



Electrolytic production of Ti–Ge intermetallics from oxides in molten CaCl₂–NaCl

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Abstract: Titanium germanium intermetallics (Ti₅Ge₃) were directly prepared from titanium oxide (TiO₂) and germanium oxide (GeO₂) powders mixture by using an electrodeoxidation process. The electrochemical experiment was carried out in a molten flux CaCl₂–NaCl at 800 °C with a potential of 3.0 V. The results show that monolithic germanide Ti₅Ge₃ intermetallic can be directly produced from TiO₂–GeO₂ or CaTiO₃–GeO₂ precursors (both molar ratios are 5:3), and the obtained Ti₅Ge₃ powders exhibit homogenous particle structure. In addition, the phase composition of the final product can be dramatically affected by the initial molar ratio of TiO₂ to GeO₂. The reaction mechanism of the electrodeoxidation process was discussed based on the experimental results. It is suggested that the electrodeoxidation process is an environmentally friendly method for the preparation of Ti–Ge intermetallics.

Key words: Ti–Ge intermetallics; oxides; electrodeoxidation; molten salt

1 Introduction

Titanium alloys are very attractive for the aerospace and chemical industries due to their lower density, high specific strength, excellent corrosion resistance, high melting point and good thermal property [1–4]. Moreover, the addition of IVA-group element into Ti-based alloys can further improve their corrosion resistance, mechanical property, and high temperature behavior [5–10]. The use of Ge alloys (i.e., germanides) for advanced applications in modern device technology is of current interest. Among these prospective applications, germanides are of interest in forming Schottky contacts on Ge [11]. FLEISCHER [7] has reported that Ti₅Ge₃ intermetallic compounds still have high strength at high temperature. ZAREMBO et al [9] and COLINET and TEDENAC [8] have studied the thermodynamic and mechanical properties of Ti–Ge

system. It was suggested that Ti–Ge intermetallic compounds have excellent mechanical and thermodynamic properties. The Ti–Ge phase diagram is shown in Fig. 1 [12]. Obviously, three intermetallic compounds, i.e., Ti₅Ge₃, Ti₆Ge₅ and TiGe₂, are stable in the Ti–Ge system. Based on the critical review of MURRAY [13] and the previous work [9,10], it is also concluded that the compounds Ti₅Ge₃, Ti₆Ge₅ and TiGe₂ are stable. Generally, the conventional process used to produce metal germanides commonly involves arc melting of the ultrapure elements Ti and Ge, which always suffered from high energy costs [10], because the conventional processes used for the preparation of Ge involve the reduction of germanium oxides or sulfides by hydrogen or carbon [14], and pure Ti is mainly produced by the Kroll process [15].

Direct extraction of metals and/or alloys from compounds without the production of hazardous substance is the trend in the future [16]. Processes with

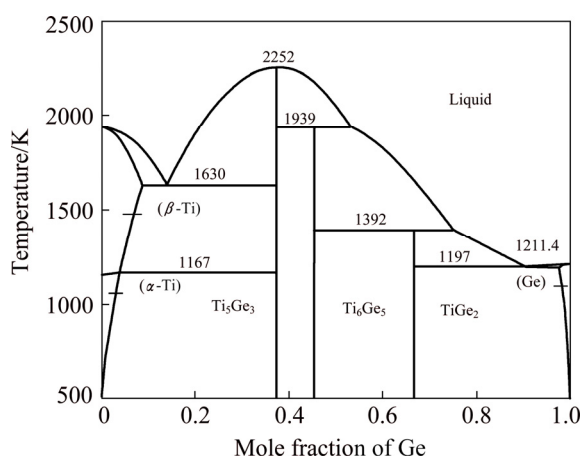


Fig. 1 Phase diagram of Ti–Ge system [12]

potential for reducing or even avoiding CO₂ emissions such as the electrodeoxidation technology would be especially desirable [5,17,18]. In recent years, the electrodeoxidation technologies have been used to produce a large number of metals and alloys in molten salts [19]. A variety of electrodeoxidation processes such as the Fray–Farthing–Chen (FFC) process and the solid oxide membrane (SOM)-assisted electrodeoxidation process are currently being investigated [15,19–25]. It has been proved that the electrodeoxidation of solid oxides in molten salts is an efficient and rapid approach for extracting metals, alloys and semiconductors [22]. The key innovation of this process is based on the thermodynamic fact that the decomposition voltages of many solid oxides are lower than those of the inorganic molten salts at high temperatures, ranging from 600 to 900 °C [15,19]. Therefore, based on the low decomposition voltage of TiO₂ and GeO₂, it is reasonable to believe that Ti–Ge intermetallics can be directly prepared from TiO₂ and GeO₂ powders mixture at 800 °C with a potential of 3.0 V by using the molten salt electrodeoxidation process.

The aim of this work is to report the success of applying the electrodeoxidation process to the preparation of titanium–germanium compounds directly from mixed TiO₂–GeO₂ powders with different molar ratios (5:3, 6:5, 1:2) in molten CaCl₂–NaCl. The effects of the stoichiometry of the initial mixtures on the characteristics of the final products were investigated. In addition, direct electrochemical preparation of Ti₅Ge₃ from CaTiO₃ and GeO₂ was also investigated. Taking Ti₅Ge₃ as an example, the specific reaction process and the formation mechanism were also described in details.

