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Preparation of zirconium by electro-deoxidization in molten salt

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Abstract：Metal zirconium was prepared by electro-deoxidization method. Using $CaCl_2$ molten salt as electrolyte, sintered ZrO_2 pallets as cathode, graphite rod as anode, the pallets were electrolyzed at 900 ℃ and 3.1 V for 8, 10 and 12 h, respectively. The mechanism of electro-deoxidization of ZrO_2 was studied preliminarily. The results show that the morphologies of cathode pallets affect the forming process of products. The process of electro-deoxidization of ZrO_2 in the molten salt is conducted step by step, from exterior of cathode to its interior and from high valence oxide to low valence oxide until to metal.

Key words: ZrO_2; zirconium; electro-deoxidization; molten salt

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1 Introduction

Zirconium is important rare metal and strategic material[1], the strategic value is that it has lower thermal neutron capture cross section. Zirconium is applied widely in atomic power reactor as cladding and structure material[2]. Because of strong affinity of zirconium and oxygen，tremendous heat energy is given out when it is combusting, it is used as important raw material of ammunition manufacture. Because of the good machine properties, zirconium is applied widely in conventional weapon as alloying agent. Zirconium powder is the important material of electronics in industry[3], especially large emissive power electronic tube. Demand of zirconium is increasing when nuclear power station is rapidly developed in China. Key problem of development of Chinese nuclear power station in the future is domestic zirconium and reducing the cost, so intensively developing sponge zirconium is the substance foundation of nuclear power station[4].

Magnesium reduction process (Kroll process) is the main manufacturing method of metal zirconium[5−6]. There are three procedures during Kroll process to produce sponge zirconium: 1) decomposition of zircon sand and preparation of $ZrCl_4$; 2) separation of Zr and Hf; 3) purification of $ZrCl_4$, and preparation of sponge zirconium by magnesium reduction process. The Kroll process has drawbacks of complicated process, high cost, high energy consumption, pollution by toxic chlorine gas，which cause higher price for zirconium and then restrict its application. So new preparation technology for zirconium and its alloy need to be developed, which is short process flow, low cost, and environmentally friendly, to make much extensive application and strong demand for zirconium and its alloy.

The report of a new process for preparing metal titanium by reduction of solid TiO_2 through molten salt electrolysis[7] attracts a lot of attention in the world, and the new process has been successfully applied to preparation of other metals. Compared with the traditional method, the new process is a one-step process, which has become research hot spots. The metal is prepared by electrochemical deoxidation from solid oxide material, for this reason, process flow is shorted, energy consumption and pollution are significantly lowered.

In this paper, the metal zirconium was prepared by electro-deoxidization method in molten salt, effect of the cathode pallets morphology on forming process of products was mainly researched, and mechanism of ZrO_2 electro-deoxidization was also studied preliminarily.

2 Experimental

2.1 Preparation of cathode pallets

The main raw materials were as follows: ZrO_2 powder (AR), Tianjin Fuchen Chemical Reagent

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Factory), anhydrous $CaCl_2$(Tianjin Baishi Chemical Reagent Factory); high purity graphite crucibles. ZrO_2 powder was pressed by cold iso-static pressing (CIP), sintered at high temperature, and then made to cathode pallets.

