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Production of NiTi shape memory alloys via electro-deoxidation utilizing an inert anode

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ABSTRACT

NiTi shape memory alloys (SMA) with equiatomic composition of Ni and Ti were prepared by electrodeoxidation, in molten calcium chloride, at 950 °C. Constant voltage electro-deoxidation was conducted using a NiTiO₃ cathode, and either a carbon anode or a novel CaRuO₃/CaTiO₃ composite inert anode. Both anode materials successfully allowed NiTi shape memory alloy to be obtained. The primary difference is that molecular oxygen was produced on the inert anode, instead of environmentally undesired CO₂ greenhouse gases on the carbon anode. Indeed, it was found that carbon could successfully be substituted with conductive calcium titanate–calcium ruthenate composites for electro-deoxidation. Furthermore, DSC was used to analyze the phase transformation of NiTi shape memory alloys, with results revealing the existence of reversible martensite–austenite phase transformations during the cooling and heating process.

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1. Introduction

NiTi alloys with equiatomic composition of Ni and Ti have high technological interest because of their ability to provide controlled material and damping properties, and from being able to change their shape with temperature or load. These properties have attracted much interest for their potential use as functional materials in many engineering applications (such as active, adaptive or smart structures), as well as certain biomedical applications [1–6]. Generally, this alloy is made through a melting method such as vacuum arc melting, which requires multiple re-melts to achieve sufficient homogeneity and to avoid segregation of the elements. NiTi shape memory alloys have also been synthesized by powder metallurgy (PM) techniques, such as self-propagating hightemperature synthesis (SHS) [1–3], hot isostatic pressing (HIP) [4], element powder metallurgy (EPM) [5], and pre-alloy powder metallurgy [6]. However, potential commercial applications have been limited by the expense of processing the alloys.

A novel electro-deoxidation technique has been developed recently. It revealed that oxygen could be electrochemically removed from solid metal oxide pellets, in CaCl₂ based molten salts, to form metal at the cathode [7,8]. A significant amount of work has since been concentrated on the electrolytic production of numerous

metals and alloys directly from their metal-oxides (such as: TiO_2 , Nb_2O_5 , SiO_2 , Cr_2O_3) [9–13]. The main advantages of the electrodeoxidation process compared to other extractive metallurgical processes include: its simplicity; its relatively low energy requirements; its relatively low labour requirements; and its capability to directly reduce a combination of different metal-oxides together to form alloys [14–21]. Chen and his coworkers have contributed to investigate the mechanism of the electro-deoxidation process. They have disclosed a three-phase interlines model to demonstrate the electrochemistry involved within the electro-deoxidation process [22–24].

NiTi alloys have been reported to be produced by electrodeoxidation [20,21]. However, shape memory effects and pseudoelastic behavior of TiNi alloy produced by the electro-deoxidation process have not been investigated in detail.

This work focuses on the production of NiTi shape memory alloys, and involves restriction of impurities like oxygen, carbon and other NiTi intermetallic compounds (such as NiTi₂ and Ni₃Ti), since the transformation temperatures are very sensitive to these impurities. Furthermore, this work offers another significant benefit, in that if a conventionally-used carbon anode is substituted for an inert anode, that molecular oxygen could be formed on the anode instead of environmentally undesired CO₂ greenhouse gases.

2. Experimental

 TiO_2 and NiO powders (Alfa Aesar) of 98+% specified purity were selected as the oxide precursor. The oxide powders were mixed

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using mortar and pestle in stoichiometric proportion. The mixed oxides were uniaxially pressed, at 5 tons using a 1.30 cm die into 1.45 g pre-formed pellets. These pellets were subsequently sintered at 1100 °C for 3 h, which ensured that the pellets had sufficient mechanical strength for connecting to an electrode. The cathode was prepared by wrapping the oxides pellet with a stainless steel wire (0.5 mm in diameter), and then connecting to a stainless steel rod (6 mm in diameter). A graphite rod with a diameter of 10 mm was used as an anode; with a conductive calcium titanate pellet doped with calcium ruthenate as the inert anode. The preparation is detailed in Refs. [25,26].

