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Synthesis and thermionic properties of tungsten–barium titanate composites

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ABSTRACT

The potential of novel tungsten–barium titanate composites as thermionic emitters is explored. Composites ranging from 20% to 80% tungsten by mass were prepared by sintering in an Ar–H_2 atmosphere. XRD and SEM studies indicate four major micro-constituents; W, $BaTiO_3$, $Ba_4(Ti,Fe)_{12}O_{27}$ and $BaWO_4$. Richardson work functions (φ_R) and Richardson constants (A_R) were determined using a Schottky diode arrangement at temperatures ranging from 1223 to 1473 K. Work functions ranged from 2.67 eV to 3.32 eV with a shallow minimum at 40% by mass W and were relatively constant (~2.7–2.8 eV) in the range 30–70% by mass W. The decrease in work function was accompanied by a strong decrease in A_R from 39.3 A cm^{-2} K^{-2} to 0.02 A cm^{-2} K^{-2} over the range 20–70% by mass W. The reduction in both φ_R and A_R was associated with the major conversion of the surface to $BaWO_4$ and $Ba_4Ti_{12}O_{27}$ during the activation treatment before emission testing.

1. Introduction

Thermionic cathodes are widely used in a variety of thermal emission and field emission devices including cathode ray tubes, sensors and electron microscopes. Each application utilizes materials tuned for the specific mode of operation (DC, pulsed, *etc.*) and the required emission current. Revived interest in thermionic energy converters for concentrated solar electricity generation or industrial waste heat recovery has caused a revival of interest in thermionic emitters for long-term stable DC emission. In this kind of application, cathode materials with high melting temperature, low vapour pressure, low thermionic work function and high electrical conductivity are necessary to sustain high emission currents; a set of properties that are rarely available in a single phase. A case in point is tungsten which has outstanding thermal stability in vacuum but also has a very high work function (~4.5 eV) which necessitates exceedingly high operating temperature for appreciable electron emission. Instead, tungsten dispenser cathodes have been developed and are particularly successful for applications such as cross-field amplifiers, magnetrons, travelling wave tubes, backward-wave oscillators, cathode-ray tubes, gas-ion lasers, electron-bombarded semiconductor (EBS) devices and X-ray tubes due to their good thermal properties and especially high emission capabilities [1]. A dispenser cathode (or a barium dispenser cathode) comprises a porous refractory metal or alloy (usually tungsten) impregnated with a barium compound. At elevated temperature a monolayer of barium forms on the tungsten as an emissive surface. A typical example is the B-type cathode in which barium calcium aluminates ($BaO{\cdot}CaO{\cdot}Al_2O_3$) have been impregnated into a tungsten matrix [2]. The aluminate supplies surface active Ba^{2+} ions which enhance electron emission by lowering the work function of tungsten to approximately 2.0 eV at around 1400 K [1,2].

Although pure oxide cathodes have work functions as low as ~1.2 eV, which would allow much lower operating temperatures, they are limited for practical applications because of their low current density capability, constrained by low electrical conductivity. This is the case even for thin films, for example a 1 μm (BaSr)O surface layer on tungsten [3]. In that investigation, the (BaSr)O film, having a work function of 1.57 eV, could produce a current density of 1.6 A cm^{-2}, this upper limit being dictated by Joule heating [4]. Dispenser cathodes are electrically conductive and have far greater DC current capability than oxide cathodes [5]. Taran et al. [6] reported a high pulsed emission current density of 230 A cm^{-2} at 2000 K for a tungsten (37% by mass)–$BaHfO_3$ composite cathode with an effective work function of 2.11 eV at 1200 K. Although they studied only pulsed emission at high temperatures, the implication of a reduction in work function suggests that other barium based perovskites are worthy of investigation for stable DC emission at lower temperatures.

One such perovskite is barium titanate ($BaTiO_3$), widely used in various electronic applications due to its ferroelectric,

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pyroelectric and piezoelectric properties [7–9]. As an oxide ceramic it exhibits five crystal structures having a melting temperature of about 1898 K. The ferroelectric property of $BaTiO_3$ thin films (1 μm thick) had been used to produce pulsed emission under high field conditions of 100 MV/m generating a current of 25 nA/cm^2 at room temperature [10,11]. Its high dielectric strength ($e_r > 1200$) and potential to act as a source of Ba, indicates that it may be suitable for use in dispenser type thermionic cathodes or to reduce the work function of refractory metal/composites.

No prior studies have been found on the development of electrode materials based on W and $BaTiO_3$ for continuous thermionic emission. In the present work, W–$BaTiO_3$ cathode materials have been fabricated through mechanical milling, pressing and sintering. This work describes the structural, chemical and thermionic properties of these composite cathode materials.

2. Experimental details

In the initial stages, cathodes were prepared from a mixture of commercial grade tungsten powder (25–50 μm diameter) combined with barium titanate (Goodfellow, Cambridge Ltd., UK, 99.9% by mass purity, particle size <45 μm). These cathodes yielded promising results however, the high specific gravity and the coarse size of the W particles made it difficult to obtain uniform mixtures leading to significant sample to sample variability. Consequently, fine W powder with particle size 0.6–1.0 μm (Sigma–Aldrich Co., Japan, 99.9 wt% purity) was found to produce stable mixtures suitable for pressing compacts. Various mass ratios of tungsten from 20% to 80% by mass and $BaTiO_3$ powders were co-milled in a high energy SPEX 8000 M ball mill with a few drops of ethanol for 60 min at a ball-to-powder mass ratio of about 5:1. Batches of milled powder having a mass of 8–10 g were compacted at 70 MPa to provide maximum green density without causing compressive failure of the compact. Sintering was carried out at 1553 K, to avoid the formation of any liquid phase component, for 4 h in a tube furnace maintaining a flow of Ar + 5%H_2 gas. On removal from the furnace, a thin dark film could be observed on all samples. This film was removed by abrading about 500 μm of the as-fired surface using SiC grinding papers prior to cleaning in an ultrasound bath. The characteristics of the as-fired and abraded surfaces are reported.