2 Experimental

Commercially available powder of titanium oxide, TiO₂ (Aldrich, ≥99.99%) and germanium oxide, GeO₂

(Aldrich, ≥99.99%) were used as raw materials. The two reagent grade oxide powders were mixed at different stoichiometric ratios and ball-milled with anhydrous alcohol for 10 h to ensure the maximum homogenization of the constituents. And about 0.3 g of the mixture was pressed to form a cylindrical pellet (10 mm in diameter and 3 mm in thickness) under a pressure load of 15 MPa. The pellet was then sintered in air at 900 °C for 4 h in a muffle furnace with a heating rate of 5 °C/min to obtain adequate strength and the desired porosity for the electrodeoxidation process. The sintered oxide pellet was sandwiched by two porous nickel foils and then attached to a Fe–Cr–Al alloy wire as a cathode. The anode was prepared by connecting a 150 mm-long and 10 mm-diameter graphite rod to a Fe–Cr–Al alloy wire. High purity CaCl₂ was produced by vacuum drying of calcium chloride dihydrate CaCl₂·2H₂O (99% purity) [26]. The eutectic mixture of NaCl–CaCl₂ was prepared by ball milling the dry pure CaCl₂ and NaCl (99% purity, $n(\text{CaCl}_2):n(\text{NaCl})=1:1$). About 160 g of the eutectic mixture was used as electrolyte in each experiment. Schematic illustration of the electrodeoxidation process for the electrosynthesis of Ti–Ge intermetallics from oxides precursors is illustrated in Fig. 2. The experiments were performed under an atmosphere of highly purified argon gas. Pre-electrolysis process was carried out before electrodeoxidation to remove the impurity contained in the molten salt. Then, the electrodeoxidation experiment was performed at 800 °C with a potential of 3.0 V. After the experiment, the samples were allowed to cool under a stream of argon gas in the furnace, then taken out of the furnace, washed with tap water to remove the residual solidified NaCl–CaCl₂ and dried under vacuum at about 90 °C.

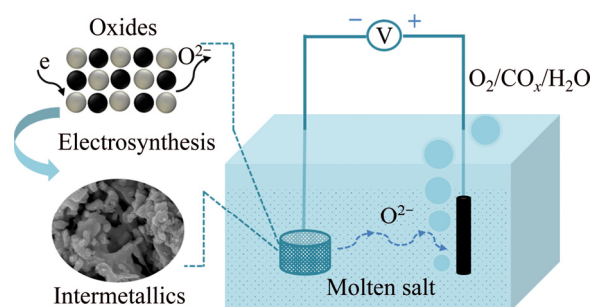


Fig. 2 Schematic illustration of electrodeoxidation process for electrosynthesis of Ti–Ge intermetallics from oxides (TiO₂/GeO₂) precursors

The phase composition of the starting materials and the products was characterized by X-ray diffraction (XRD, D8 Advance, Bruker) with the incidence beam angle of 2° in the range of 10°–80°. The surface morphology and elemental composition of the products were characterized by scanning electron microscopy

(SEM, JEOL JSM-6700F, Japan) and energy dispersive X-ray spectroscopy (EDX, Oxford INCA EDS system), respectively. A BioLogic HCP-803 electrochemical workstation was used to control and record the current-time curve during the electrodeoxidation process.

3 Results and discussion

3.1 Influence of sintering on raw material and current features

The influence of sintering on the raw material composition was investigated firstly to confirm whether there were new compounds generated during the sintering process. The XRD pattern of the mixed oxide pellet ($n(\text{TiO}_2):n(\text{GeO}_2)=5:3$) after being sintered at 900 °C for 4 h is given in Fig. 3. It is apparent that no peaks occurred other than those of the starting oxides, which indicates that the sintering process cannot influence the composition of the pellet precursor. Figure 4 shows the current-time curve recorded during the electrolysis of $5\text{TiO}_2-3\text{GeO}_2$ mixture pellet. Obviously, at the beginning of the electrodeoxidation process, the current increases with the expanding of the electrochemical three-phase interlines (3PIs) reaction area [23,27]. Then, the current decreases from approximately 1900 mA to around 400 mA after 30 min of electrolysis. After that, the reduction current gradually decreases and tends to be constant at a stable level (background current). It can be seen that the background current is approximately 200 mA. After being electrolyzed for different time, the XRD patterns of the pellet's outer and inner parts are shown in Fig. 5. It can be seen from Fig. 5(a) that the outer part of the pellet reduced for 5 h mainly contains Ti_5Ge_3 . In addition to Ti_5Ge_3 , the inner part of the reduced pellet still contains CaTiO_3 , Ge and Ti_6Ge_5 . To completely electrolyze the inner part of the pellet to form Ti_5Ge_3 , longer electrolysis time (8 h) is needed (Fig. 5(b)). It is obvious that the electrodeoxidation process for the pellet's interior is

