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Innovative sintering process for fabrication of thermochromic smooth VO₂ ceramics

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Abstract

In this paper, a pyrolysis method is used to synthesize high quality VO₂ powder. Black carbon and V₂O₅ powder are mixed and annealed at 650°C or 800°C under argon flow to initiate a carbo-reduction reaction. The 650°C VO₂ powder presents submicron particle size with an amorphous fraction estimated at 11.5%. With the increase of the annealing temperature up to 800°C, grains become larger than the micron while the crystallinity goes up to 98.5% (i.e. amorphous fraction drops to 1.5%). This one-step process allows the preparation of quantities up to 10 g of VO₂ powder and should be easily transferable to large-scale production. An innovative sintering process is then adopted to produce high quality thermochromic VO₂ ceramics from the as-prepared VO₂ powder. First, SPS process is used to obtain high-density VO₂ pellet. Then, the VO₂ pellet is post-annealed in a homemade induction furnace at 1300°C under a controlled atmosphere to allow grain growth by coalescence and improve pellet surface quality. According to a surface topography analysis, the mean amplitude roughness parameter (Ra) of the obtained VO₂ ceramic is found to be 2.93 ± 0.01 nm. A large resistance change by three orders of magnitude along the phase transition is observed, which makes the as-prepared smooth VO₂ ceramic a promising candidate for various applications requiring optical and/or electronic switching behaviour depending on temperature.

Keywords

Vanadium dioxide, large-scale powder synthesis, sintering process, smooth ceramic, thermochromic behaviour

1. Introduction

Thermochromic materials exhibit a reversible change in optical properties as a function of temperature. Among them, VO₂ shows a first-order metal–insulator transition (MIT) from a low-temperature monoclinic phase to a high-temperature tetragonal phase at around 68°C, which is closer to room temperature than any other thermochromic inorganic materials. Moreover, the transition temperature of VO₂ can be tuned to ambient temperature by doping with metal ions such as W⁶⁺ [1], Nb⁵⁺ [2] or Mo⁶⁺ [3]. The phase transition is associated with abrupt changes in electrical, magnetic, thermal and optical properties. All of these characteristics make VO₂ an ideal candidate for a wide variety of technologies including smart radiator devices [4], adaptive infrared camouflage [5], smart windows [6].

Many methods have been explored to synthesize VO₂ powder including combustion [7, 8], hydrothermal [9] and pyrolysis [10]. However, due to the numerous valences of the vanadium element, several oxides such as VO, V₂O₃, V₄O₇, VO₂, V₆O₁₃, V₃O₇, V₂O₅, etc. can be obtained during the synthesis process [11]. In spite of several efforts, the synthesis of pure VO₂ powder has been so far limited to few grams scale [12] being a restricting factor for commercial utilization. Thus, developing a cost-efficient, reproducible and large-scale technique to produce stoichiometric VO₂ powder remains a big challenge.

VO₂-based ceramics represent a great interest for thermistors, electric current inrush limiters [13] and switching devices [14]. Nevertheless, the fabrication of VO₂

ceramics appears difficult to achieve because of the thermal instability of the oxide. Indeed, the sintering of VO₂ powder at high temperature to obtain dense ceramics, while maintaining the pure VO₂ phase, does require a precise control of the oxygen pressure (cf. Ellingham diagram [Fig.1](#)). Only few studies on the synthesis of VO₂-based ceramics are reported in the literature [15, 16, 17]. Spark plasma sintering (SPS) has proved to be an efficient method to develop high-density ceramics in a short time and at moderate temperatures. Recently, Kato et al. [17] applied SPS at 500°C as a sintering process to obtain VO₂ pellets with high relative densities exceeding 90%. Nevertheless, the as-prepared pellets exhibit grain size below 10 μm with a rough surface that excludes any characterizations requiring mirror-polished surface such as ellipsometry. Also, considering optical applications, the pellet surfaces are required to be smooth enough, so that no scattering phenomenon is observed.

In the current work, in a first stage, a pyrolysis method was used to synthesize high quality VO₂ powder. V₂O₅ was mixed with carbon and annealed in a flowing Ar atmosphere to allow a carbothermal reduction process. Carbon content was adjusted depending on the operating temperature to obtain a pure VO₂ (M1) phase. The crystal structure, the morphology and the phase transition properties of the synthesized powders were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC), respectively. The one-step process allows the preparation of quantities up to 10 g of VO₂ powder and should be easily transferable to large-scale production.

In a second stage, the as-prepared powder was used to elaborate very high quality VO₂ ceramics through two successive steps. Firstly, SPS process at 700°C allowed the shaping of pellets with high densities; then, a fast annealing step at 1300°C under adequate oxygen partial pressure was performed using a homemade induction furnace to

initiate grain growth. The surface morphology and the thermochromic behaviour of the final ceramics were studied by optical profilometry and resistivity measurements, respectively. The main aim of this work is to demonstrate the benefits of using a two-steps sintering process to obtain functional VO₂ ceramics with a high surface quality.

2. Experimental section

2.1. Synthesis of VO₂ powder

V₂O₅ powder was synthesized by a thermolysis of vanadyl ethylene glycolate (VEG) precursor in air atmosphere [18]. V₂O₅ nanoparticles powder was then uniformly mixed with soot (carbon black; bulk density: 80–120 g.L⁻¹) purchased from Alfa Aesar. The mixture was annealed into the constant-temperature zone of a horizontal tube furnace. The heating and cooling rates were fixed at 10°C/min and 5°C/min, respectively. The dwell time was fixed at 10 hours. Two different temperatures were tested (650°C and 800°C) and the C/V₂O₅ molar ratio was adjusted depending on the operating temperature. The carbothermic reduction of V₂O₅ leads to VO₂ formation. Throughout the process, Ar gas was introduced into the furnace at a flow rate of 0.2 L/min providing an oxygen-free atmosphere (P_{O₂} = 10 Pa). The phase composition of each annealed sample was assessed by XRD. This one-step annealing process allows the easy-preparation of up to 10 g of VO₂.

