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Gel-combustion synthesis of $CoSb_2O_6$ and its reduction to powdery Sb_2Co alloy

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Abstract: Sb_2Co alloy in powdery form was synthesized *via* reduction with gaseous hydrogen of the oxide $CoSb_2O_6$, obtained by the citrate gel-combustion technique. The precursor was an aqueous solution of antimony nitrate, cobalt nitrate and citric acid. The precursor solution with mole ratio Co(II)/Sb(V) of 1:2 was gelatinized by evaporation of water. The gel was heated in air up to the temperature of self-ignition. The product of gel combustion was a mixture of oxides and it had to be additionally thermally treated in order to be converted to pure $CoSb_2O_6$. The reduction of $CoSb_2O_6$ by gaseous hydrogen yielded powdery Sb_2Co as the sole phase. The process of oxide reduction to alloy was controlled by thermogravimetry, while X-ray diffractometry was used to control the phase compositions of both the oxides and alloys.

Keywords: $CoSb_2O_6$; Sb_2Co; gel-combustion; intermetallic compound; thermogravimetry; X-ray diffraction.

INTRODUCTION

Sol–gel techniques and their variances: gel-combustion techniques, are widely used to produce nano-dispersed, simple or combined, oxides serving as high temperature superconductors,[1] ferrites,[2,3] electrode materials for lithium batteries,[4] catalysts,[5,6] *etc*. The reduction of oxides by heating in a hydrogen atmosphere presents an already known procedure of powder metallurgy, enabling the synthesis of powders of pure metals or alloys.[7–15]

Sol–gel techniques, being faster and more effective, are replacing more and more classical solid-state synthesis procedures. Namely, the low mobility of atoms in solids is the basic obstacle in the synthesis of solid materials through classic solid-state reactions, where the relatively coarse starting mixtures of the solid compounds require either a long time or high temperatures to achieve interdiffu-

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sional homogenization on the molecular level. Sol–gel techniques enable intimate precursor mixtures that are homogeneous on the molecular level to be obtained, leading to a final product with only little additional treatment. The citrate gel-combustion method was already used to synthesize the complex oxide compounds $LiMn_2O_4$[4] and $NiWO_4$,[16] while a two-step procedure, involving both gel-combustion synthesis of oxide mixtures and their reduction to alloys, was used recently to obtain Ni–W[16] and Ni–Mo[17] alloys. The hypothesis underlying this two-step route may be expressed as follows: the gel-combustion procedure provides a mixture of oxides homogeneous on the molecular level, which yields immediately a thermodynamically stable alloy upon reduction. This idealized performance assumes low temperature synthesis of an alloy without the need for any additional thermal treatment to relax its structure.

The intermetallic compound $CoSb_2$ is a representative of the arsenopyrite class of compounds.[18] This alloy is also known as a semiconductor material of relatively low thermal conductivity and high thermoelectric power.[19,20] For semiconductor investigations, large crystals of $CoSb_2$ were synthesized earlier by Feschotte *et al.*[20] by the gradient-freeze technique. The intermetallic compound $CoSb_2$ recently became additionally interesting as an anodic material for Li-ion batteries, being of high theoretical Faradic capacity (amounting to even 530 mA g^{-1}), as well as nice cyclability, if prepared in a nano-dispersed or amorphous form.[21–25] Xie *et al.*[22] published the synthesis of a nano-dispersed alloy based on levitation melting and ball milling of the solidified bulk alloy. Somewhat later, Xie *et al.*[23] published the solvothermal synthesis, in which a solution of $CoCl_2 \cdot 6H_2O$, $SbCl_3$ and $NaBH_4$ in anhydrous ethanol was placed in an autoclave and thermostated for a certain time, whereby Sb_2Co alloy as a precipitate, which was filtered, washed and vacuum-dried, was obtained.