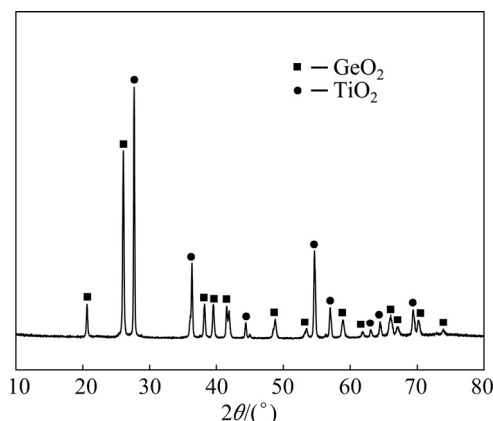


Fig. 3 XRD pattern of $5\text{TiO}_2-3\text{GeO}_2$ mixture pellet after being sintered at 900 °C for 4 h

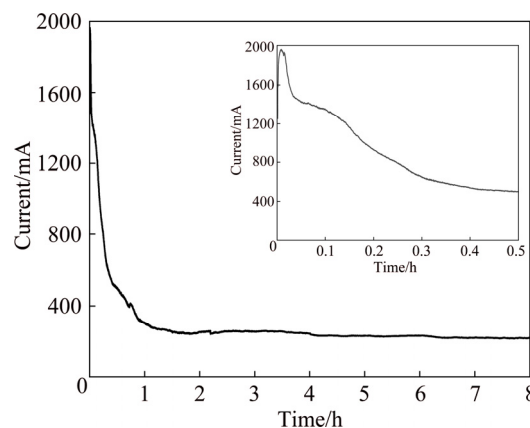


Fig. 4 Typical current-time curve recorded during electrolysis of $5\text{TiO}_2-3\text{GeO}_2$ mixture pellet under 3.0 V at 800 °C (The inset is initial part of current-time curve)

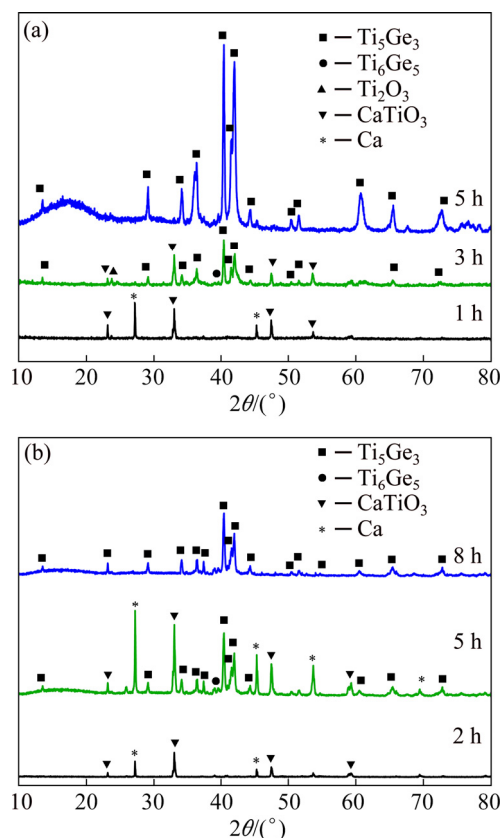


Fig. 5 XRD patterns of outer (a) and inner part (b) of $5\text{TiO}_2-3\text{GeO}_2$ mixture pellet after being electrolyzed under 3.0 V at 800 °C for different time

slower than that for the pellet's surface. Generally, the electrodeoxidation reaction occurs in the region of electronic conductor/oxide-compounds/electrolyte 3PIs and the 3PIs expand gradually from the surface to the center of the pellet [27].

3.2 Influence of reaction time and raw materials on final products

To investigate the influence of reaction time on the final products, the electrodeoxidation of mixed powders ($n(\text{TiO}_2):n(\text{GeO}_2)=5:3$) was carried out at 800 °C with a

constant voltage of 3.0 V for 2, 4, 6, and 8 h, respectively. Figure 6 shows the XRD patterns of the cathode pellets after being electrolyzed for different time. Obviously, the product electrolyzed for 2 h contains Ge, but no metallic Ti phase is observed. This observation may imply that GeO_2 was firstly electrodeoxidized to Ge following reaction (1):

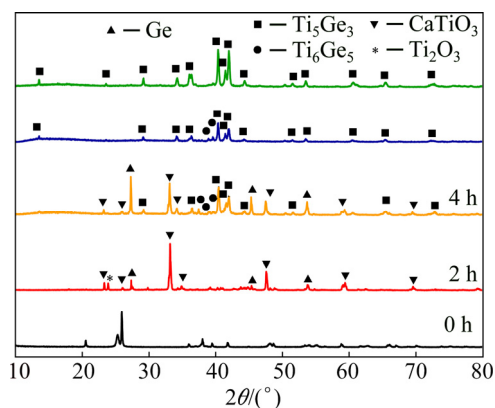
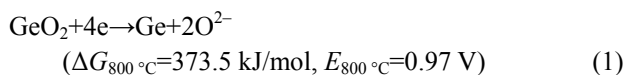
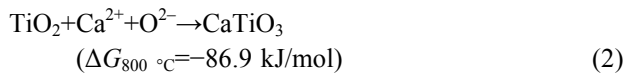
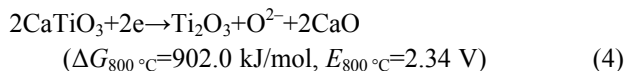
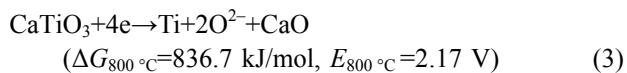


