Journal of Alloys and Compounds 495 (2010) 537–540

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis of hydrogen tungsten bronzes H_xWO_3 by reactive mechanical milling of hexagonal WO_3

Facundo J. Castro [a], Florent Tonus [b], Jean-Louis Bobet [b], Guillermina Urretavizcaya [a,*]

[a] Centro Atómico Bariloche (CNEA, CONICET), Instituto Balseiro (UNCuyo), Av. Bustillo 9500, San Carlos de Bariloche, Argentina
[b] Institut de Chimie de la Matière Condenseé de Bordeaux (ICMCB), CNRS (UPR 9048), Université de Bordeaux I, 87 Avenue du Dr. A. Schweitzer, 33608 Pessac Cedex, France

ARTICLE INFO

Article history:
Received 18 July 2008
Received in revised form 14 October 2009
Accepted 15 October 2009
Available online 24 October 2009

Keywords:
Hydrogen tungsten bronzes
Mechanical alloying
Hydrogen absorbing materials

ABSTRACT

Recently, we have reported the formation of hydrogen tungsten bronzes by reactive mechanical milling monoclinic tungsten (VI) oxide under hydrogen atmosphere. In this work we report the milling of hexagonal WO_3 under H_2 atmosphere. Our main results are the structural transformation of the hexagonal oxide to the high temperature polymorph of WO_3 with orthorhombic structure, and the formation of different hydrogen tungsten bronzes at distinct milling times. The bronzes seem to be formed from the orthorhombic oxide, and compared with the bronzes obtained by milling monoclinic WO_3 are rather unstable after short exposure to air. The materials are characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and total hydrogen content determination.

1. Introduction

Tungsten trioxide is a compound that exhibits several polymorphic forms. Each one is stable in a definite temperature range [1]. Monoclinic WO_3 is the stable polymorph at room temperature and in the range 17–330 °C. These polymorphs can reversibly transform into each other but not in the hexagonal structure, because the hexagonal forms of WO_3 do not belong to the polymorph series. Gerand et al. obtained hexagonal WO_3 for the first time by dehydration of $WO_3 \cdot 1/3H_2O$ hydrate [2]. Other forms to synthesize hexagonal WO_3 are described in Refs. [3–5].

Hydrogen tungsten bronzes [6–15] are non-stoichiometric materials with formula H_xWO_3 (x in the range from 0.1 to 0.6) in which hydrogen atoms are incorporated into the structure of tungsten (VI) oxide. From a crystallographic point of view, they belong to the family of tungsten bronzes [6,16–18], in which different electropositive elements such as alkaline metals, alkaline earth metals, transition metals and rare earths are intercalated among the WO_6 octahedra. These materials show a very rich crystallographic chemistry and very interesting electronic properties due to its metallic conductivity, produced by the electron mobility [12,14,15]. Most of the applications are concentrated on their electrochromic properties. The traditional methods to obtain hydrogen tungsten bronzes are reported in Refs. [7,8]. Recently, the mechanochemical synthesis route has been successfully used for bronze formation, by milling monoclinic WO_3 with liquid hydrocarbons (*e.g.* xylene) under air [15], or by direct synthesis by milling monoclinic WO_3 under hydrogen atmosphere [19].

In this paper we report the synthesis of hydrogen tungsten bronzes by milling hexagonal WO_3. As an additional motivation for studying the milling of hexagonal WO_3, a sort of cyclic behavior was observed [20] when milling under hydrogen or under argon a different variety of hexagonal WO_3 (JCPDS card no. 85-2460). There it is reported that the amount of hexagonal oxide diminishes during the first milling hours, but then grows with subsequent milling.

2. Experimental

The starting powder was hexagonal WO_3 synthesized according to the method of Solonin et al. [4]. Briefly, $CuWO_4$ was obtained after heat-treating a mechanical mixture of monoclinic WO_3 (Aldrich, 99+%) and CuO (Sigma–Aldrich, 99+%) 30 h at 850 °C under air; after that, the tungstate was reduced to a mixture of Cu and hexagonal H_xWO_3 by heating it under flowing H_2 for 5 h at 300 °C; then, the copper was washed away of the mixture by using concentrated HNO_3; finally, the bronze was decomposed into hexagonal WO_3 by heating it for 1 h at 375 °C under air.