A dense alumina crucible (Almath Ltd.) was then placed inside an Inconel[®] vertical tubular reactor. This crucible contained 240 g of vacuum-dried CaCl₂ salt produced from calcium chloride dihydrate (Fisher). It was calculated that 96.6% removal of the theoretical amount of water was achieved from the calcium chloride di-hydrate, by heating from 100 °C to 200 °C over a 3-day period, with the condensate measured to have a pH comparable to distilled water.

The water-cooled upper end of the reactor was sealed with a stainless steel cover with silicone-sealed feed-through for the thermocouple and the electrodes (attached to the electrical connection leads). The sealed reactor system was continually flushed through with argon gas (Air Products), which had been dried over calcium sulphate granules. The reactor was then heated at a constant rate of $2 \,^{\circ}$ C min⁻¹ by the furnace (Lenton), to further remove some of the residual moisture in the salt, until a temperature of 950 $\,^{\circ}$ C was reached.

After the operating temperature had been attained, the system was left to stabilize for 2 h. Thereafter, the oxide pellet was slowly lowered into the electrolyte. The selected anode was then immersed to the molten salt. The power supply (Instek, PSM-3004) was then connected to the anode and cathode connection leads. After 25 min had elapsed from the immersion of the oxide pellet, a constant voltage of 3.0V was applied between the anode and the cathode with the corresponding current measured. The anode potential was measured versus a molybdenum reference wire. A Rapidox 2100 oxygen analyzer (Cambridge Sensotec) was used to detect and record the oxygen composition of the gases generated from the calcium titanate-calcium ruthenate composite anode. Prior to off-gas measurement, the oxygen analyzer was calibrated by passing two sufficiently different gas mixtures with known oxygen concentration through the analyzer; the calibration was completed when the check reading was within a 50 ppm tolerance limit.

Electro-deoxidation was terminated after 6–8 h, and the electrodes and thermocouple were removed from the melt into the upper part of the reactor. After removal of the electrodes from the reactor, the reactor was allowed to cool. Then, the electrodes were removed from the reactor and washed under a gentle vacuum (100 mbar) using a 5-day washing procedure, involving: water for the 1st day; 25% concentrated acetic acid for the 2nd and 3rd days; water again for the 4th day; and acetone for the final day. Such a vigorous washing procedure is required to remove salt from within the pores of the cathode, and prevent subsequent fragmentation of the electrodes caused by hydration of the calcium chloride, and to ensure the accurate weighing of the electrodes. Sometimes, a simpler washing procedure was also used.

Finally, the analyses were carried out using the following instruments and procedures. The phase composition of the cathode samples was determined through X-ray diffraction analysis (Phillips, PW1050). The micro-structural composition of the reduced samples was analyzed by scanning electron microscopy, coupled with energy dispersive X-ray analysis (JEOL, JSM-5800LV). The acceleration voltage was set to 15 keV, using detected secondary electron emissions. Oxygen content of the products was



Fig. 1. SEM image and XRD pattern of mixing oxides sintered at 1373 K for 3 h.

quantitatively determined using Eltra ONH-2000 analyzer. A DSC full name (TA Instrument) was used to identify the reversible phase transformation of cathodic product.

3. Results and discussion

In order to successfully produce alloys by the electrodeoxidation process, the homogeneity of starting materials is the key factor. An important objective was to prepare equiatomic composition of NiTi alloy. Thermodynamic calculations show that for a stoichiometric composition of the two oxides, TiO₂ can react with NiO to form NiTiO₃.

$$TiO_2 + NiO = NiTiO_3, \qquad \Delta G^\circ = -10, 183 J \text{ mol}^{-1} \text{at} 1100 \,^\circ\text{C} \quad (1)$$

The pellets of mixed TiO_2 and NiO were sintered at $1100 \,^{\circ}C$ for 3 h. The product was analyzed by the X-ray diffraction (XRD) technique, with the results shown in Fig. 1a indicating that all peaks visible in this figure pertain to a single phase of NiTiO₃. Only negligible amounts of the raw material phase could be observed in the diffraction traces. It has been reported that the single phase of the oxide will produce a homogenous alloy [27]. Fig. 1b presents the SEM image of the oxides pellet as-prepared and unreduced. The porosity of the presented pellet allows for the penetration of molten salt, which is beneficial to the diffusion of O^{2-} .