Fig. 6 XRD patterns of $5\text{TiO}_2\text{-}3\text{GeO}_2$ mixture pellet after being electrolyzed under 3.0 V at 800°C for different time

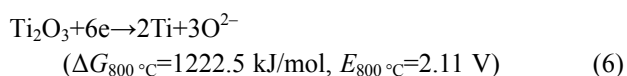
However, during the electrodeoxidation process, TiO_2 would convert into CaTiO_3 following Reaction (2):



The products obtained from 2–6 h electrolysis consist of Ti_5Ge_3 , Ti_6Ge_5 , CaTiO_3 and Ti_2O_3 (see Fig. 6), which may suggest that Reactions (3) and (4) occurred, i.e., Ca-containing intermediate compounds (CaTiO_3), were reduced to $\text{Ti/Ti}_2\text{O}_3$ [20] and CaO .



Then, CaO would dissolve into molten $\text{CaCl}_2\text{-NaCl}$ following Reaction (5), and Ti_2O_3 was further reduced to Ti following Reaction (6):



Generally, two simultaneous processes are involved during the synthesis of Ti_5Ge_3 , i.e., (1) Ge reacts with Ti to form Ti_5Ge_3 and Ti_6Ge_5 at the experiment temperature (Reactions (7) and (8)); (2) the formed Ti_6Ge_5 further reacts with Ti to form Ti_5Ge_3 (Reaction (9)).

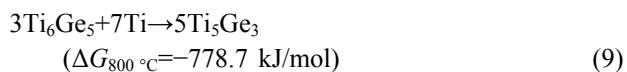
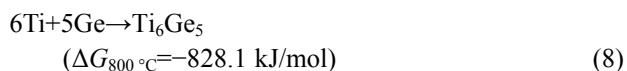
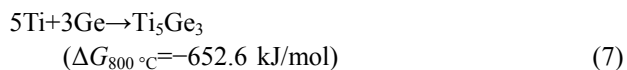


Figure 7 shows the typical SEM image and its

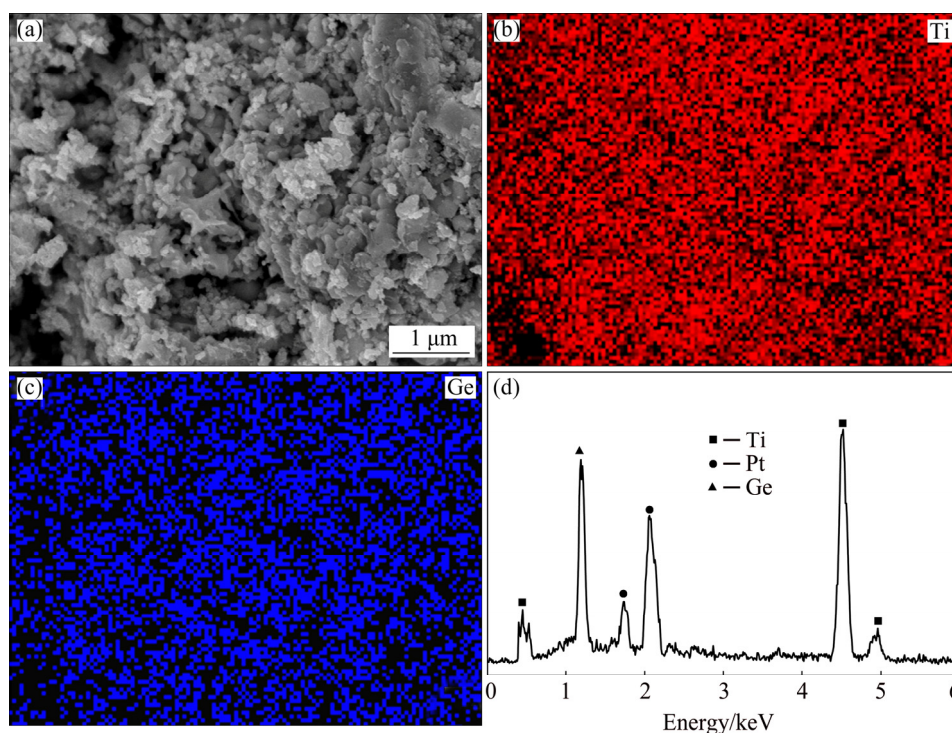


Fig. 7 SEM image of completely electrolyzed product (electrolyzed for 8 h) obtained from mixed powder pellet ($n(\text{TiO}_2):n(\text{GeO}_2) = 5:3$) under 3.0 V at 800°C (a), elemental maps of Ti (b) and Ge (c) corresponding to (a), and EDS spectrum (d) measured over image (a)