The milling was done in a Uni-Ball-Mill II (Australian Scientific Instruments) apparatus. Around 17 g were milled under 5 bar of hydrogen using a ball to powder weight ratio of 20:1. The milling lasted up to 200 h. Periodically, the milling chamber was opened within a glove box with controlled oxygen and moisture content, and a small amount of powder was taken out for analysis.

The milling products were characterized by X-ray diffraction (XRD) using an hermetic sample holder under Ar atmosphere on a Philips PW 1710/01 instrument with Cu Kα radiation (graphite monochromator) and by differential scanning calorimetry (DSC) in a TA 2910 apparatus with a heating rate of 10 °C/min under flowing Ar (122 ml/min). Elemental identification was made by energy dispersive X-ray analysis (EDS, Philips Electronic Instruments). Additionally, the total amount of hydrogen in some samples was determined using a Leco RH-404 instrument.

---

* Corresponding author. Tel.: +54 2944 445100; fax: +54 2944 445199.
E-mail address: urreta@cab.cnea.gov.ar (G. Urretavizcaya).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.10.109

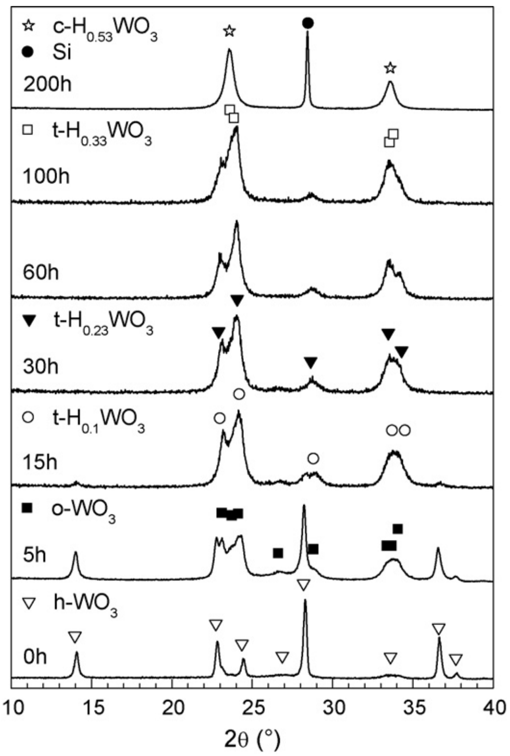

Fig. 1. XRD patterns of the milled materials as a function of milling time. In some patterns Si was used as a standard. For clarity, only the most intense reflections of the different cards are displayed; also for clarity in some cases their relative intensities are slightly modified.

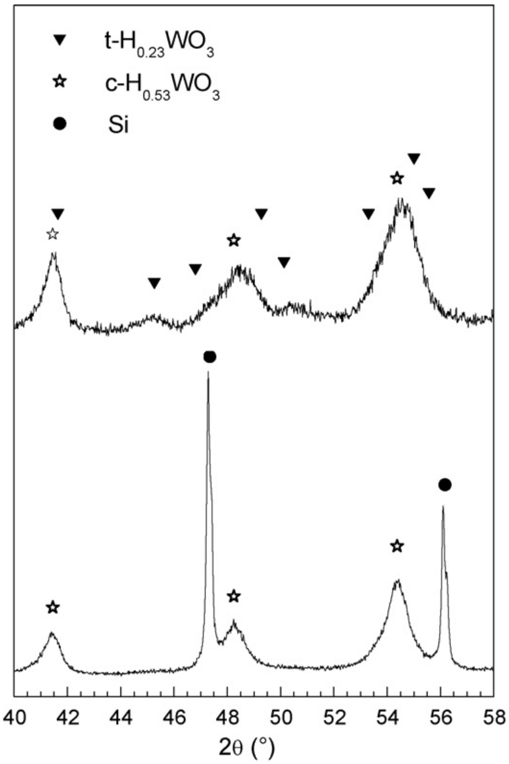

Fig. 2. Partial view of the XRD patterns of the 200 h milled material: bottom as-milled material, top after three days within an Ar filled glove box. Si used as a standard. The symbols of cards positions only denote 2θ location.

