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The thermogravimetric analysis of Sn–W bronzes [1]

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Abstract

For tin–tungsten bronzes Sn_xWO_3 prepared both under mild, aqueous conditions and by a high temperature solid state reaction, the degree of hydration, the amount of X-ray amorphous byproducts and the value x have been determined quantitatively by thermogravimetric reduction in hydrogen. This is clearly more precise than the oxidation in oxygen, as the latter is not complete at 1050°C and is accompanied only by a much smaller change in mass.

INTRODUCTION

Metal–tungsten bronzes are nonstoichiometric compounds which have a nominal composition M_xWO_3. The crystal structure and many properties of a bronze depend on its constitutents, but the insolubility of these reduced metal–tungsten oxides causes great difficulties in finding a reliable and practical analytical technique.

Since the first reports of the tungsten bronzes, there have been a number of papers that describe different analytical methods. Most of them are principally based on selecting suitable reagents for decomposition of the bronzes, for example the method of Philipp [1, 2] uses ammoniacal silver nitrate, that of Raby and Banks [3] uses bromine trifluoride, Bernoff [4] uses a mixture of $NaNO_3$ and Na_2CO_3 and Brimm [5] employs ammonium sulfate and sulfuric acid for digesting the bronzes.

In addition a microprocess using KOH for determining the lower oxidation degree [6] and electron probe microanalysis for the metal:tungsten ratio [7] have been introduced.

Recently we have developed a new method for preparation of

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[1] Dedicated to Hans Georg Wiedemann.

tin–tungsten bronzes under mild conditions [8]. Because in these phases tin oxide and tungsten oxide can be formed as byproducts, the precise chemical analysis of compounds such as Sn_xWO_3 is all the more difficult. By adopting the methods of Bernoff and Conroy [4] and Plies [9] who directly weigh samples after heating in hydrogen or oxygen gas, we have tried to use thermogravimetric analysis in different atmospheres for determination of the tin content. Some results of this investigation are presented below.

EXPERIMENTAL

Bronzes Sn_xWO_3 were prepared by the reaction of metallic tin and tungstic acid suspended in distilled water [8]. The powder products were then heated in evacuated ampules for transformation into single crystals.

A Mettler TG 2000 thermobalance was used for thermogravimetric analysis (TGA). The powder or finely powdered crystal samples of 40–50 mg mass were heated in alumina crucibles in flowing oxygen or hydrogen (40 ml min^{-1}). In order to avoid the problems caused by water retained in the powder samples, the TGA had to be performed up to 500°C in nitrogen gas until all remaining water had escaped from the bronzes. Scan speeds of 5°C min^{-1} were applied up to 900°C or 1000°C.

The final products and the intermediate phases in different temperature regions were examined by X-ray powder diffraction with a Guinier–de Wolff camera, using Gu Kα radiation and silicon as an internal standard.

RESULTS AND DISCUSSION

At first an attempt was made to measure the gain in mass from the TG curve after heating Sn_xWO_3 under flowing O_2. However there are two factors which prevented us from using the data from the TGA in oxygen. The first is that the increase in mass for Sn_xWO_3, if completely oxidized, totals only 4%, which introduces a greater error. The second is that the TG curve in O_2 rises continuously up to 1050°C, the upper temperature limit of our thermobalance. Clearly, the oxidation of the bronze is not yet finished at this temperature. It is probable that the first oxidized products SnO_2 and WO_3 form on the surface of the sample and prevent O_2 from reacting further with the interior of the sample. Indeed, electron diffraction shows that in samples heated to 1050°C, crystalline bronze is still present.