elemental maps (Ti and Ge) as well as EDS spectrum of the Ti_5Ge_3 product synthesized from a mixed powder pellet ($n(\text{TiO}_2):n(\text{GeO}_2)=5:3$). It can be seen that Ti and Ge elements are uniformly distributed in the product. In addition, Fig. 6 also demonstrates that CaTiO_3 occurred as an intermediate product during the synthesis of Ti_5Ge_3 . Therefore, based on this observation, we try to use $\text{CaTiO}_3\text{-GeO}_2$ as precursors to produce Ti_5Ge_3 . Figure 8 shows the current–time curve of the electrolysis of $5\text{CaTiO}_3\text{-3GeO}_2$ mixture pellet. It is found that the electrolysis of $5\text{CaTiO}_3\text{-3GeO}_2$ only needs 6 h. The current efficiency which can only be used as a general evaluation for the electrolysis process is defined as the ratio of the theoretical charge for reducing all oxides contained in the pellet and the total charge passed through the electrolytic cell. The current efficiency for Ti_5Ge_3 production from $5\text{TiO}_2\text{-3GeO}_2$ electrolyzed for 8 h is calculated to be 37.8%. As a comparison, the current efficiency for Ti_5Ge_3 production from $5\text{CaTiO}_3\text{-3GeO}_2$ electrolyzed for 6 h is calculated to be 40.2%. Figure 9(a) shows the XRD patterns of the mixed CaTiO_3 and GeO_2 powders ($n(\text{CaTiO}_3):n(\text{GeO}_2)=5:3$) after being electrolyzed for different time. Apparently, the reaction process of $\text{CaTiO}_3\text{-GeO}_2$ is similar to that of $\text{TiO}_2\text{-GeO}_2$, and Ti_5Ge_3 can be obtained as final

products. Figure 9(b) shows the XRD patterns of Ti_5Ge_3 obtained from different raw materials, i.e., $\text{CaTiO}_3\text{-GeO}_2$ and $\text{TiO}_2\text{-GeO}_2$. Obviously, the two Ti_5Ge_3 are similar. Figures 9(c) and (d) show the typical SEM image and EDS spectrum of the Ti_5Ge_3 synthesized from $5\text{CaTiO}_3\text{-3GeO}_2$ powder. The SEM image indicates that the Ti_5Ge_3 particles possess homogenous structure, and there is no other impurity elements contained in the product (Fig. 9(d)).

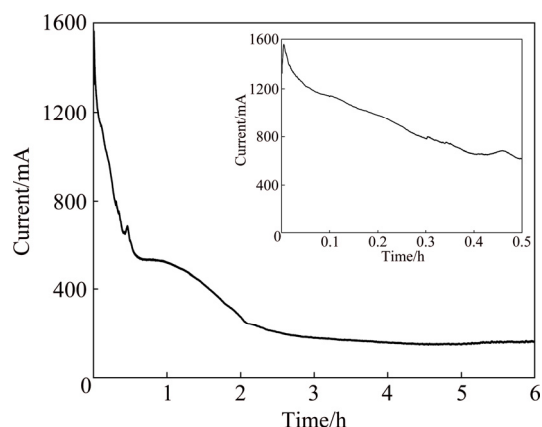


Fig. 8 Current–time curve recorded during electrolysis of $5\text{CaTiO}_3\text{-3GeO}_2$ mixture pellet under 3.0 V at 800 °C (The inset is initial part of current–time curve)