The NiTiO₃ pellet was connected to a stainless steel lead to form the cathode with carbon initially selected as the anode, with 3 V applied for the electro-deoxidation process of NiTiO₃. Fig. 2 presents the relevant current and anode potential time profiles, recorded during electrochemical reduction experiments performed using a carbon anode. The current profile commences with a current peak of significant magnitude that extends for approximately



Fig. 2. The current profile of electro-deoxidation based on carbon anode.

2 h, and this is followed by a current shoulder, and then, the gradual decline of current leading to the background levels.

The overall process can be explained by the oxygen initially within the cathode ionized to oxygen ions that dissolve in the melt.

$$NiTiO_3 + 6e^- = NiTi + 3O^{2-}$$
(2)

The oxygen ions then diffuse through the melt to the carbon anode where discharge takes place and reacts with carbon to form CO_2 .

$$C + 30^{2-} = 1.5CO_2 + 6e^-$$
(3)

In this work, a composite mixture of 0.5CaTiO₃/0.5CaRuO₃ was used as anode in the electro-deoxidation process to produce NiTi shape memory alloy. It was discovered that calcium titanate (CaTiO₃), which is a poor electrical conductor on its own, becomes a much better conductor when combined with calcium ruthenate (CaRuO₃) [25]. The 0.5CaTiO₃/0.5CaRuO₃ anode was fabricated as described in previously reported work [26]. Fig. 3 represents the variation of oxygen evolution and respective current-time profile



Fig. 3. The oxygen evolution and current profile of electro-deoxidation based on CaRuO₃/CaTiO₃ composite anode.



Fig. 4. Anode potentials on carbon and CaRuO₃/CaTiO₃ composite anodes.

obtained on the CaTiO₃/CaRuO₃ anode. The current–time curves are similar to those obtained using a carbon anode. From reference to Fig. 3a, it can be seen that molecular oxygen was produced instead of the environmentally undesired carbon oxide greenhouse gases. Moreover, the variation of oxygen was in accordance with the trend of the analogous current versus time profiles, with the exception of some spikes, which could be explained by unstablization of the oxygen sensor. The liberation of oxygen on the CaTiO₃/CaRuO₃ anode demonstrates that the anodic reaction is described through Eq. (4).

$$30^{2-} = 1.50_2 + 6e^{-} \tag{4}$$

The CaTiO₃/CaRuO₃ anode in a calcium chloride–calcium oxide melt, oxygen is evolved. Previous studies also showed that CaTiO₃/CaRuO₃ anodes functioned satisfactorily in calcium chloride–calcium oxide melts, with no sign of attack or decomposition after electrolysis [26]. This is a very significant advance on other materials that have been investigated which either corrode or accumulate highly resistive films [28].

The liberation potentials of CO_2 and O_2 based on reactions (3) and (4) were calculated by HSC chemistry and were determined to be 1.60 V and 2.62 V versus Ca^{2+}/Ca , respectively. The anode potentials on the carbon and $CaTiO_3/CaRuO_3$ anodes were measured during electrolysis. From Fig. 4, it is apparent that the anode potential on the $CaTiO_3/CaRuO_3$ anode is approximately 1.6 V, and



Fig. 5. XRD patterns of the cathodic product after electro-deoxidation based on carbon anode (a) and CaRuO₃/CaTiO₃ composite anode (b).



Fig. 6. SEM (a) and Ni (b), Ti (c) and O (d) mapping of the cathodic product after electro-deoxidation based on CaRuO₃/CaTiO₃ composite anode.

is higher than the corresponding measurement on the carbon anode of 1.2 V. Theoretically, the anode potential on an inert anode should be 1 V higher than that on carbon anode. The testing result in our work is showing there is only 0.4 V difference based on the anodes. This could be essentially due to the over-potential required for the liberation of O_2 on the CaTiO₃/CaRuO₃ anode is much lower than that of the liberation of CO₂ on the carbon anode. The result denotes that oxygen evolution on the CaTiO₃/CaRuO₃ material is kinetically less demanding than the generation of carbon oxides on carbon; and may partially offset the theoretical $\sim 1 \text{ V}$ lower cell operation capability of graphite anodes compared with oxygen evolving anodes for the electro-deoxidation process. A similar result was obtained when a SnO₂ based anode used [28].