2.2 Electrolysis experiments and characterization

Proper quantity anhydrous $CaCl_2$ was put into a high purity graphite crucible, then the crucible was put into a stainless steel reactor which was filled with argon and heated to 900 ℃ by temperature-programmed tube furnace, during electrolysis, sintered ZrO_2 sample pallets cathode which was hanged on the electrode leader was inserted into molten $CaCl_2$ in graphite crucible, anode was d 20 mm×3 mm graphite rod, the pallets were electrolyzed at 900 ℃ at a constant voltage for 8, 10 and 12 h, respectively. Electrolysis electric supply was WYK-3030 DC voltage-stabilized power supply. After electrolysis, the product was cleaned in 1% HCl solution and distilled water by ultrasonic cleaning machine separately, then it was rinsed with distilled water, dried in low temperature electric baking oven at 100 ℃. The microstructure and morphology of the cathode products were studied by JSM-6400 scanning electron microscope (SEM). The contents of the products were analyzed by INCA X-sight energy dispersive spectrum (EDS). Phase composition of the products was studied by D/max 2200PC X-ray diffractometer(XRD). The diffractive conditions were as follows: anode was Cu target and the diffraction angle (2θ) was in rang of 10°−80°, the scanning speed was 2°/min, the electron acceleration voltage was 40 kV, the work current was 40 mA.

3 Results and discussion

3.1 Effect of morphology of cathode pallets on product

Fig.1(a) and (b) show the SEM images of ZrO_2 pellet before and after electrolysis separately. It is shown that the morphology of sintered ZrO_2 pallet is agglomerated particle which were packed together and the size of the particles is 3−5 μm. After electrolysis at 3.1 V for 12 h, the particles grow to about 5−10 μm, whose morphology has converted to porous nodular structure, that is typical sponge zirconium structure. Fig.1(c) shows the XRD pattern of the product. Contrast analyses on XRD patterns of product and zirconium standard patterns, XRD patterns of the product dovetails nicely with zirconium standard patterns, namely, the product is metal zirconium. The composition of the products was analyzed by EDS, the results show that the composition of metallic zirconium is 94%(mass fraction). As zirconium is similar to titanium in that it has considerable solubility for oxygen in the solid state, it takes more time for the oxygen to diffuse in the zirconium granules to get pure metallic zirconium, from now on how to prepare pure metallic zirconium is the main research subject.

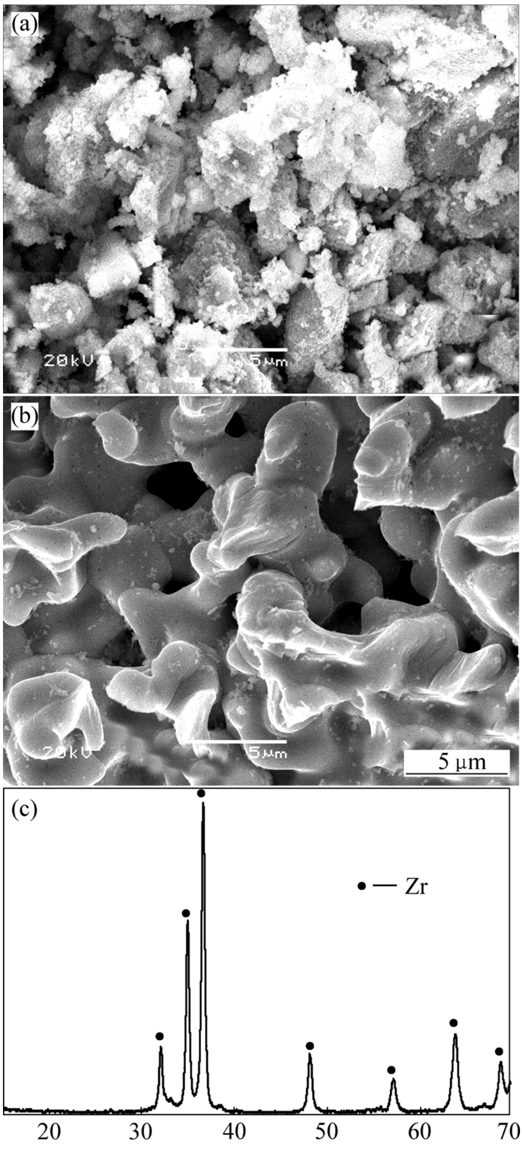

Fig.1 SEM images of ZrO_2 pellet before (a) and after(b) electrolysis at 3.1 V for 12 h in molten $CaCl_2$ at 900 ℃and XRD patterns of product (c)

