mechanisms were also discussed.

Key words: molten salt electrolysis; high-purity titanium; powder; valence; electrocrystallization

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1 Introduction

High-purity titanium powder is the titanium material with purity reaching or exceeding 4N grade (99.99%). In addition to the universal properties of titanium, such as high melting point, low density, good corrosion resistance, and nonmagnetic, the high-purity Ti powder possesses excellent mechanical, electronic, biological, adsorbent properties, etc [1,2]. Therefore, the high purity Ti powder is now widely used in powder metallurgy, biofabrication, integrated circuit target, high vacuum suction, etc. Up to now, the demand for high purity Ti powder is rapidly increasing with the development of various high-tech areas. Consequently, investigation into the preparation of high-purity Ti powder has profound importance [3].

At present, the traditional procedures for preparation of high-purity titanium powder have two main steps. The first step is the preparation of high purity bulk Ti material from raw Ti by hot reduction (Kroll method) [4−6], thermal cracking of Ti halogenated salt [7], electron beam fusion [8], molten salt electrolysis of $TiCl_4$ [2,9,10], electrochemical reduction of TiO_2 [11−15]. The second step is atomizing the high purity Ti melt. However, the conventional procedures have the following insufficients. First, the traditional procedures are complex trival, low yield rate, limiting the practical industry production. Second, the traditional methods have high requirements for raw material, which inevitably increase the cost. Third, the two steps would easily lead to the impurities pollution, which seriously deteriorate the purity of Ti powder. Fourth, the traditional methods have a purification limitation that some impurities could not be removed thoroughly. For example, the electron beam fusion could not easily remove the Fe, Ni, O elements. Fifth, the powder characterisations by traditional methods could not be controlled easily. Above all, it is obvious that the traditional Ti preparation produces are currently severely hindering the development of Ti industry, and a new preparation method for preparation high-purity Ti is necessary.

The molten salt electrolysis (MSE), not only can produce high purity Ti from Ti sponge, but also can prepare Ti powder flexibly by cathodic reduction of the Ti from ion to crystal, exhibiting advantages in the

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preparation of high-purity Ti powder. Our previous work has preliminary reported preparaing high-purity titanium by MSE [10]. However, the valence variation, electrocrystallization mechanisms, and the electrocrystallization are not investigated, although the above scientific issues are very important in deeply understanding and controlling the electrolytic powder quality. In this work, the high-purity Ti powder is prepared by MSE. The valence state evolution of Ti ion, impurities distribution and the effects of electrolytic conditions on the powder characterizations are studied.

2 Experimental

Figure 1 shows the molten salt electrolysis apparatus schematically. The MSE equipment included charging, electrolytic and vacuum systems. The anode was a nickel basket which contained titanium sponge and the cathode was the pure titanium. During the electrolysis process, at the anode, the Ti sponge lost electron and became low valence Ti ion, accordingly deposited on the cathode by reduction reaction, and thus Ti powder can be obtained. The following is the detailed experimental procedures. First, the molten salt, which was composed of NaCl and KCl, was dried in vacuum to remove the H and O elements before the electrolysis. After drying, the electrolyzer was heated and then a certain amount of $TiCl_4$ was added and reacted with the Ti sponge, forming the $TiCl_3$, $TiCl_2$ and attendant NaCl−KCl−$TiCl_x$ molten salt. The electrolysis experiment was performed by direct-current power supply at Ar protecting atmosphere. The electrolysis temperature was 500−800 °C. The electrolysis time was 28−41 h. When the electrolysis was finished, the anode and the cathode were all shifted up immediately from the molten salt. At last, the electrolysis product was cleaned to remove the molten salt and obtain Ti powder. After electrolysis, the elemental compositions were detected by inductively coupled plasma-atomic emission spectrometry (ICP-AES), glow discharge mass spectrometry (GD-MS) and electron probe micro-analysis (EPMA). The morphology of titanium powder was analyzed by scanning electron microscopy (SEM). The valence state was analyzed by X-ray photoelectron spectroscopy (XPS). The inner microstructure of electrodeposited titanium was characterized by focused ion beam (FIB) and transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM) with selected area electron diffraction (SAED) pattern.

3 Results and discussion

3.1 Ti valence states evolution

In order to disclose the valence state evolution of Ti ion, the molten salts were extracted for XPS analysis at electrolysis time of 10, 20 and 30 h respectively, and the results are shown in Fig. 2. The various valences and contents of titanium at different electrolysis stages are listed in Table 1. At electrolysis time of 10 h, there are two peaks, indicating the existence of +3 and +4 valences of titanium (Fig. 2(a)). When the electrolysis time is extended to 20 h, there are four peaks and at least three kinds of valence, corresponding to +1, +3 and +4 valences (Fig. 2(b)). When the electrolysis time is further increased to 30 h, the three Ti peaks reveal the valence states of +1 and +3.

At the earlier stage of electrolysis, the main valence of Ti is +4 with the content of 87.6%, and the Ti content of +3 valence is only 12.37%, while there is no existence of +2 valence Ti. It can be understood by considering the chemical reaction equilibrium constants between Ti ion and Ti, as shown in Table 2. There are four chemical reactions between Ti ion and Ti. It can be seen that the equilibrium constant of +2 valence Ti generation is lower

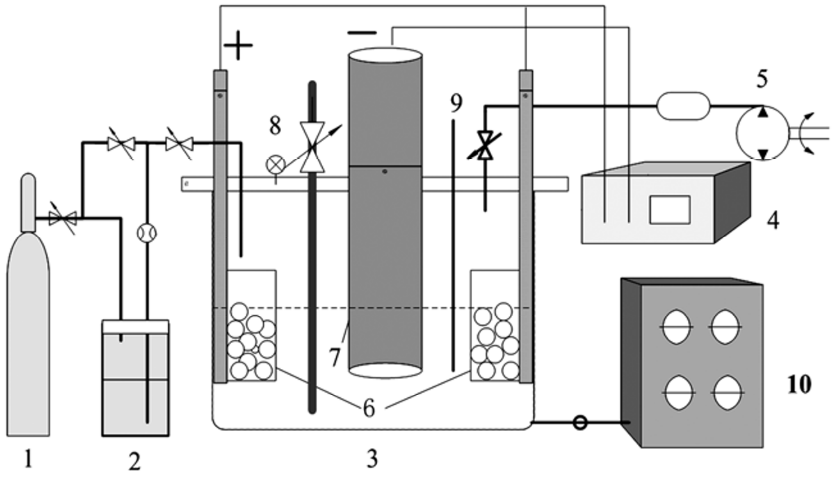

Fig. 1 Apparatus diagram of molten salt electrolysis: 1—Ar gas; 2—$TiCl_4$ storage tank; 3—MSE refining slot; 4—DC power supply; 5—Vacuum pump; 6—Anode basket; 7—Cathode plate; 8—Vacuum gauge; 9—Thermocouple; 10—Temperature control device