2.2. Fabrication of VO₂ ceramics

SPS has proved to be an efficient method to sinter materials with optimal microstructures. Thus, this sintering process was used to prepare thermochromic pellets.

VO₂ powder sample of 0.8 g was loaded into a carbon die of 10 mm inner diameter and heated to 700°C at 100°C/min under vacuum. The dwell time was 15 min and a uniaxial pressure of 100 MPa was applied during the process. At the end, a rapid cooling at 300°C/min was performed. The as-prepared high-density pellets were then post-annealed at 1300°C under a controlled atmosphere to increase grain size by high-temperature coalescence phenomenon. Pellets were put inside a platinum cylinder and the heating from room temperature to the desired temperature was achieved in only 30 secs thanks to a homemade induction furnace. The cooling of the platinum cylinder from 1300°C to room temperature lasted around 5 min. High purity Ar and O₂ gas were introduced into the furnace during the process by using two flow sensors. Oxygen partial pressure was adjusted to proceed inside the thermodynamic stability domain of VO₂. The use of very fast kinetics for the annealing process aims to preserve stoichiometric VO₂ phase, i.e. avoiding the formation of other vanadium oxides such as V₆O₁₃, V₈O₁₅, V₂O₅, etc. Finally, the obtained ceramics were mechanically polished by 600, 1200, 2400, 4000 grit discs successively, and mirror-polished surface was obtained using a felt polishing disc combined with a liquid suspension of alumina.

2.3. Characterization

The crystal structure of the as-prepared samples was determined by a PANalytical X' Pert PRO diffractometer using the Cu-K α radiation source ($\lambda = 1.5423 \text{ \AA}$), with a divergent slit of 1° and a receiving slit size of 0.1 mm in a 2 θ range from 8° to 80°. Moreover, to determine the degree of crystallinity of the samples, Rietveld refinements were achieved using FullProf software.

The morphology of the as-prepared powders was observed by SEM using a TESCAN Vega II microscope.

Thermal analysis was carried out by differential scanning calorimetry using DSC 8000 PERKIN ELMER at a scan rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ over the temperature range $30\text{-}110^{\circ}\text{C}$. To test the repeatability and to detect the potential switching fatigue, VO_2 powders were subjected to three measurement cycles.

The oxygen partial pressure used during powder synthesis and ceramics preparation was measured by a MicroPoas® sensor (zirconia sensor with a built-in metal reference, in our case Iridium).

The experimental density of VO_2 ceramics was calculated from their weight and geometrical size, while their surface morphology was observed by a Leica DMI3000 M optical microscope and a WYKO NT1100 optical profiling system.

Resistance *versus* temperature through VO_2 ceramics was measured with a two probes system. Two small probes were connected to two platinum discs circling the ceramic sample. The current was then applied from a power generator through the probes and the voltage difference was measured by a KEITHLEY multimeter. Resistance measurements were carried out *versus* temperatures ranging between 20 and 120°C while a thermocouple was positioned right next to the sample to determine the exact value of the sample temperature.

3. Results and discussion

3.1. Study of VO_2 powders synthesized at 650°C and 800°C

3.1.a Structural and morphological properties

[*Fig.2*](#) presents XRD patterns of the samples obtained at 650°C using different $\text{C}/\text{V}_2\text{O}_5$ molar ratios. At a $\text{C}/\text{V}_2\text{O}_5$ molar ratio of 0.50 , the as-prepared sample consists of VO_2 (JCPDS 44-0252) and V_6O_{13} (JCPDS 43-1050), indicating that the amount of C is not high-enough to entirely reduce the V_2O_5 raw material to the VO_2 target phase. Similar

result was earlier reported by Wu et al. [7]. As the C/V₂O₅ molar ratio increases to 0.75, all the X-ray peaks match with the VO₂ monoclinic phase, showing a complete transformation of V₂O₅ into VO₂. Finally, with increasing the C/V₂O₅ up to 1.00, the reduction process becomes too efficient leading to the appearance of V₈O₁₅ impurity (JCPDS 18-1448) besides VO₂.

To determine the crystallinity of the VO₂ powder obtained at 650°C, quantification analysis using Rietveld refinement with the Fullprof program was performed. A precise amount of a well-known sample (100% crystallinity rate, in our case Silicon, but it could also be NIST Reference, for example LaB6 NIST SRM 660a), mixed at 10 wt% with the VO₂ powder, was used as reference to calculate the proportion of crystalline and amorphous parts in the as-prepared VO₂ powder. The Rietveld refinement is depicted in [Fig.3a](#). The calculated data match perfectly the experimental one, as confirmed by the good-quality fit (R_{Bragg} agreement factor = 8.98%). The weight percent of the VO₂ crystalline part was estimated at 88.5%, the amorphous part being so 11.5%.