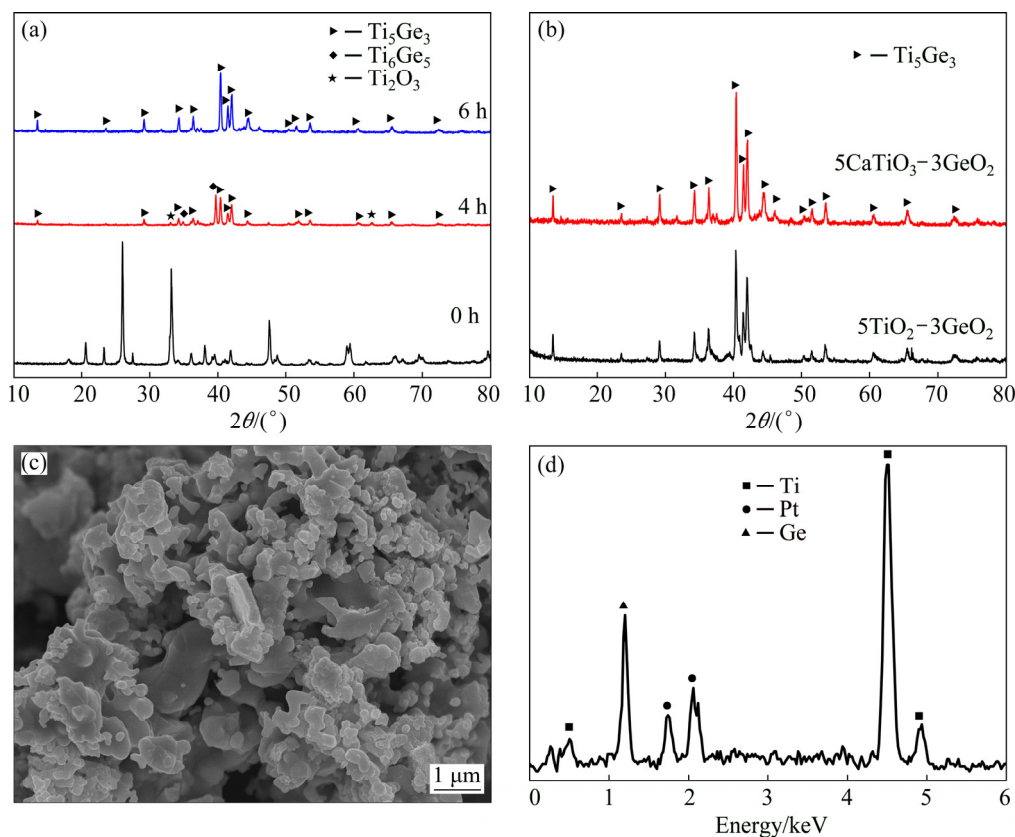


Fig. 9 XRD patterns of mixed $5\text{CaTiO}_3\text{-3GeO}_2$ powder pellet electrolyzed for different time under 3.0 V at 800 °C (a), XRD patterns of final products obtained from different raw materials under 3.0 V at 800 °C (b), SEM image of completely electrolyzed products (electrolyzed for 6 h) from mixed $5\text{CaTiO}_3\text{-3GeO}_2$ powder pellet under 3.0 V at 800 °C (c) and EDS spectrum (d) of obtained Ti_5Ge_3 product corresponding to (c)

3.3 Electrochemical synthesis of Ti_xGe_y

Electrolysis of TiO_2 - GeO_2 pellets with different starting stoichiometries, i.e., molar ratios of TiO_2 to GeO_2 =5:3, 6:5, 1:2, was also carried out at 800 °C for 8 h with a potential of 3.0 V. The XRD patterns and the SEM images of the completely electrolyzed products are shown in Figs. 10 and 11, respectively. A summary of germanide phases formed after electrolysis and the serial number of SEM images/XRD patterns with different starting molar ratios of TiO_2 to GeO_2 are listed in Table 1. Figure 10 reveals that a single-phase Ti_5Ge_3 intermetallic

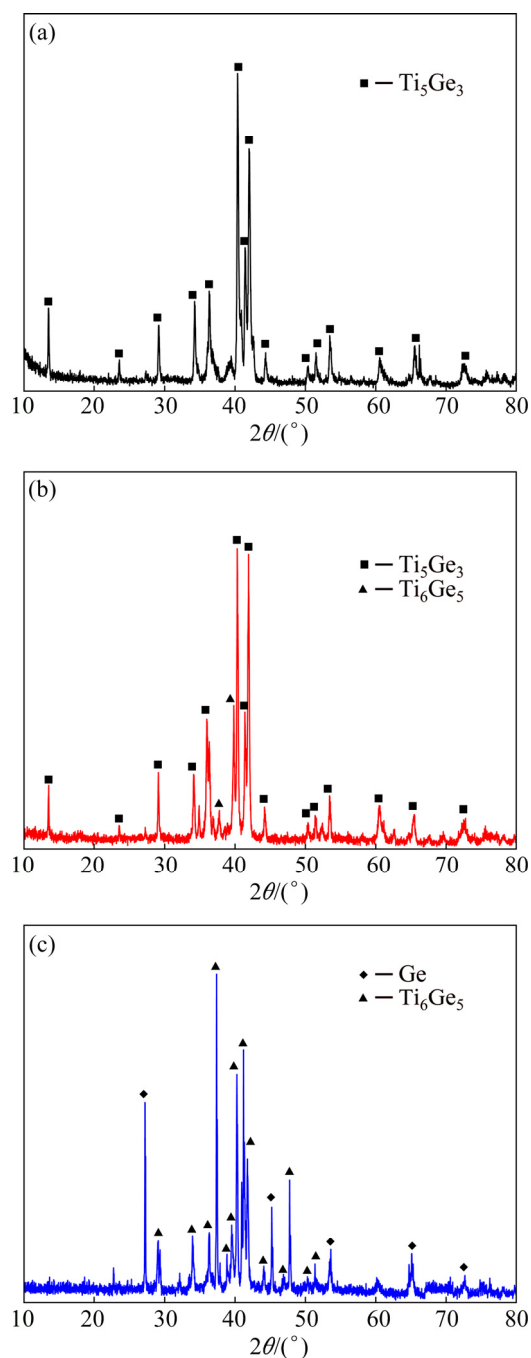


Fig. 10 XRD patterns of products completely electrolyzed for 8 h under 3.0 V at 800 °C from powder mixtures with different starting molar ratios of TiO_2 to GeO_2 : (a) 5:3; (b) 6:5; (c) 1:2