The electro-deoxidation was ended after 8 h, and the product was analyzed by XRD. Fig. 5 shows the XRD pattern of cathodic products prepared using carbon anode (Fig. 5a) and CaTiO₃/CaRuO₃ anode (Fig. 5b). The results reveal that the cathodic product is near the equiatomic composition of NiTi alloys. There are two phases



Fig. 7. DSC curves of the as-prepared NiTi specimen.

of B2 and B19' in the product prepared based on carbon anode. In comparison, the product prepared based on the CaTiO₃/CaRuO₃ anode only shows the presence of a B2 phase. These results demonstrate that the feasibility of producing equiatomic composition of NiTi alloy through electro-deoxidation.

Moreover, conventional electro-deoxidation process carried out using a carbon anode, have the significant disadvantage of the anode corroding during electrolysis, from oxygen ions diffusing through the molten salt to the anode where they discharge and react with carbon to produce carbon dioxide.

This work focused on the preparation of near-equiatomic NiTi alloy based on the inert anode. The photograph and SEM image of the as-prepared NiTi alloy by the CaTiO₃/CaRuO₃ anode are shown in Fig. 6a. It is clear that the cathodic product has a reflective appearance, and the NiTi alloy, was more dense compared with conventional results. Fig. 6b and c clearly shows uniform mapping of Ni and Ti elements. Also Fig. 6d demonstrates that a 1000 ppm Ca is remaining in the product. The electro-deoxidation process was performed with a cell voltage of 3V, which is higher than the decomposition potential of CaO. The deposition of Ca may indicate that the salt used is not fully purified, but contains a small amount of CaO. Furthermore, Fig. 6e shows only negligible amount of Ru (600 ppm) is co-depositing on the cathode, and clarifies that CaTiO₃/CaRuO₃ is quite stable and can be considered an inert anode for use in this electro-deoxidation process. The oxygen content in the cathodic products using both carbon and CaTiO₃/CaRuO₃ anodes was measured by an Eltra ONH-2000 analyzer, with the results showing that less than 3000 ppm oxygen remains in the products. For the cathodic products based upon the carbon anode, the average content of oxygen is approximately 2100 ppm, while for the CaTiO₃/CaRuO₃ anode this is approximately 2900 ppm.

NiTi alloys have also been produced by a conventional electrodeoxidation process using carbon anodes [20,21]. However, shape memory effects and pseudoelastic behavior of near-equiatomic TiNi alloy associated with the reversible martensite–austenite phase transformation have not yet been reported. We have investigated the reversible martensite–austenite phase transformation properties of the cathodic products produced by the electrodeoxidation process using a CaRuO₃/CaTiO₃ inert anode. Fig. 7 shows the DSC curve of the cathodic product. The starting temperature was 80 °C, with a negative scan initially performed. While cooling the specimen results in two exothermic peaks upon peaks (*Pa* and *Pr*). There is only endothermic peak (*Pm*) upon heating. The two step transformation of B2 \rightarrow R-phase (*Pa*) and subsequent R-phase \rightarrow B19' (*Pr*) may occur upon cooling [29]. This indicates that, upon cooling, the austenitic phase B2 transfers to rhombohedral phase (R-phase) at *Pa*, R-phase to martensitic phase at *Pr*. The reverse transformation occurs from martensitic phase directly to the austenitic phase B2 at *Pm*. The DSC results demonstrate that the NiTi alloys have shape memory effects associated with the reversible martensite–austenite.

4. Conclusions

The production of a NiTi shape memory alloy (SMA) with near-equiatomic composition of Ni and Ti via electro-deoxidation in molten calcium chloride at 950 °C was achieved and reproducible. Constant voltage experiments were conducted with a conventionally-used carbon anode, and also with a novel CaRuO₃/CaTiO₃ anode material. The two significant differences between the results, is the evolution of molecular oxygen on the inert anode instead of environmentally undesired carbon oxide greenhouse gases on the carbon anode, and the lack of contamination of the product by carbon. Hence, the conductive calcium titanate-calcium ruthenate composites can be considered a substitute for conventionally-used carbon anodes for electro-deoxidation. Moreover, DSC was used to analyze the phase transformation of near-equiatomic NiTi alloy with results revealing the existence of reversible martensite-austenite phase transformations during the cooling and heating process.

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