3. Results and discussion

The structural evolution of the material during milling, as determined by XRD, is presented in Fig. 1. For clarity only the 2θ range 10–40 is shown. Phase identification by XRD is a difficult task in this case, due to the combined effect of the great quantity of WO_3 polymorphs and hydrogen tungsten bronzes with very similar XRD patterns, and due to the microstructural characteristics produced by milling that render XRD patterns with broad peaks. In Table 1 we summarize the phases that undoubtedly are present in the material. The starting material has been clearly identified as hexagonal WO_3 (JCPDS 33-1387). However, the diffractogram also shows very small reflections that correspond to untransformed monoclinic oxide (JCPDS 43-1035). After 5 h of milling a fraction of the starting hexagonal WO_3 (JCPDS 33-1387) transforms to orthorhombic WO_3 (JCPDS 20-1324). Orthorhombic WO_3 is the stable phase in the temperature range 330–740 °C [1]. We do not know why the hexagonal oxide transforms to the high temperature structure of the oxide during a milling performed at room temperature, but it is not uncommon to obtain metastable phases by mechanical milling [21]. After 15 h of milling, orthorhombic WO_3 and a small amount of hexagonal oxide are present in the sample; additionally, a small amount of tetragonal $H_{0.23}WO_3$ (JCPDS 42-1261) can be seen. Moreover, the presence of tetragonal $H_{0.1}WO_3$ (JCPDS 23-1448) though not clearly seen, cannot be discarded (peak superposition). After 30 h, the starting hexagonal oxide disappears, some orthorhombic oxide remains, and the reflections of $H_{0.23}WO_3$ can be clearly seen. Additionally, the pattern does not allow us to clearly ascertain if there is some tetragonal $H_{0.33}WO_3$ (JCPDS 23-1449) or not. When the milling reaches 60 h, no oxide (nor hexagonal, neither orthorhombic) remains in the sample. At this milling time the entire pattern can be explained by the reflections of $H_{0.23}WO_3$, but again, nothing can be said about $H_{0.1}WO_3$ and $H_{0.33}WO_3$. After 100 h small reflections of cubic $H_{0.53}WO_3$ bronze (JCPDS 42-1260) start to appear, coexisting with $H_{0.23}WO_3$. Finally, after 200 h, the diffraction pattern corresponds to cubic bronze $H_{0.53}WO_3$ (please note that there is a mistake in the formula for this compound in the JCPDS card: it reads $H_{0.23}WO_3$ instead of $H_{0.53}WO_3$, as reported in the original paper). Interestingly, in the case of the 200 h milled material, the diffractogram obtained right after milling showed only the cubic bronze, but the diffractogram of the same material after three days within a glove box with controlled amounts of O_2 (less than 5 ppm) also showed the reflections of tetragonal bronze $H_{0.23}WO_3$, indicating that the cubic bronze is rather unstable (Fig. 2). A small contamination with Fe from the milling chamber

Table 1
Phases identified in the XRD patterns as a function of milling time. A check mark (√) indicates that the phase is present and a vertical bar (|) designates a phase that is present in a small amount (small peaks).

Milling time	0	5	15	30	60	100	200	200[a]
Hexagonal, WO_3, JCPDS 33-1387	√	√	|					
Monoclinic, WO_3, JCPDS 43-1035	√							
Orthorhombic, WO_3, JCPDS 20-1324		√	√	√				
Tetragonal, $H_{0.23}WO_3$, JCPDS 42-1261			|	√	√	√		√
Cubic, $H_{0.53}WO_3$, JCPDS 42-1260						|	√	√

[a] After being stored within a glove box for three days.