The current—time plot of electrolysis of ZrO_2 is shown in Fig.2. The current density is higher at the very beginning of electrolysis, but decreases few minutes latter, from then on, the variation of current density is very slowly, after 250 min, current increases slightly. The rate of extraction of ZrO_2 by electrolysis in molten salt was determined by the following factors[8]: ① the transfer rate of oxygen ion from particle or Zr-O solid solution to cathode surface; ② the transfer rate of charge or electrolyte among pores of cathode; ③ diffusion rate of O^{2-} dissolved in molten $CaCl_2$ among pores of solid cathode; ④ the transfer rate of O^{2-} from outer surface of cathode to anode through electrolyte; ⑤ the electrochemical reaction rate of ZrO_2.

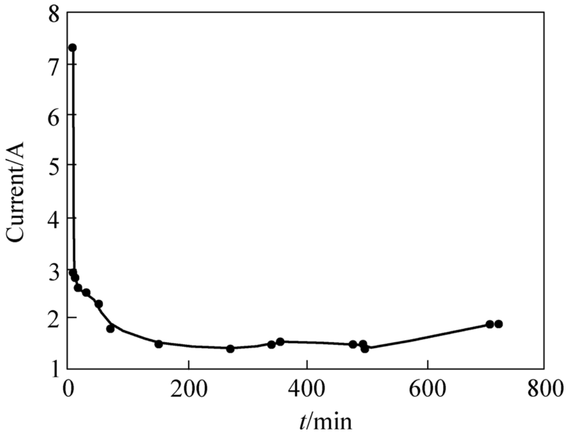

Fig.2 Current—time plot of electrolysis of ZrO_2 in molten $CaCl_2$(900 ℃, 3.1 V, 12 h)

Owing to that at the beginning, the reaction occurs on the surface of cathode, the reaction rate is controlled by electrochemical reaction, therefore at the very beginning, the current density is higher, then with the removal of the oxygen in cathode and electrochemical reaction, there is a layer of product formed on the surface. At the same time, the deoxidization reaction of ZrO_2 is exothermic reaction, so the metal zirconium product is slightly sintered which leads to the compaction of metal zirconium layer, this would hinder further permeation of molten $CaCl_2$ and transfer of oxygen ion to pallet surface, so the current density is decreased. Once all external ZrO_2 is deoxidized to metal zirconium, the current density of electrolysis would tend to stable. During this process, the deoxidization rate depends on diffusion of oxygen ion from interior of particles to interface of zirconium/molten salts. At the very beginning of electrolysis, the reaction is controlled by step ⑤, when a layer of zirconium metal is formed on the surface of pallet, the electrolysis reaction is controlled by steps ①−④. Increasing the diffusion rate of oxygen ion in cathode pallet will improve electrolysis rate, so grain size and porosity of pallet would affect the rate of electrolysis, electrolysis rate would be improved if porosity and active area of the cathode are increased properly. From current-time plot, after electrolysis 250 min, the current increases slightly, because the graphite anode is eroded during electrolysis. After experiment, there is a layer of black carbon on the surface of $CaCl_2$, emerging of black carbon wasted part of electrolysis current and decreases electrolysis efficiency.

3.2 Process and mechanism of metal zirconium

Zirconium oxide is an insulator, and as its main valence state is four, it is difficult to introduce electron into the oxide structure. FRAY and CHEN[9] found that reduction started at the point adjacent to the lead wire, and then propagated quickly on the surface of the pallet leading to the formation of a porous zirconium metal surface layer, by further reduction of the oxide, gradually penetrated through the pallet. This surface metallization process was found to correspond approximately to an initial current peak against time, as zirconium has considerable solubility for oxygen in the solid state, it takes several hours for the oxygen to diffuse in the zirconium granules to the metal/salt interface.