To achieve full crystallinity, the synthesis temperature was increased up to 800°C. The C/V₂O₅ molar ratio was reduced to 0.5 to overcome the effect of the thermal reduction temperature (cf. [Fig.1](#)). As shown from Rietveld analysis of the corresponding XRD pattern ([Fig.3b](#)), VO₂ is fully crystallized in the monoclinic system and the weight percent of the crystalline fraction was then estimated at 98.5%. For the 800°C annealed VO₂ powder, the diffraction peak at $2\theta = 27.85^\circ$, corresponding to the (011) Miller indexes for VO₂(M1) (S.G. : $P2_1/c$), is slightly thinner than the other peak showing (011) preferred orientation. The average full width at half maximum (FWHM) of the main diffraction peak decreases from 0.159° for the 650°C-sample to 0.126° for the 800°C-sample, showing an increase of the average crystallite size with the increase of the thermal

treatment temperature. So, increasing synthesis temperature from 650°C to 800°C allows to strongly improve quality of VO₂ powder, leading to pure crystalline powder devoid of any amorphous content.

The morphologies of VO₂ powders synthesized at 650°C and 800°C are shown in [Fig.4](#). 650°C-VO₂ powder ([Fig.4a](#)) consists of submicron particles forming large aggregates of about 10 µm diameter. While the annealing temperature increases from 650°C to 800°C, the crystallites with clear boundaries become larger with a diameter of about 2-10 µm ([Fig.4c](#)), being in agreement with the XRD peak shape evolution presented above. The aggregation effect decreases drastically and well-isolated VO₂ particles are observed. Higher temperature provides sufficient energy for the grain growth and the very large increase of the crystallite size for the 800°C-sample as compared to the 650°C one, also improves drastically the particles dispersion. Similar results were reported on VO₂ powder preparation in the literature [18, 12, 19, 20].

3.1.b Thermal analysis of thermochromic phase transition

It is well-known that the first order phase transition of VO₂, associated with a large variation of latent heat, occurs at around 68°C [21]. The DSC analysis of the two synthesized VO₂ powders was performed using the same scanning conditions (rate: 10°C/min and atmosphere: N₂), for both heating and cooling stages. To test repeatability, 3 cycles were carried out for each sample. The DSC curves are displayed in [Fig.5](#). During heating and cooling cycles, endothermic and exothermic peaks are clearly visible for both samples. By convention, the phase transition temperature (T_c) is taken as the average of endothermic and exothermic peak positions. Thus, the phase transition temperature for the two VO₂ powders is about 66°C, which is very close to the transition temperature of bulk VO₂ [21]. The similarity of the DSC curves throughout the 3 cycles for the two samples illustrates a behaviour of very high-reversibility. The main difference between

the two samples is the shape of the peaks. Indeed, VO₂ synthesized at 800°C ([Fig.5b](#)) presents perfectly symmetrical peaks with high enthalpy values (42-43 J/g) whereas the 650°C-sample, exhibits DSC peaks with only 35-38 J/g enthalpy values with a back asymmetry (the end of the phase transition in both heating and cooling cycles seems to be spread in temperatures). The slight differences observed comparing the two different samples could be attributed to a better crystallinity obtained for the high annealing temperature, the significant amorphous fraction for the low-thermally treated sample being not submitted to the phase transition.

To conclude on these first results dealing with the preparation of two powder samples (synthesized using 650°C or 800°C treatment temperature) and their physico-chemical characterizations, pure polycrystalline VO₂(M1) powder was successfully synthesized using carbothermic reduction of V₂O₅ adjusting in an adequate way the C/V₂O₅ ratio, which varies with the synthesis temperature. The 650°C VO₂ powder presents submicron particle size with an amorphous fraction estimated at 11.5%. With the increase of the annealing temperature up to 800°C, grains (with faceted aspect showing their monocrystalline behaviour) become larger than the micron while the amorphous fraction drops to 1.5%. Nevertheless, the crystalline quality improvement negligibly affects the thermochromic behaviour of the as-prepared VO₂ compounds. Thereafter, the objective was to prepare high quality VO₂ ceramics from the VO₂ synthesized powder using SPS process.

3.2. Study of VO₂ pellets fabricated by SPS

Pellets from the two previously synthesized VO₂ powders were prepared using SPS with similar sintering conditions (temperature: 700°C, applied pressure: 100 MPa,

dwel time: 15 min). The sintering conditions were chosen from a preliminary parametric analysis varying applied pressure, final temperature and dwell time. Typically, decreasing the pressure, the temperature or dwell time leads to a decrease of the reached density; however, beyond 700°C with 15min dwell time (increasing the temperature and/or the dwell time) the density remains constant whereas the electrical contrast at the phase transition starts to decrease. This performance worsening may result from an excessively reducing SPS process leading to anionic vacancies creation in the VO₂ crystalline framework. Sintering was carried out in vacuum, a gauge allows the accurate control of the chamber's pressure during the whole process. [Fig.6a](#) shows the evolution of the chamber's pressure as a function of temperature during the SPS sintering process. In the case of the 650°C VO₂ powder, the increase in chamber's pressure during the sintering process could be due to the reaction between the residual carbon still present in the powder and the oxygen of VO₂, leading to the formation of CO/CO₂ gas mixtures. This would indicate that a small quantity of carbon is not consumed during the carbothermic process when the synthesis temperature is only 650°C. However, for the 800°C VO₂ powder, the chamber's pressure remains stable during the entire process meaning no carbo-reduction reaction associated with CO/CO₂ gases takes place. Thus, another benefit of using 800°C instead of 650°C annealing temperature to prepare VO₂ powder is to fully remove the carbon from the powder sample avoiding further carbo-reduction reaction during SPS process.

[Fig.6b](#) shows the XRD patterns of the two pellets obtained after SPS process applied to the two VO₂ powder samples. Pure polycrystalline VO₂(M1) is maintained when sintering is performed on the powder synthesized at 800°C. However, from the 650°C powder, the presence of the V₆O₁₁ phase (JCPDS 18-1451) confirms the reduction of VO₂ during SPS

sintering. Consequently, VO₂ powder synthesized at 800°C was thereafter systematically used to prepare VO₂ pellets by SPS process.