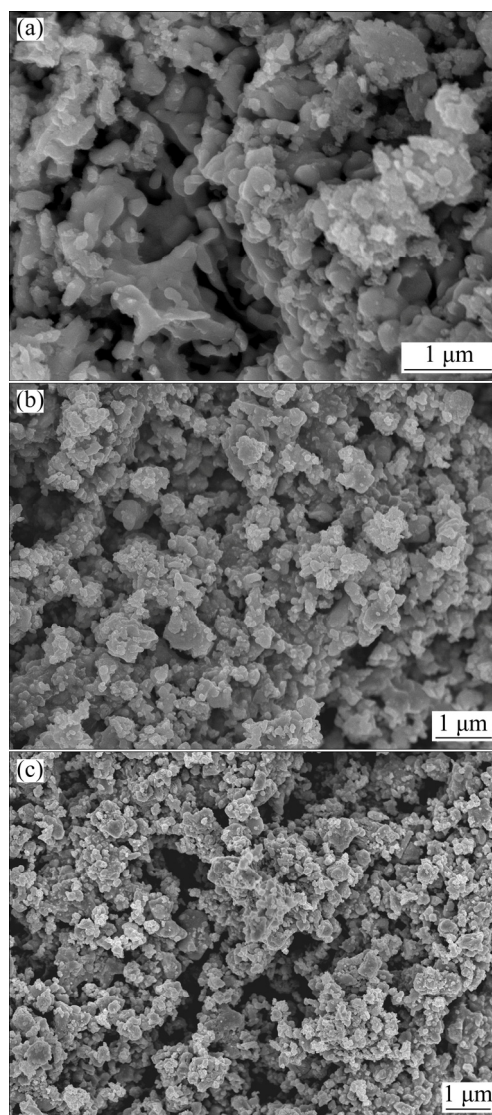


Fig. 11 SEM images of products completely electrolyzed for 8 h under 3.0 V at 800 °C with different starting molar ratios of TiO_2 to GeO_2 : (a) 5:3; (b) 6:5; (c) 1:2

Table 1 Summary of germanide phases of electrolytic products and serial number of SEM images/XRD patterns with different starting molar ratios of TiO_2 to GeO_2 under 3.0 V at 800 °C

TiO_2/GeO_2 molar ratio	Phase	XRD pattern	SEM image
5:3	Ti_5Ge_3	Fig. 10(a)	Fig. 11(a)
6:5	Ti_5Ge_3 - Ti_6Ge_5	Fig. 10(b)	Fig. 11(b)
1:2	Ti_6Ge_5 -Ge	Fig. 10(c)	Fig. 11(c)

is obtained when the TiO_2/GeO_2 molar ratio is 5:3, and two germanide phases, i.e., Ti_6Ge_5 and Ti_5Ge_3 , are formed as the product when TiO_2/GeO_2 molar ratio equals 6:5. The final product consists of Ti_6Ge_5 and pure metal Ge when TiO_2/GeO_2 molar ratio is 1:2. It should be noted that the XRD results cannot prove that the

oxygen content has been completely removed during electrolysis, a small amount of oxygen component may still exist in the products due to the fact that the molten salt electrolysis is difficult to completely remove the oxygen element. Figure 11 reveals that all final products possess porous morphologies. Additionally, the microstructures of the products obtained from different starting stoichiometries have slight differences. As shown in Fig. 11, the single-phase Ti_5Ge_3 obtained from $5TiO_2-3GeO_2$ exhibits homogenous particle structure, which shows a slight difference from the SEM images (Figs. 11(b) and (c)) of the other two products. The reason may be attributed to their different phase compositions.

3.4 Formation mechanisms

Based on the experimental result, a mechanism for the formation of Ti_5Ge_3 from TiO_2/GeO_2 by the electrodeoxidation process was suggested and summarized in Fig. 12. During the electrolysis, the intermetallic Ti_5Ge_3 was formed following a multi-step process, i.e., at the beginning of the electrolysis, when the applied voltage is higher than the decomposition potential of GeO_2 (GeO_2 0.97 V, TiO_2 1.94 V at 800 °C [28]), GeO_2 was firstly electrodeoxidized to Ge at 800 °C. Simultaneously, $CaTiO_3$ was formed during the electrodeoxidation process. Subsequently, $CaTiO_3$ compounds were reduced to $Ti-Ti_2O_3$ and CaO . Then, Ti_2O_3 was reduced to Ti, the formed Ti and Ge would react to form Ti_6Ge_5 and Ti_5Ge_3 . It is worth noting that there is a general trend that Ti_6Ge_5 was formed firstly during the electrolysis process, then the formed Ti_6Ge_5 would further react with Ti to form Ti_5Ge_3 if there is enough Ti. This experimental observation is supported by previous thermodynamic considerations [9,11,29]. In addition, the Gibbs free energy change of the reaction $5Ti+3Ge \rightarrow Ti_5Ge_3$ is negative at the electrolysis

temperature [11], which means that the electrodeoxidation-generated Ti and Ge can react to form Ti_5Ge_3 . Therefore, it is reasonable to believe that two reaction routes, i.e., $Ti, Ge \rightarrow Ti_5Ge_3$ and $Ti, Ge \rightarrow Ti_6Ge_5$, $Ti \rightarrow Ti_5Ge_3$ coexist during the electro-synthesis process.