The intention of the present study was to synthesize Sb_2Co alloy in the powdery form by reduction of a mixed oxide $CoO–Sb_2O_5$ synthesized by combustion of the corresponding citrate gel. This was an attempt to surmount the disadvantages of the classic metallurgical melt-solidification route, which requires closed conditions due to a pronounced ability of antimony to sublime,[22,25] as well as to avoid the relatively complex solvothermal synthesis.[23]

EXPERIMENTAL

The chemicals used in this study: Sb, $Co(NO_3)_2 \cdot 6H_2O$ and citric acid, were purchased from Merck. 1 g of metallic powdery Sb (8.214 mmol) was mixed with 5.178 g of citric acid (24.6 mmol) and 1 ml of concentrated nitric acid, and 2 ml of distilled water was added. The antimony was dissolved quantitatively under slight heating. Then 1.1952 g $Co(NO_3)_2 \cdot 6H_2O$ (4.107 mmol) was added to the solution to obtain a mole ratio Sb:Co of 2:1. The solution was dried at 80 °C for 24 h to gelatinize. The dry gel was heated in air up to self-ignition, which occurred at about 300 °C, yielding a dark-gray powder, which was expected to be the oxide mixture. This powder was isothermally treated for 30 min in air at a predetermined temperature, in order to remove traces of carbon, which also unavoidably consolidated the crystal structure. A small part of the oxide sample was used to prove thermogravimetrically the conditions of reduction with gaseous hydrogen. A TA Instruments Model 2090 TG–DTA device was used to obtain a TG curve under a flow of the gas mixture Ar + H_2 (25 vol.%). From the TG curve, the final temperature of reduction was determined. Then, the whole oxide mass was placed in a quartz tube which was protruded through a horizontal furnace and the reduction gas stream (Ar + H_2 (25 vol.%)), at a constant flow rate of 70 ml min^{-1}, was established through the tube. After heating up to the temperature required for complete reduction, a gray powder was obtained, which was expected to be Sb_2Co. X-Ray analysis for the purposes of this study was performed by means of a Philips PW 1710 diffractometer, using $CuK_{\alpha1,2}$ line (λ = 1.54056 Å) in the 15–70° 2θ range, in steps of 0.05° with an exposition of 3 s. The morphology of alloy was observed using a Jeol JSM-840A scanning electron microscope.

RESULTS AND DISCUSSION

As is known from inorganic chemistry, CoO and Sb_2S_5 may form the complex oxide compound $CoSb_2O_6$. This compound was expected to be the direct product of the gel-combustion synthesis described in the Experimental section, in view of the hypothesis that the gel-combustion procedure provides homogenization on a molecular level. The powdery product of the gel-combustion procedure described in the Experimental section was treated isothermally at 700 °C during 30 min in order to remove traces of carbon and then was subjected to X-ray diffraction analysis in order to examine the phase composition. The XRD diffracttogram (Fig. 1) evidenced not only the expected pure $CoSb_2O_6$, but a mixture of $CoSb_2O_6$, Sb_2O_3 and CoO, which were identified based on JCPDS cards 18-0403, 72-1854, and 75-0418,[26] respectively. The appearance of the compound $CoSb_2O_6$ confirms the expectation that the gel-combustion procedure leads to a very intimate mixture of oxides, able to react mutually and to build a thermodynamically stable compound. However, the appearance of free simple oxides indicates that the temperature developed during the gel combustion was insufficient to provide

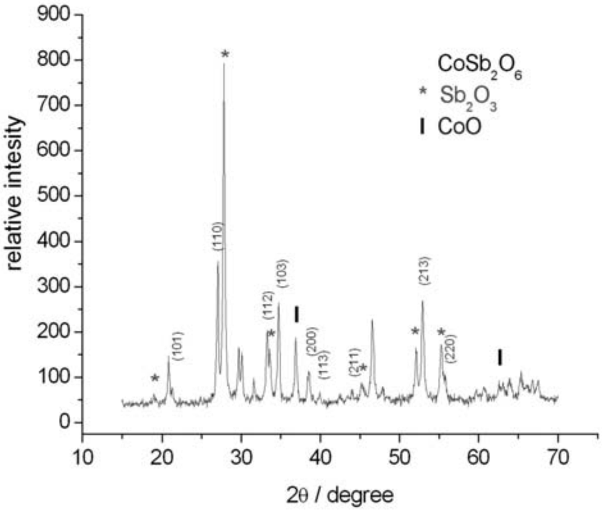

Fig. 1. X-Ray diffractogram of the oxide mixture obtained by citrate gel-combustion, upon thermal treatment at 500 °C. The diffraction lines of $CoSb_2O_6$, Sb_2O_3 and CoO are labeled by Miller indices ($CoSb_2O_6$) or by marks, shown in the inserted legend.

for complete conversion of simple oxides to their product, $CoSb_2O_6$. The appearance of the lower-valence oxide Sb_2O_3 is most probably due to the partial reduction of Sb_2O_5 by the carbon appearing as a product of incomplete combustion of citric acid.