The VO₂ pellet's surface was then polished by the successive steps described in the experimental part. The specific density of the VO₂ pellet was estimated equal to 97%. The polished surface was then analyzed by an optical microscope. [Fig.7a](#) shows the top-view micrograph of the surface morphology of the VO₂ pellet. Despite the numerous polishing steps, a high surface roughness remains. Our hypothesis is that despite the high density, the inter-grain mechanical cohesion prevents from the polishing that instead proceeds by tearing the grains. It is worth noting that the size of the obtained particles is below 10 μm, i.e. a quite similar size than the raw powder one. Thus, using SPS process, a densification up to 97% can be associated with negligible grain growth as previously reported for other compounds in literature [22]. Particles rearrangement by rotation and sliding, caused by the applied pressure (100 MPa) during the sintering process, could explain the pellet's high-density value. Furthermore, densification of the microparticles may also occur by local plastic deformation at their contact points [23]. The electronic resistance of the VO₂ pellet *versus* temperature was then recorded ([Fig.7b](#)). The compound transits from semi-conductive state to metallic state during the heating process. Consequently, the resistance of the VO₂ pellet decreases over two orders of magnitude across the phase transition. On heating, the transition temperature is estimated to 72°C about, while the reversible transformation during the cooling occurs at around 64°C, which results in hysteresis loop. The average transition temperature is thus 68°C, i.e. equal to the theoretical value of bulk VO₂.

3.3. Post-annealing of VO₂ pellets at 1300°C

Aiming to improve the surface quality, the high-density VO₂ pellet was annealed at 1300°C for 1 h under a controlled atmosphere to allow grain growth by coalescence. The partial pressure of oxygen was fixed at 100 Pa to preserve the pure VO₂ phase. A picture of the homemade induction furnace used for the post-annealing is shown in [Fig.8a](#). This system allows to reach 1300°C in only 30 secs, avoiding formation of undesired vanadium oxides during the heating. A top-view micrograph of the surface morphology of the annealed VO₂ ceramic is shown in [Fig.8b](#). Large grains with smooth surface and average diameters above 50 µm, delimited by planar grain boundaries, are observed. However, localized black spots are also visible and could correspond to small cavities, which are the residues of the deepest holes on the raw surface. Optical profilometer was thereafter used to further evaluate surface quality of the sample and to obtain quantitative parameter through roughness coefficient.

3D optical profilometry image of the sample, with an analysed area of 110 x 150 µm², is shown in [Fig.9a](#). Grain boundaries and cavities, with a blue colour in the image (negative depth in regard of the average height), can be clearly visualized. According to the surface topography analysis, the mean amplitude roughness parameter (Ra) was found to be 69.65 ± 0.01 nm. The 2D profile along the dotted red segment crossing horizontally the image is plotted in [Fig.9a](#). Height level decreases down to – 200 nm for two surface accidents, corresponding to the occurrence of a cavity and a grain boundary. These irregularities are responsible for the high value of Ra. Measurements were then performed in a smooth sub-region delimited by two grain boundaries, i.e. corresponding to the surface of a single grain ([Fig.9b](#)). The surface roughness parameter is significantly reduced to Ra value of only 2.93 ± 0.01 nm, which is even lower than typical roughness of VO₂ thin films deposited by physical vapour deposition (PVD) on flat substrates [24,

25, 26, 27]. Thus, the annealing step promoted grain growth by grain boundary diffusion and allowed to obtain a very low roughness surface.

The crystal structure of the annealed sample was then checked by XRD analysis ([Fig.10a](#)). Monoclinic VO₂(M1) phase is still present which means that the partial pressure of oxygen was properly adjusted during annealing to maintain the thermochromic allotropic form. It is interesting to note that the obtained VO₂ ceramic exhibits a strong preferential (011) crystallographic orientation. It suggests a preferential grain growth orientation during the post-annealing process, through the radial plane of the pellets and according to a crystallographic direction of the VO₂ structure. The (011) orientation corresponds to the edge-sharing [VO₆] octahedral chains. It can be so assumed that the grain growth mechanism proceeds through an alignment of the octahedral chains on either side of the grain interfaces before the coalescence of the two grains. Finally, the thermochromic behaviour of the VO₂ ceramic was evaluated by resistance *versus* temperature measurements ([Fig.10b](#)). A resistance drop over 3 orders of magnitude is observed in the phase transition process, in heating mode. The variation of the electrical contrast at the phase transition is comparable to the best recent results reported on VO₂ ceramics or films [28, 29, 30, 31]. The transition temperature is 68.0°C and 64.9°C for the heating and cooling process, respectively, revealing a hysteresis width of only 3.1°C, much narrower than for dense VO₂ thin films reported in literature [28]. This extremely narrow hysteresis width can be attributed to the crystallographic orientation observed by XRD [32]; a phase-transition cooperative mechanism between neighbouring grains oriented along the same crystallographic axis can be considered. Such thermochromic properties are very promising for applications requiring a fast and no delayed switching behaviour such as sensors or detectors.