It should be noted that $TiGe_2$ was not produced during the electrolysis of $1TiO_2-2GeO_2$, (as shown in Figs. 10(c) and 13). The foregoing study [29] suggested that if sufficient time was given for the reaction to continue, Ti_6Ge_5 would transform to $TiGe_2$ by the reaction with the excess Ge available according to the reaction of $7Ge+Ti_6Ge_5 \rightarrow 6TiGe_2$. However, the reaction is a very slow solid-state reaction at the electrolysis temperature. In the work of JAIN and KAO [10], it was suggested that hundreds of hours were needed to synthesize $TiGe_2$ at 900 °C. Therefore, it is difficult to form $TiGe_2$ in molten salt electrodeoxidation process because the electrolysis time is insufficient for the solid transformation from Ti_6Ge_5 to $TiGe_2$.

4 Conclusions

- 1) Ti_xGe_y intermetallic compounds were synthesized by direct electrodeoxidation of mixed TiO_2-GeO_2 powders in molten $CaCl_2-NaCl$ at 800 °C with a potential of 3.0 V.
- 2) The reaction mechanism for the synthesis of Ti_5Ge_3 is a multi-step process, which generally includes the electrodeoxidation of GeO_2 , the formation of $CaTiO_3$ compounds, the electrodeoxidation of $CaTiO_3$ compounds and the formation of Ti_5Ge_3 intermetallic.
- 3) Single-phase Ti_5Ge_3 can be obtained from $5TiO_2-3GeO_2$ and $5CaTiO_3-3GeO_2$.
- 4) The results imply that the molten salt electrodeoxidation process is a fast and environmentally friendly process for the production of Ti_xGe_y intermetallic.

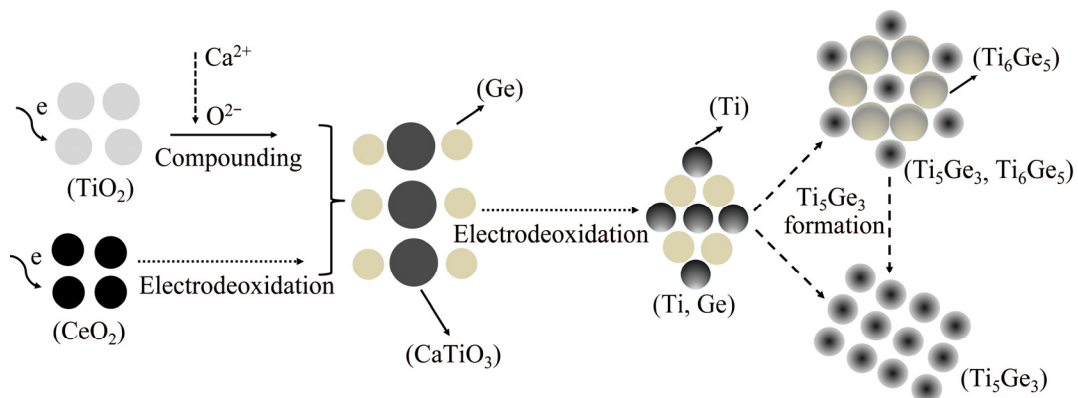


Fig. 12 Schematic illustration of formation mechanism of Ti_5Ge_3 from $5TiO_2-3GeO_2$ during electrodeoxidation process under 3.0 V at 800 °C

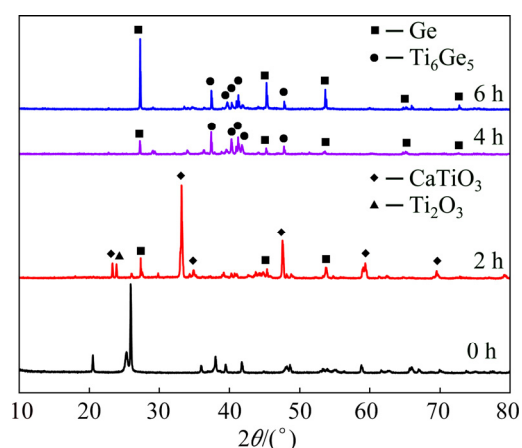


Fig. 13 XRD patterns of $1\text{TiO}_2\text{-}2\text{GeO}_2$ electrolyzed under 3.0 V at 800 °C for different time

Acknowledgments

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CaCl₂-NaCl 熔盐中电解氧化物制备 Ti-Ge 金属间化合物

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摘要: 采用电解脱氧工艺, 以不同比例的 TiO₂ 和 GeO₂ 混合物为前驱体, 在电压为 3.0 V、温度为 800 °C 的电解条件下, 制备 Ti-Ge(Ti_xGe_y)金属间化合物。在同样电解条件下, 以 5TiO₂-3GeO₂ 或 5CaTiO₃-3GeO₂ 为前驱体时, 均可电解得到 Ti₅Ge₃ 金属间化合物。获得的电解产物表现出相对均匀的晶粒结构。此外, 初始原料(TiO₂/GeO₂)的摩尔比对最终电解产物有非常大的影响。根据实验数据, 详细阐述电解脱氧制备 Ti_xGe_y 金属间化合物的相关反应机理。结果表明, 电解脱氧工艺是一种环境友好的制备 Ti_xGe_y 金属间化合物的方法。

关键词: Ti-Ge 金属间化合物; 氧化物; 电解脱氧; 熔盐

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