In order to examine whether the obtained oxide mixture, in spite of its complexity, may yield the expected Sb_2Co alloy, the complete product of gel-combustion was subjected to reduction. Namely, the lower the temperature used in the procedure, the lower is the expected mean particle radius of resulting product.

The procedure of reduction was checked first by thermogravimetry. For this purpose, the oxide mixture was subjected to reduction within a thermobalance, in a stream of the gaseous mixture Ar + H_2 (25 %). The mass change during linearly programmed heating is shown in Fig. 2. Obviously, reduction accompanied by mass loss proceeds in one step and finishes at 650 °C. This TG curve shows that the mass loss amounts to 20 %, confirming that a part of the Sb existed as Sb_2O_3 in the initial product. Namely, the mass loss which corresponds to the conversion $CoSb_2O_6 \rightarrow Sb_2Co$ amounts to 24 %. The TG data in Fig. 2 show that a temperature of at least 650 °C is required to finalize the reduction of the oxides. Bearing this fact in mind, the whole amount of the oxide product obtained by gel-combustion was reduced in a stream of the gaseous mixture Ar + H_2 (25 vol.%) at 800 °C, and then cooled to room temperature, keeping it permanently under the reducing gas stream to avoid re-oxidation.

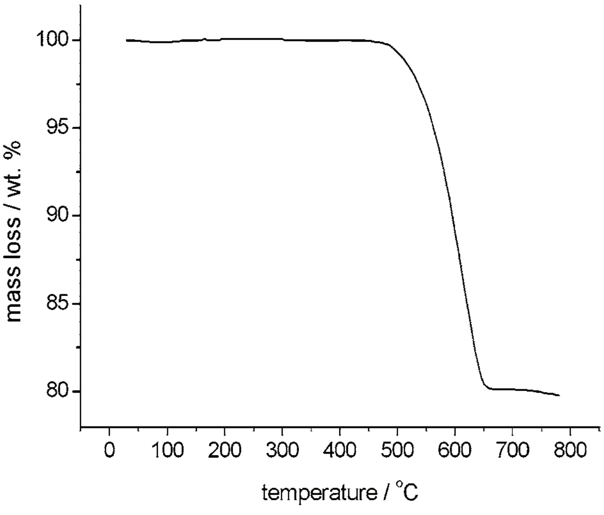

Fig. 2. Thermogravimetric curve obtained during the heating of the oxide mixture $CoSb_2O_6$, Sb_2O_3 and CoO in an Ar + H_2 (25 vol. %) stream at a heating rate of 15 °C min^{-1}.

The X-ray diffractogram of the obtained alloy, shown in Fig. 3, evidences that the resulting alloy was a mixture of Sb_2Co (monoclinic, JCPDS card No. 29-0126)[26] and SbCo (JCPDS card No 33-0097).[26] On the basis of the relative intensities, Sb_2Co was in excess. A real explanation for the complexity of the phase composition illustrated in Fig. 3 is the presence of simple oxides in the initial oxide mixture, as visible in Fig. 1. At least, free antimony oxide present in the initial mixture yields elementary Sb during reduction, which may evaporate at 800 °C and deteriorate the expected mole ratio Sb:Co of 2:1. This explains the appearance of SbCo besides of Sb_2Co in the final alloy.

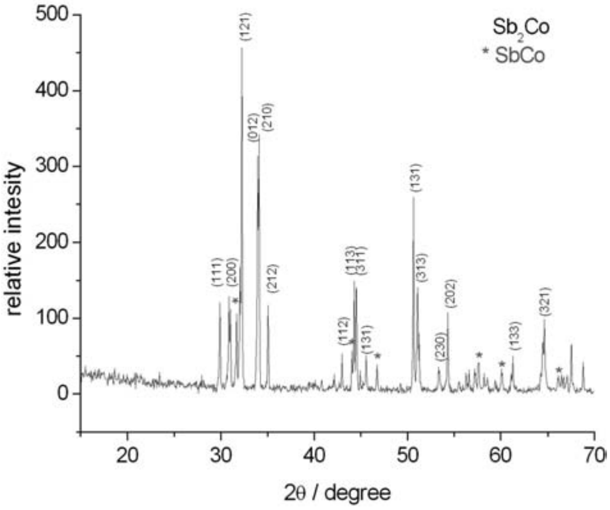

Fig 3. X-Ray diffractogram of the alloy obtained by the chemical reduction of the product of the gel-combustion procedure. The diffraction lines of Sb_2Co are labeled by Miller indices, while those of SbCo are labeled by an asterisk.