4. Conclusion

High quality polycrystalline VO₂ powder was synthesized using a carbothermal reduction process of V₂O₅ / carbon soot mixtures. The influence of the synthesis temperature on crystallographic and thermochromic properties was investigated by XRD and DSC techniques, respectively. Pure VO₂ monoclinic phase was successfully obtained at different annealing temperatures, with various grain sizes and crystalline fractions as long as the carbon content was well adapted to the treatment temperature. VO₂ powder synthesized at 800°C is fully crystallized (i.e. no amorphous content) and exhibits an intense thermochromic behaviour. An innovative sintering process using two successive stages was thereafter performed to obtain high quality VO₂ ceramics from the as-prepared powder. First, SPS process was used to obtain high-density VO₂ pellet. Then, the VO₂ pellet was post-annealed in an induction furnace at 1300°C for 1 h under a controlled atmosphere to allow grain growth by coalescence and improve the surface quality. The obtained VO₂ ceramic presents a smooth surface (i.e. low roughness) with large grain size above 50 µm. The large resistance change, by three orders of magnitude along the monoclinic to rutile phase transition, and the very narrow hysteresis width associated to the pellet preparation process represent a breakthrough. Both these properties make the as-prepared VO₂ ceramic a promising candidate for various applications relying on thermally induced optical and/or electronic switching as smart sensors, radiators or transistors, adaptive infrared camouflage, cool roofs for smart buildings.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures :

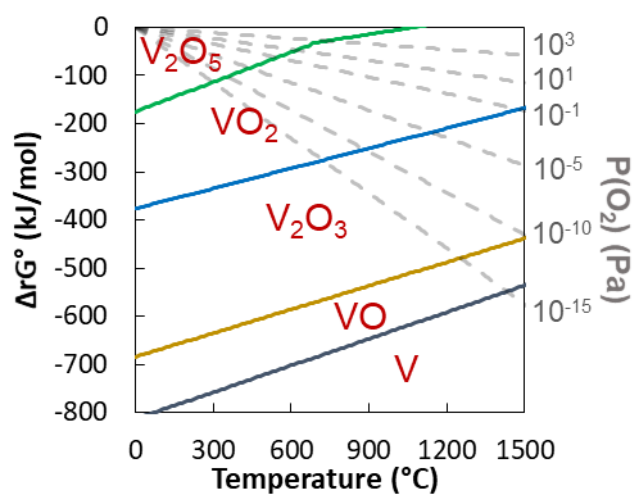


Fig. 1. Ellingham diagram of vanadium (not all existing oxides are displayed for clarity).

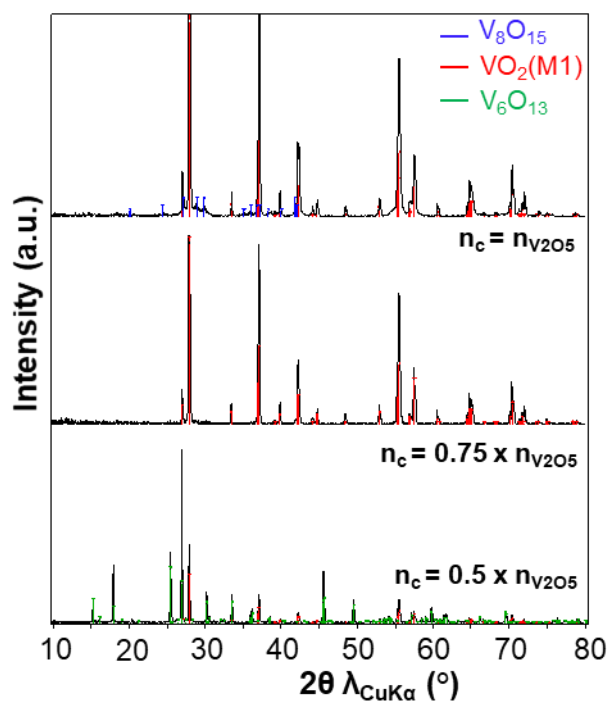


Fig. 2. X-ray diffraction patterns of the samples obtained from thermal treatment at 650°C for 10 h of various C- V_2O_5 mixtures with different C/ V_2O_5 molar ratios ($n_c/n_{\text{V}_2\text{O}_5}$).