It was therefore decided to employ reduction in hydrogen. The TGA curves in flowing N_2–H_2 demonstrate a mass loss process. Step by step the Sn_xWO_3 samples were completely reduced to the elements tin and

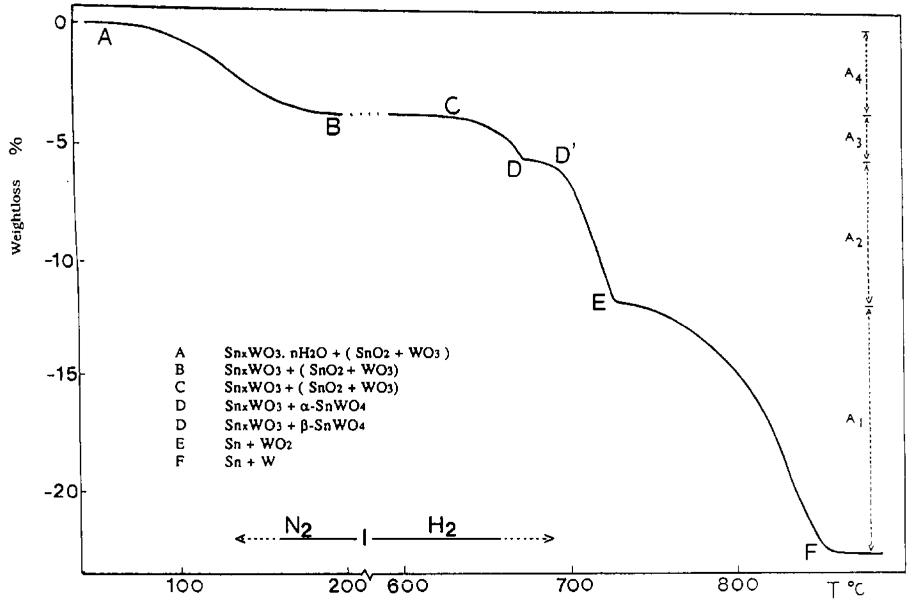

Fig. 1. TG curve of Sn_xWO_3 powder in H_2 ($x = 0.31$).

tungsten. Figure 1 shows the dependence of the sample mass on the temperature and the different reduced intermediates and products.

The process A–B is a simple dehydration. The reduction from D′ to F is also clear at a glance. The transformation of $SnWO_4$ from α to β type (D–D′) has no effect on the change in mass. The C–D step, after which the phase $SnWO_4$ has been observed, is not yet quite clear. Theoretically in this case and under reducing atmosphere, there may be many possibilities for formation of this tin tungstate, for example the direct reaction of tin dioxide with tungsten oxide or the oxidation of some Sn_xWO_3 by SnO_2, etc. Obviously the reaction is very complex and it is almost impossible to determine separately the amount of $SnWO_4$ formed from all possible reactions. For calculating the content of tin in bronze, however, we could state from D′, assuming the amount of $SnWO_4$ to be Δ.

Thus, from both reactions (1) and (2), occurring in D′–E and E–F, respectively

$$Sn_xWO_3 + \Delta SnWoO_4 \xrightarrow{H_2} (x + \Delta)Sn + (1 + \Delta)WO_2 + (1 + 2\Delta)H_2O \tag{1}$$

$$(1 + \Delta)WO_2 \xrightarrow{H_2} (1 + \Delta)W + 2(1 + \Delta)H_2O \tag{2}$$

we can derive a proportion equation

$$\frac{2(1 + \Delta)}{1 + 2\Delta} = \frac{A_1}{A_2} \tag{3}$$

where A_1 and A_2 indicate the mass losses in mg (see Fig. 1). Then, setting the value Δ obtained from eqn. (3) (ranging from 0 to 0.1, depending on the experimental conditions) in eqn. (4), the required value of x can be calculated.

$$\frac{(3+4\Delta)\mathrm{O}}{(x+\Delta)\mathrm{Sn}+(1+\Delta)\mathrm{W}+(3+4\Delta)\mathrm{O}}=\frac{A_1+A_2}{B_\mathrm{w}-A_3-A_4} \tag{4}$$

where O, Sn and W are the relative atomic masses of oxygen, tin and tungsten, respectively; B_w is the initial mass of the sample in mg; A_3 is the mass loss in mg from the step C–D; and A_4 is the water content in mg of step A–B.

By this method we have investigated a series of samples. For the Sn_xWO_3 powder, in the preparation of which the Sn/H_2WO_4 ratio was 0.33:1, the value of x calculated according to the TG curve in Fig. 1 is equivalent to 0.31.