To study the reduction process of ZrO_2, the morphology of different zone of non-completely reduction pallet were compared(Fig.3). SEM images of center is particle morphology Fig.3(a), no porous nodular structure, in intermediate zone of cross section, there is half porous nodular structure and half particle morphology Fig.3(b), the morphology of edge zone is completely porous nodular structure Fig.3(c), the change of morphology shows that the reduction reaction is processed from exterior to interior of the pallet. To further study the reduction process of ZrO_2, the pallets were electrolyzed at 900 ℃ and 3.1 V voltage for 8, 10 and 12 h, respectively, XRD patterns of the products are shown in Fig.4. From Fig.4, we know that the process of electro-deoxidization of ZrO_2 in the molten salt is conducted step by step, from high valence oxide to low valence oxide until to metal. From the products of different electrolysis time, the process of reduction is supposed as follows: the products electrolyzed for 8 h are Zr, Zr_3O, $Ca_2Zr_7O_6$, $ZrCl_2$, ZrCl, CaO and $Ca(OCl)_2$. At beginning, a great deal of O^{2-} deoxidized from ZrO_2 diffuse to anode, Ca^{2+} in the molten $CaCl_2$ diffuse to cathode。The possible reaction involved in reduction process is: $Ca^{2+} + ZrO_2 + O^{2-} \rightarrow CaZr_nO_m$, perhaps other amorphous oxides mesophase are produced during the reduction process. With the electrolysis time goes by, $CaZr_nO_m$ is deoxidized pretty fast, the content of CaO in pore of pallet is increased, then, low valence oxides like ZrO, Zr_3O, $ZrCl_2$ and ZrCl are produced. With further reduction of $CaZr_nO_m$ and producing of metal zirconium, CaO in pore of pallet is dissolved in molten $CaCl_2$ and transferred from pallet cathode to molten $CaCl_2$. After electrolysis for longer time, the metal zirconium is produced from exterior to interior. After electrolysis for 8 h, the pallets are delaminated obviously, the out layer is metallic zirconium, the inner layer is mesophase. The products electrolyzed for 10 h are Zr, Zr_3O, ZrO and

ZrCl, that is to say, after electrolysis for 10 h, $CaZr_nO_m$ is deoxidized gradually until it is exhausted, so the products are metal zirconium and little low valence oxide. The products electrolyzed for 12 h are mainly metal zirconium and very little ZrO, the content of ZrO is so low that the XRD peak of it is almost invisible**.** As zirconium is similar to titanium in that it has considerable solubility for oxygen in the solid state, it taks more times for the oxygen to diffuse in the zirconium granules to get pure metallic zirconium. So the study will focus on how to optimize the electrolysis condition to prepare purity metallic zirconium and to improve the current efficiency and production efficiency.