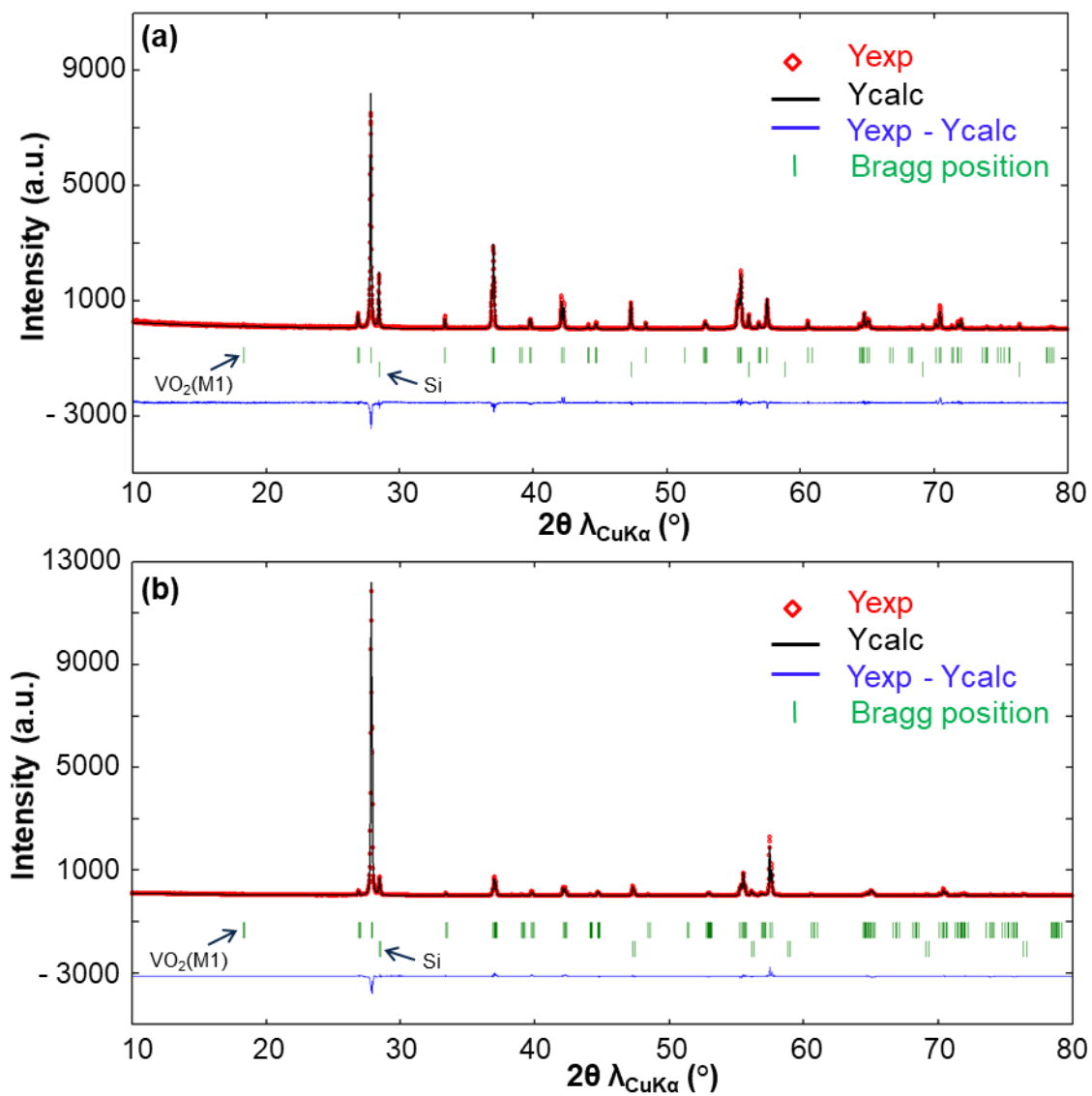


Fig. 3. Rietveld refinements of XRD data of accurate amount of silicon reference mixed with VO₂ annealed at 650 °C (a) and 800 °C (b).

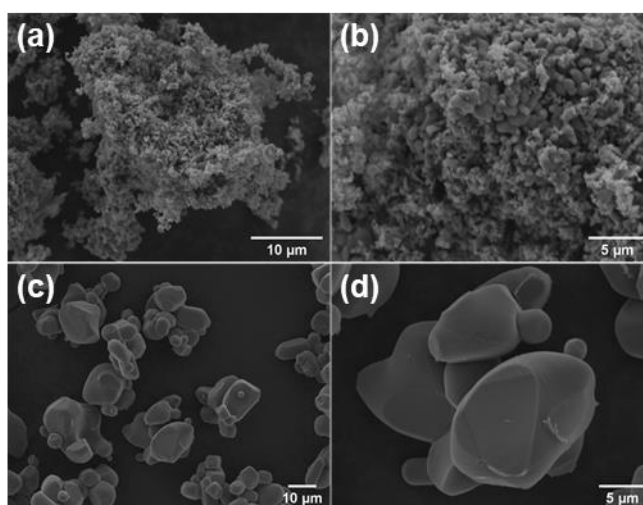


Fig. 4. SEM images of VO₂ powder synthesized at 650 °C (a,b) and 800 °C (c,d).

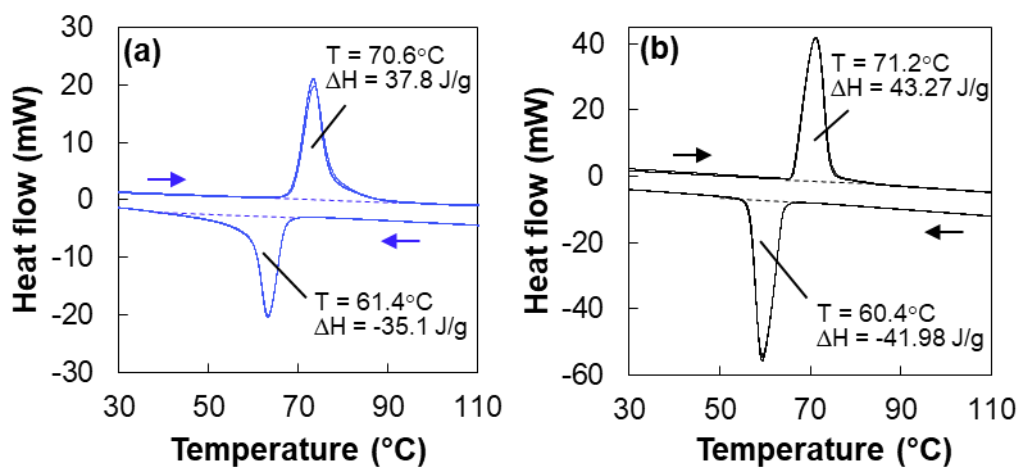


Fig. 5. DSC curves of VO₂ powder synthesized at 650 °C (a) and 800 °C (b).