As expected, single crystal samples have a very similar TGA curve excluding the dehydration process. Figure 2 shows the H_2 reduction procedure to a crystal sample obtained from the same powder as that in Fig. 1. With similar calculations the result was $x = 0.33$, greater than that from the powder bronze. Probably this is evidence that by heating the powder for a long time in the evacuated ampule more Sn has been incorporated into the lattice tunnels.

For comparison we have also recorded the TGA of Sn_xWO_3 prepared by means of reported solid state reactions [10]. Corresponding to the fact that

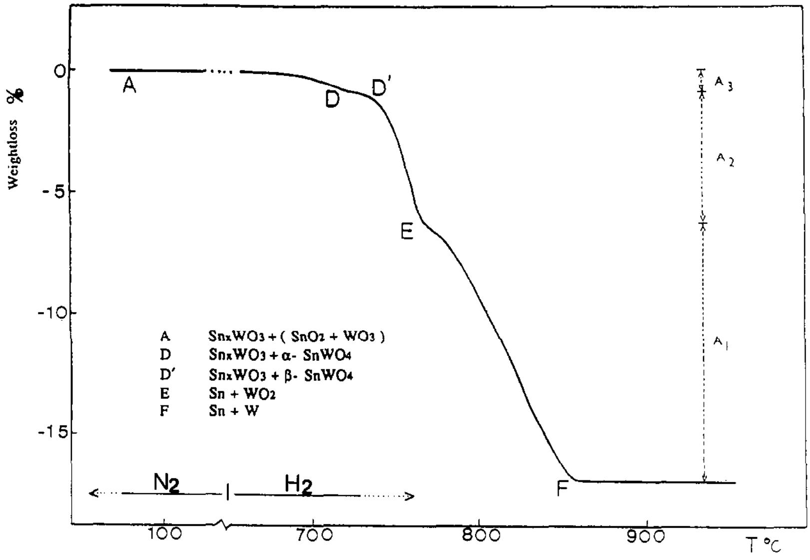

Fig. 2. TG curve of single crystalline Sn_xWO_3 in H_2 ($x = 0.33$).

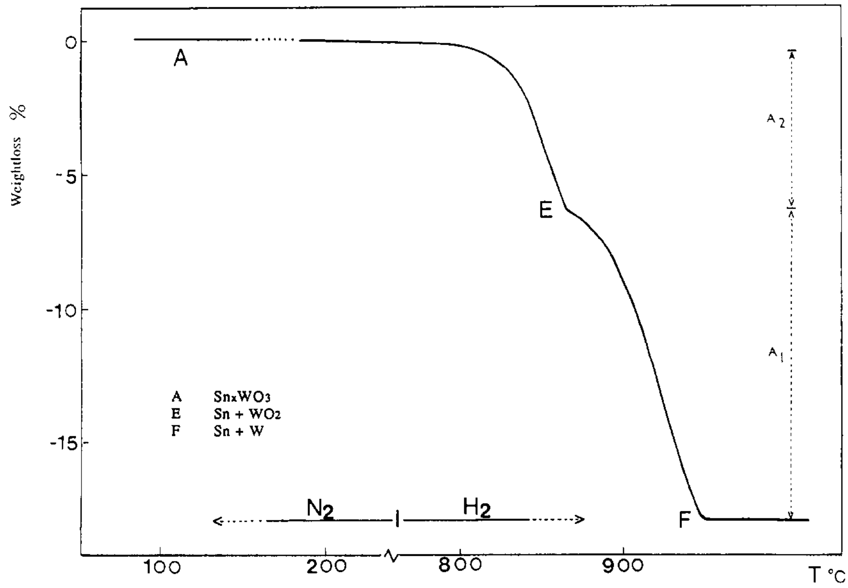

Fig. 3. TG curve in H_2 of single crystalline Sn_xWO_3 prepared from Sn and WO_3 ($x = 0.26$).

the TG curves include only the A–E–F reduction, the ratio A_1/A_2 is now exactly 2 (Fig. 3). Here the Δ value is evidently zero.

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