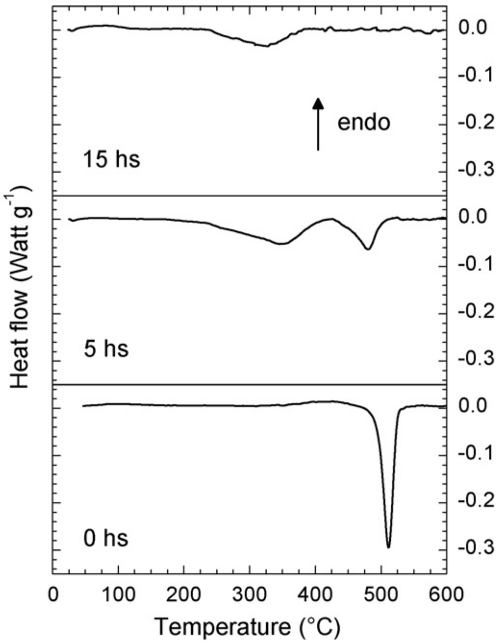

Fig. 3. DSC curves of the samples milled up to 15 h.

or balls was detected by EDS (<1 wt.%) and observed by XRD as a small peak that can be assigned to the more intense reflection of $FeWO_4$ ($2\Theta = 30.5°$, JCPDS 85-1354) in the sample milled 200 h.

The evolution of the milled material was also characterized by DSC measurements. The results can be grouped in two sets. In the first set, from 0 to 5 h of milling time (Fig. 3), only exothermic peaks are observed, and they can be linked with phase transformations of the oxide to the monoclinic structure. In the second set, from 30 to 200 h of milling time (Fig. 4), only one endothermic event is observed, and it is assigned to the decomposition of the tetragonal bronzes formed during milling. The DSC run corresponding to 15 h is a transition case, where an endothermic event at low temperature is observed together with an exothermic peak at high temperature. The thermogram corresponding to the starting material presents only one exothermic event with a minimum located at 511 °C. As was checked by XRD, this peak corresponds to the transformation of the hexagonal phase into the monoclinic structure (JCPDS 43-1035). The area under this peak gives an approximate value of the phase transformation enthalpy equal to −31.3 J/g. After 5 h of milling we see that two peaks appear in the thermogram. The first one, which occurs at lower temperatures, corresponds to the transformation of the orthorhombic oxide formed by milling into the monoclinic structure, the second one to the transformation of the original hexagonal WO_3 to the monoclinic structure. It is interesting to note that the second peak coincides in shape with the peak associated with the hexagonal to monoclinic transformation of the starting material, but it has smaller area, and it is a little bit shifted towards lower temperatures. The area reduction is a consequence of the diminished amount of hexagonal oxide due to the transformation to the orthorhombic structure; the temperature shift seems to be a typical milling effect, as has been reported several times for different systems [21]. The thermogram of the 15 h milled material presents one endothermic event at low temperatures and only one exothermic event around 300 °C. The endothermic peak corresponds to the decomposition of the tetragonal hydrogen tungsten bronze, whereas the exothermic event corresponds to the orthorhombic to monoclinic transformation. We do not see a second exothermic event associated to the hexagonal to monoclinic transformation of the oxide probably due to the too small amount of hexagonal oxide that remains.

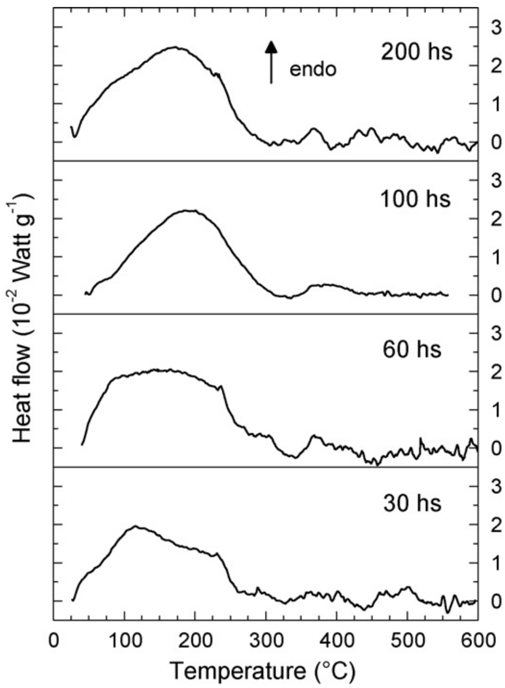

Fig. 4. DSC curves of the samples milled from 30 to 200 h.