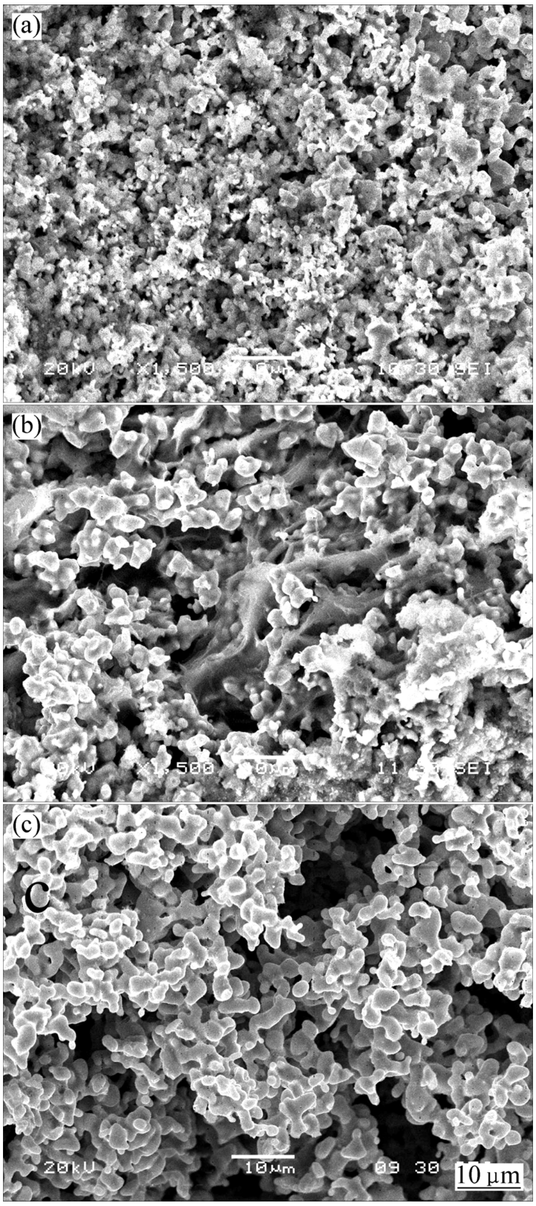

Fig.3 SEM images of different zone on cross section of product prepared from ZrO_2 by electrolysis at 3.1 V in molten $CaCl_2$ at 900 ℃ for 8 h: (a) Center zone; (b) Intermediate zone; (c) Edge zone of cross section

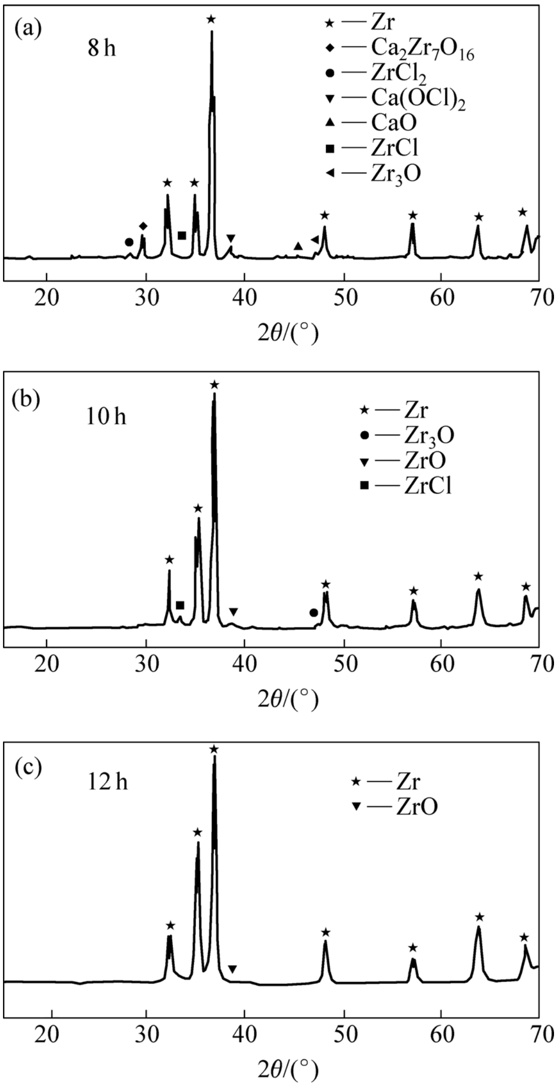

Fig.4 XRD patterns of products prepared from ZrO_2 by electrolysis at 3.1 V in molten $CaCl_2$ at 900 ℃ for 8 h(a), 10 h(b) and 12 h(c)

4 Conclusions

1) Metal zirconium can be prepared by electro-deoxidization of ZrO_2 in molten salts, current efficiency will be improved if enhancing the activity of cathode pallet and optimizing the electrolysis condition and design of electrolytic cell. The electro-deoxidization of solid ZrO_2 is a novel process to prepare the metal zirconium.

2) The process of electro-deoxidization of ZrO_2 in the molten salt is conducted step by step, from exterior of cathode to its interior, and from high valence oxide to low valence oxide until to metal, media products are $CaZr_nO_m$ and CaO.

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