To avoid these obstacles, an attempt was made to simplify the phase composition of the oxides by an additional thermal treatment. Therefore, the oxide product obtained upon gel-combustion was treated isothermally at a temperature of 1000 °C in an air stream for 30 min, under the expectation that the simple oxides CoO and Sb_2O_3, appearing together with $CoSb_2O_6$, would mutually react *via* a solid-state reaction to yield pure $CoSb_2O_6$. After this treatment, the oxide product was examined by X-ray diffraction and the diffractogram, shown in Fig. 4, indeed evidenced only one phase, $CoSb_2O_6$.

The monophase powder $CoSb_2O_6$ was then subjected to reduction. A thermogravimetric curve of the reduction of a small sample of the same oxide, presented in Fig. 5, shows a mass loss of 24 %, which is in accordance with the calculated value for complete reduction of $CoSb_2O_6$ to metal. Generally, there is no remarkable difference in the shape between this TG curve of the monophase oxide and the one presented in Fig. 2 for the multiphase oxide mixture. Therefore, the oxide $CoSb_2O_6$ was reduced in the same way on heating in an Ar + H_2 (25 %) stream at 800 °C for 30 min. After cooling to room temperature, the mass was examined by X-ray diffraction and SEM. The X-ray diffractogram presented in Fig. 6 indicates the presence of Sb_2Co only, although the relatively low signal-to-noise ratio indicates its low crystallinity degree. Its SEM microphotograph, Fig. 7, shows that the particle diameter amounted to a few micrometers and that the relatively high temperature of 800 °C, required for oxide reduction, caused partial particle agglomeration by sintering.

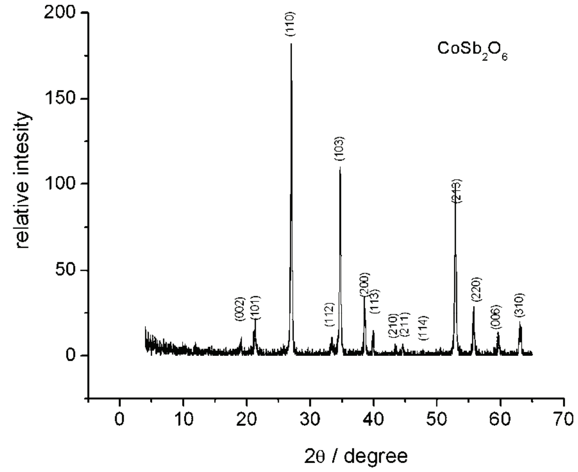

Fig 4. X-Ray diffractogram of the product of gel-combustion after thermal treatment at 1000 °C. Only the reflections of $CoSb_2O_6$, labeled by Miller indices, may be observed.

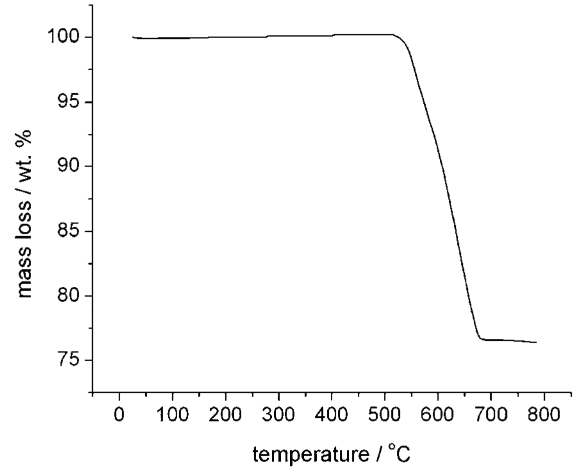

Fig 5. Thermogravimetric curve obtained during the heating of the stoichiometric oxide $CoSb_2O_6$ in an Ar + + H_2 (25 vol.%) stream at a heating rate of 15 °C min^{-1}.