Fig. 4 presents the thermograms of the second set (i.e. materials ball milled for 30–200 h). As before, the endothermic event at low temperatures is associated with the decomposition of the bronzes synthesized during milling. Despite the apparent irregularity in the shape of the thermograms, they are very similar to those obtained after milling monoclinic WO_3 [19]. The area under the endothermic event can be used to determine the amount of hydrogen in the bronze (x value in H_xWO_3, Fig. 5), using the same procedure described in Ref. [19]. The figure shows that the amount of hydrogen in the material grows with milling time, in general agreement with the phases identified by XRD. However, the amount of hydrogen determined by DSC is rather below the expected composition of the material. For example, the 60 h milled material presented a XRD pattern that corresponds almost completely to $H_{0.23}WO_3$, but the x value estimated from DSC measurements is only 0.14. The 100 h milled material has an XRD pattern with reflections that seem to belong to $H_{0.23}WO_3$ and $H_{0.53}WO_3$; regardless of this, the x value from DSC is 0.17. Finally, the XRD pattern of the 200 h milled

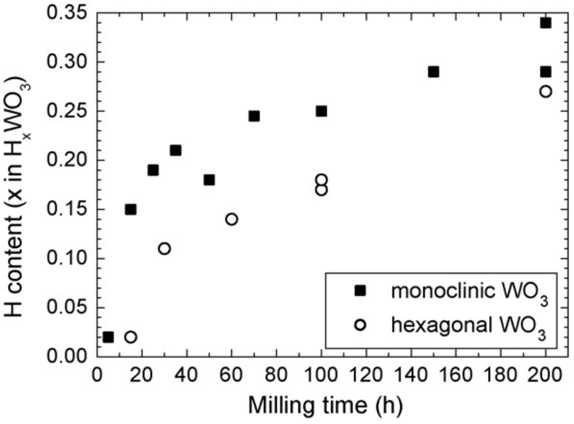

Fig. 5. Hydrogen content as a function of milling time determined from DSC for the milling of hexagonal WO_3 (open circles) and for the milling of monoclinic WO_3 (filled squares) [19].

material corresponds to $H_{0.53}WO_3$ and only after three days we can see small reflections associated with $H_{0.23}WO_3$; notwithstanding this, the *x* value from DSC is 0.27. It seems that the bronzes obtained by milling the hexagonal WO_3 are rather unstable upon short exposure to air, as was mentioned above in connection with Fig. 2 and the 200 h milled material. The XRD patterns have been made on samples never exposed to air, whereas the DSC capsules, though prepared and closed within a glove box, have been transferred to the DSC apparatus under air, and it seems that a short exposure to air for a few minutes is enough to decompose an appreciable amount of bronze. Moreover, the estimation of the *x* value by means of total hydrogen content determination (LECO) agrees with the DSC results. As an example, in the case of the 200 h milled sample, the *x* value given by LECO is 0.28, in good agreement with the DSC value (i.e. 0.27). It has to be mentioned that the samples have also been transferred to the LECO instrument under air.

Also in Fig. 5 we compare the evolution of *x* values for this milling and the milling done using monoclinic WO_3 as starting material [19]. We see that in both cases the general trends of the *x* values as a function of milling time are similar. However, in this case, the *x* values are slightly delayed in milling time, and a bit shifted towards lower *x* values. The delay and the XRD results, suggest that the hydrogen bronzes are formed from the orthorhombic oxide not from the hexagonal WO_3. If this were the case, the delay could be interpreted as the time needed to start synthesizing orthorhombic WO_3 from the hexagonal phase. The lower *x* values can be a consequence of the greater instability of the bronzes obtained from the orthorhombic oxide upon short exposures to air.