The phases present in the W–$BaTiO_3$ composite cathodes were analyzed by X-ray diffraction (Philips 1710) using CuK_α radiation ($\lambda = 0.15406$ nm), operating at an accelerating voltage of 40 kV, an emission current of 40 mA and a scanning rate of 0.025°/s. Phase identification utilized the International Centre for Diffraction Data (ICDD) database. The phase identification was confirmed by Rietveld analysis which also supplied quantitative phase analysis using the method of Hill and Howard [12]. The crystallite size of the samples was estimated by using the Scherrer equation:

$$d = 0.89\lambda / B\cos\theta$$

where d is the mean crystallite diameter, λ the wavelength of the X-rays, B the broadening of the full-width at half-maximum of the diffraction peak (FWHM), and θ the diffraction angle. The tungsten peak having the highest intensity, at about 40° 2θ, was used for this purpose.

The chemical composition of samples was measured by means of energy dispersive X-ray analysis (EDX) using a Philips XL30 SEM with Oxford ISIS EDS system operated at accelerating voltages of 15–25 kV. The surface morphology of the as-fired and abraded pellets was characterized using secondary electron and backscattered electron imaging. Elemental mapping of the abraded surfaces was carried out using JEOL JSM-6100 SEM with Oxford ISIS EDS system. Post-emission surfaces were examined in a ZEISS Sigma VP FE-SEM.

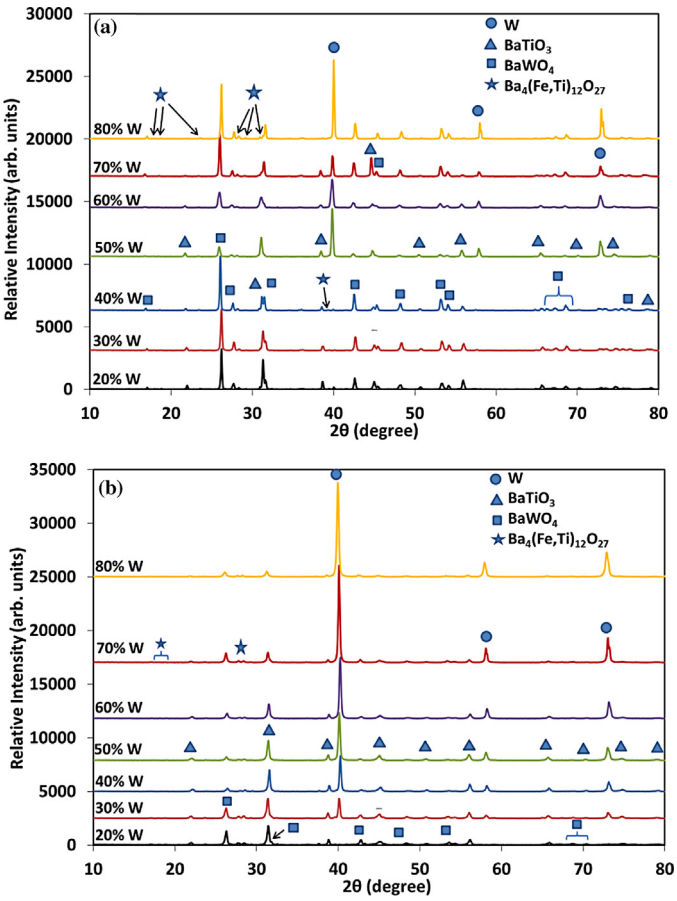

Fig. 1. XRD patterns of W–$BaTiO_3$ composite cathodes having different mass fraction of tungsten from (a) as-fired surfaces and (b) abraded surfaces. Note that the identifying marks for each phase are applicable to all peaks at the same 2θ location across all samples.

Electrical resistivity of the pellet samples (4.5–6.0 mm thick and about 17 mm diameter) were estimated by the four-wire sensing method using a precision multimeter. The cylindrical pellets were abraded and later painted with commercial silver glue. Two electrical wires were attached on each of the circular faces of the samples and resistivity was measured by conduction through the samples.

Thermionic emission to evaluate the emission constants was performed on abraded samples in a Schottky device in the temperature range of 1223–1473 K using a 3 mm gap between the emitter and the collector. The collector itself had a diameter of 6 mm. Vacuum was maintained at $<1 \times 10^{-3}$ Pa during testing and prior to data collection the samples were activated for 1 h at 1473 K to allow any conversion reactions and/or migration of species to occur over the freshly abraded emissive surface. DC emission testing was carried out by applying accelerating voltages in the range of 0–300 V during a series of constant temperature holds. Schottky and Richardson plots were used to find the Richardson work function of the W–$BaTiO_3$ samples according to ASTM Standard F83 [13].

3. Results

3.1. Sample characterization

XRD patterns of the as-fired and abraded surfaces of the samples are shown in Fig. 1. Both the as-fired and abraded surfaces contain three main phases namely, tungsten, barium titanate ($BaTiO_3$), barium tungstate ($BaWO_4$) and a phase which matched barium-iron titanate ($Ba_4Fe_{1.917}Ti_{10.083}O_{27}$) in the ICDD XRD database. This phase is Fe substituted $Ba_4Ti_{12}O_{27}$ [14–16] (also known as $BaTi_3O_7$)