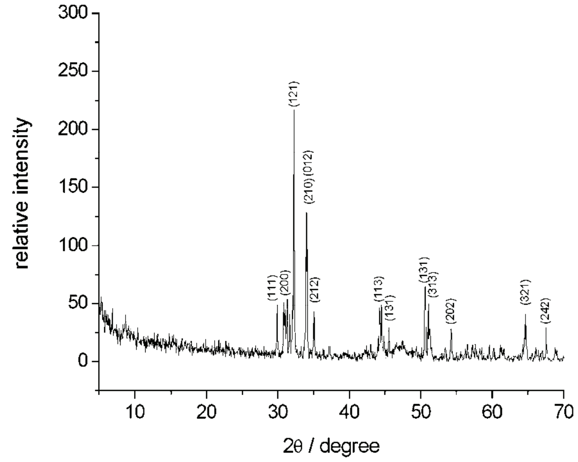

Fig 6. X-Ray diffractogram of the product of the reduction of $CoSb_2O_6$. The reflections from the different crystallographic planes of Sb_2Co are labeled by the corresponding Miller indices.

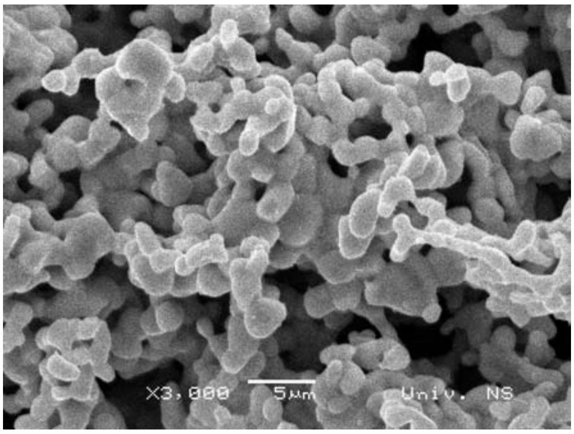

Fig. 7. An SEM microphotograph of the Sb_2Co alloy.

CONCLUSIONS

The intention of this study was first to synthesize an intimate mixture of CoO and Sb_2O_5, expecting to obtain $CoSb_2O_6$, and then to reduce it to the intermetallic compound Sb_2Co in powdery form. The gel-combustion procedure was used for the synthesis of the oxide mixture. The conditions of oxide reduction were controlled thermogravimetrically, while the phase composition of solid products was controlled by X-ray diffraction. For the gel-combustion product, purified from carbon residues by heating in air at 700 °C, X-ray diffractometry evidenced a multiphase system, consisting of the mixture $CoSb_2O_6$ + CoO + Sb_2O_3. Its reduction in a hydrogen atmosphere at 800 °C yielded a two-phase metallic product composed of SbCo and Sb_2Co. In order to improve the procedure, the oxide mixture obtained by the gel-combustion procedure was additionally treated by annealing at 1000 °C. This treatment provided the monophase oxide $CoSb_2O_6$. Its reduction in a hydrogen atmosphere at 800 °C yielded the monophase alloy Sb_2Co. This method requires a reduced number of time consuming steps in comparison to the solvothermal method.

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ИЗВОД

СИНТЕЗА $CoSb_2O_6$ МЕТОДОМ САГОРЕВАЊА ГЕЛА И РЕДУКЦИЈА ДО ПРАШКАСТЕ ЛЕГУРЕ Sb_2Co

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Легура Sb_2Co у форми праха синтетисана је редукцијом оксида $CoSb_2O_6$ добијеног методом сагоревања цитратног гела. Полазни водени раствор направљен је од антимон-нитрата, кобалт-нитрата и лимунске киселине. Полазни раствор са молским односом Co(II)/Sb(V)

1:2 преведен је у гел упаравањем воде. Гел је загреван на ваздуху до температуре самопаљења. Производ сагоревања је смеша оксида, и морао је да се додатно третира термички да би се превео у чист $CoSb_2O_6$. Редукцијом $CoSb_2O_6$ у атмосфери водоника добијена је прашкаста легура Sb_2Co као чиста фаза. Процес редукције оксида до легура контролисан је термогравиметријски, док је фазни састав оксида и легура испитиван дифракцијом X-зрака.

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