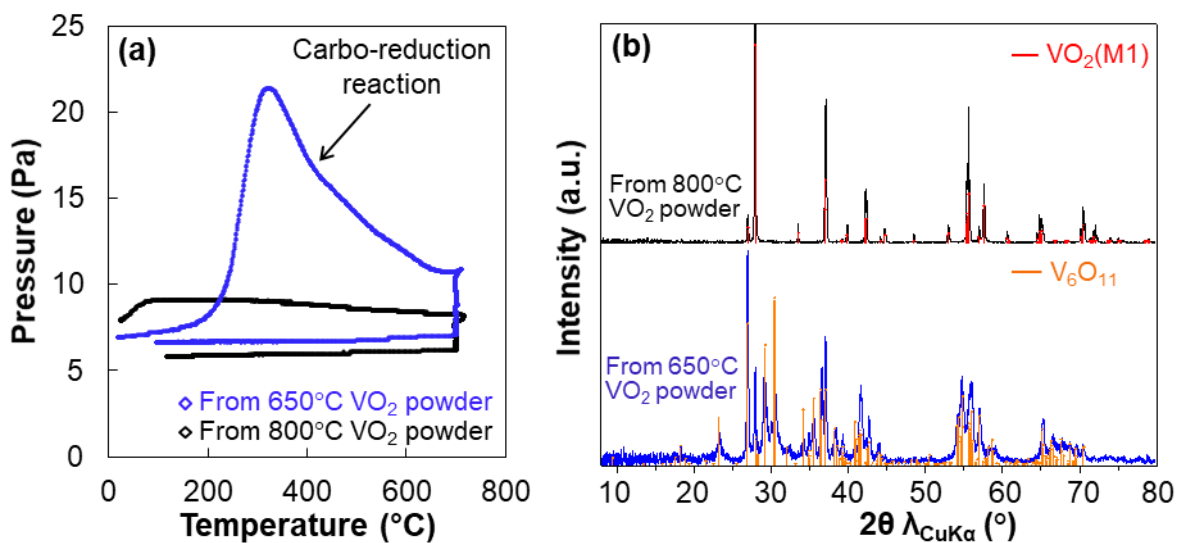


Fig. 6. Evolution of the chamber's pressure vs temperature during SPS from VO₂ powder synthesized at 650 °C and 800 °C (a) and XRD patterns of the obtained pellets (b).

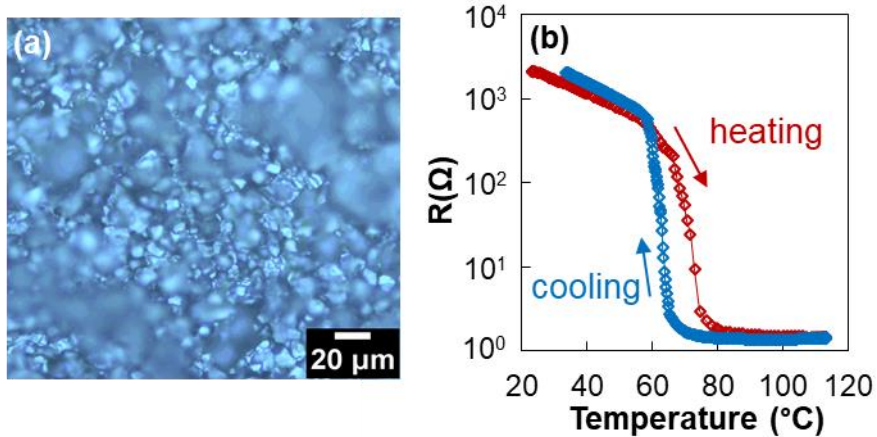


Fig. 7. Optical microscope image of the pellet surface (a) and its electric resistance vs temperature (b) for a VO₂ pellet obtained by SPS process applied to the VO₂ powder synthesized at 800 °C.

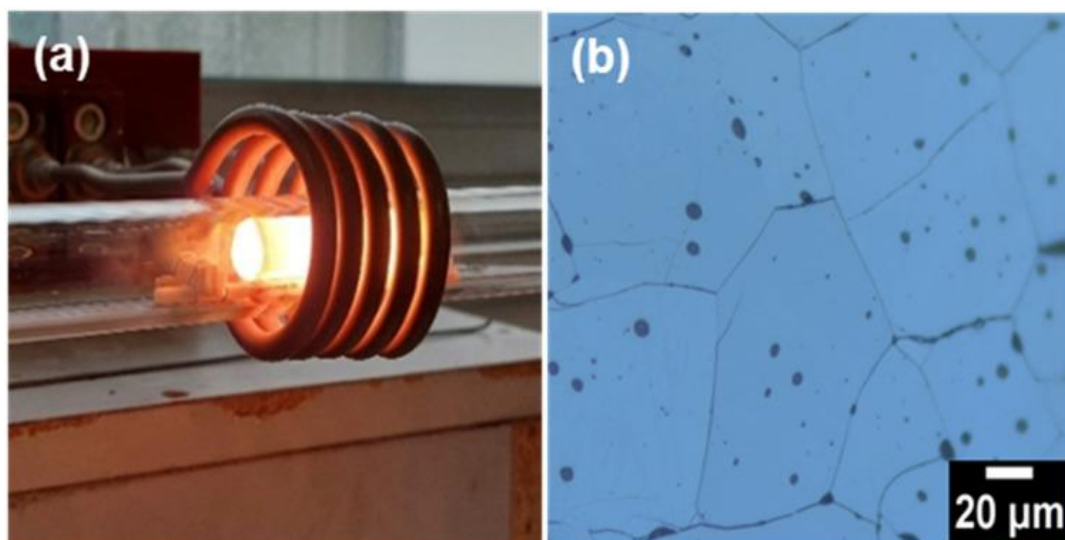


Fig. 8. The homemade induction furnace used for annealing (a) and optical microscope image of VO₂ ceramic obtained after annealing for 1 h at 1300 °C under controlled atmosphere ($P_{O_2} = 100$ Pa) (b).