As a final remark, we do not observe in this case any cyclic behavior when milling hexagonal WO_3 under H_2 [20]. Maybe the reason for the absence of cyclic behavior could be the use of a different hexagonal WO_3. While the hexagonal oxide of [20] corresponds to the form reported by Oi et al. [5], in this case it corresponds to the form originally synthesized by Gerand et al. [2], which as far as we report here transforms irreversibly towards the orthorhombic structure.

4. Conclusion

The milling of hexagonal WO_3 under hydrogen atmosphere has given as main results the transformation of the oxide to the high temperature polymorph of WO_3 with orthorhombic structure, and the synthesis of hydrogen tungsten bronzes with different hydrogen contents. The bronzes seem to be produced from the orthorhombic oxide. The amount of hydrogen in the milled material as a function of milling time shows an evolution similar to the one observed when milling monoclinic oxide [19], but slightly delayed in time due to the formation from orthorhombic WO_3 and a little bit shifted towards lower values (instability of the bronzes formed from orthorhombic oxide). No cyclic behavior during milling was observed.

Acknowledgments

We gratefully thank H. Corso for the LECO measurements. We also acknowledge the SECYT - ECOS cooperation program for partial financing this work.

References

[1] A.F. Wells, Structural Inorganic Chemistry, third edition, Clarendon Press, Oxford, 1962.
[2] B. Gerand, G. Nowogrocki, J. Guenot, M. Figlarz, J. Solid State Chem. 29 (1979) 429–434.
[3] W. Han, M. Hibino, T. Kudo, Bull. Chem. Soc. Jpn. 71 (1998) 933–937.
[4] Y.M. Solonin, O.Y. Khyzhun, E.A. Graivoronskaya, Crystal Growth Des. 1 (2001) 473–477.
[5] J. Oi, A. Kishimoto, T. Kudo, M. Hiratani, J. Solid State Chem. 96 (1992) 13–19.
[6] F.R. Gamble, T.H. Geballe, in: N.B. Hannay (Ed.), Treatise on Solid State Chemistry, vol. 3, Plenum Press, New York, London, 1967, pp. 89–165.
[7] O. Glemser, C. Naumann, Z. Anorg. Allg. Chem. 265 (1951) 289–302.
[8] P.G. Dickens, R.J. Hurdicht, Nature 215 (1967) 1266–1267.
[9] P.J. Wiseman, P.G. Dickens, J. Solid State Chem. 6 (1973) 374–377.
[10] P.G. Dickens, J.H. Moore, D.J. Neild, J. Solid State Chem. 7 (1973) 241–244.
[11] M.V. Susic, Y.M. Solonin, J. Mater. Sci. 23 (1988) 267–271.
[12] L.A. Aleshina, L. Ya. Berezin, N.B. Inyushin, V.P. Malinenko, A.D. Fofanov, Sov. Phys. Solid State 31 (1989) 2048–2053.
[13] E. Cazzanelli, C. Vinegoni, G. Mariotto, A. Kuzmin, J. Purans, Solid State Ionics 123 (1999) 67–74.
[14] M.S. Whittingham, Solid State Ionics 168 (2004) 255–263.
[15] S. Takai, N. Hoshimi, T. Esaka, Electrochemistry 72 (2004) 876–879.
[16] P. Hagenmuller, in: J.C. Bailar Jr., H.J. Emeléus, R. Nyholm, A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, vol. 4, Pergamon Press, Oxford, 1973, pp. 541–605.
[17] J. Wang, G. Liu, Y. Du, Mater. Lett. 57 (2003) 3648–3652.
[18] W. Ostertag, C.V. Collins, Mater. Res. Bull. 2 (1967) 217–221.
[19] G. Urretavizcaya, F. Tonus, E. Gaudin, J.-L. Bobet, F.J. Castro, J. Solid State Chem. 180 (2007) 2785–2789.
[20] F.J. Castro, J.-L. Bobet, J. Alloys Compd. 366 (2004) 303–308.
[21] C. Suryanarayana, Prog. Mater. Sci. 46 (2001) 1–184.