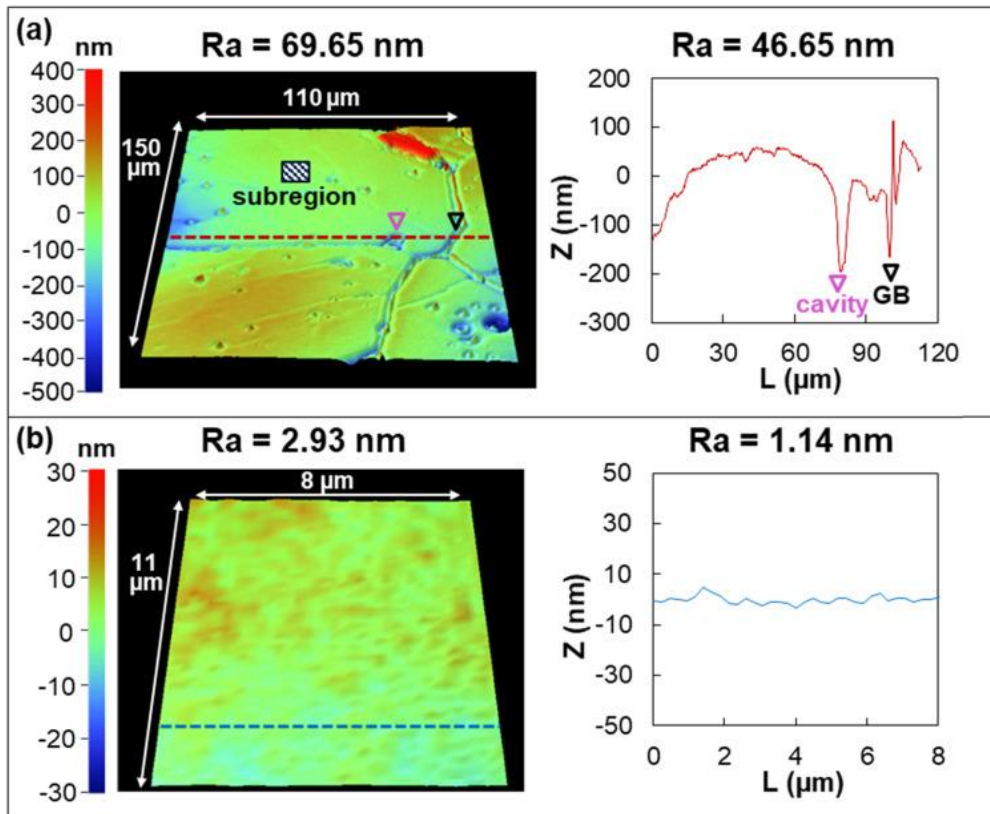


Fig. 9. 3D surface image and 2D profile of VO_2 ceramic obtained after annealing for 1 h at 1300°C under controlled atmosphere of SPS VO_2 pellet; analysis performed on an area of $110 \times 150 \mu\text{m}^2$ (a) and analysis performed on a smooth sub-region ($11 \times 8 \mu\text{m}^2$) (b).

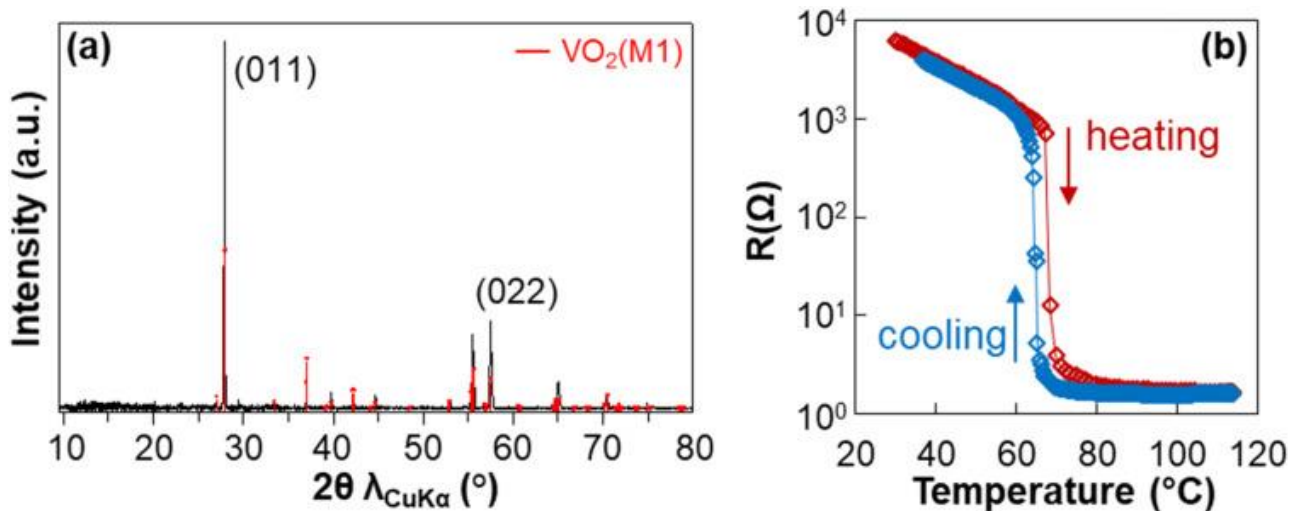


Fig. 10. XRD pattern (a) and electric resistance vs temperature (b) of VO_2 ceramic obtained after annealing for 1 h at 1300°C under controlled atmosphere of VO_2 pellet obtained by SPS process applied to the VO_2 powder synthesized at 800°C .