Phase Equilibria, Thermal Analysis, and Reactivity of Tin Tungsten Bronzes and Related Phases

I. J. McCOLM, R. STEADMAN, AND C. DIMBYLOW

School of Materials Science, University of Bradford, Bradford BD7 1DP, England

Crystal chemistry and phase relations of the bronze forming region of the Sn–W–O system have been investigated. Above 780°C the tin bronzes Sn_xWO_3 are shown to be thermally unstable and an equilibrium diagram is established at 700°C which shows that the composition limits of the tetragonal phase are $0.21 \leqslant x \leqslant 0.29$. Below $x = 0.21$ a series of single and two phase regions containing orthorhombic bronzes exists for which the composition limits have been established. In the range $0.29 \leqslant x \leqslant 0.76$ the system comprises the tetragonal bronze, $Sn_2W_3O_8$ and $SnWO_4$, while above 0.76 there is no bronze, only $Sn_2W_3O_8$, $SnWO_4$ and free Sn. The phase $Sn_2W_3O_8$ has been isolated and shown to have a hexagonal unit cell, $a = 7.696$ Å, $c = 18.654$ Å. The evidence of differential thermal analysis and X-ray studies suggests that this hexagonal phase arises from the decomposition of the tungsten bronze phase and is itself decomposed to cubic $SnWO_4$ above 700°C. Small thermal effects observed in the DTA scans of tin-containing tetragonal bronzes are interpreted in terms of an order–disorder phenomenon arising from asymmetric tunnel occupancy by Sn^{2+} ions caused by the presence of the lone pair of electrons. Hydrogen reduction of Sn_xWO_3 has been shown to result in complete removal of oxygen, producing $Sn + \alpha\text{-}W$ in the range 600–850°C. Some activation energy data are given for the reduction process.

Introduction

Since the first report of a tin tungsten bronze phase by Gier et al. (*1*), there have been a number of papers that reveal the complex nature of this ternary system, (*2–5*). All this work raises some questions regarding phase equilibria, composition limits and the general reactivity of the Sn_xWO_3 bronzes. This paper reports data from some experiments aimed at establishing the composition ranges of the bronze phases, their thermal stability and their reactivity to hydrogen and oxygen. These experiments are a necessary preliminary to our aim of establishing the behaviour of europium and tin as joint guest ions in tungstic oxide bronzes (*6*).

Some of the questions raised by the earlier work are concerned with the possible meta-stability of a hexagonal phase reported by Gier but not found by McColm and Steadman (*1*, *2*). Can its appearance in some situations

be related to the unique family of orthorhombic tin bronzes (*3*, *4*)? Other points of interest arising in this system are concerned with the decomposition products of the tin bronzes, because in general, when either the decomposition temperature or the electron concentration in the band system of a bronze is exceeded excess guest metal is removed by disproportionation into a lower bronze and a tungstate phase (*7*, *8*). However, at the outset no stable tin tungstate phase was known. Hydrogen reduction of the sodium bronzes has been shown to proceed through higher sodium content bronzes to finally a mixture of $\alpha + \beta$ tungsten and Na_2WO_4 (*9*). The course of such a reaction was therefore of interest in comparison to the sodium system.

During the progress of this work Jeitschko and Sleight (*10*) reported on the preparation of a polymorphic tin tungstate $SnWO_4$, the higher temperature β-cubic form of which had

185

an X-ray powder pattern identical to one of the decomposition products in this work. Hence, we are now able to add to the information on the $SnWO_4$ phase. The low melting point of $SnWO_4$ and its subsequent decomposition are complicating factors in studies of tin bronzes that may have led in the past to some of the apparent anomalies with respect to composition ranges and phase equilibria.

We have determined the equilibrium diagram for the Sn–W–O system in the regions close to the Sn_xWO_3 bronze phases at 700 and 1000°C by means of single crystal and powder X-ray techniques, optical microscopy, differential thermal analysis and chemical analyses. The DTA results, when considered together with single crystal X-ray data and work on similar phases not containing tin, suggest that an order–disorder phenomenon specific to tin tungsten bronzes may occur as a result of asymmetry arising from the lone pair of electrons on the Sn^{2+}.

Hydrogen reduction of the tin bronzes in the range 600–850°C results in complete removal of the oxygen leaving a $Sn + \alpha\text{-}W$ residue which can easily be separated and analysed. Thus, this method, while being used to study the dependence of the reaction kinetics on the tin content of the bronzes, has been found to be a convenient analytical procedure for these phases. Some of these data are presented below.

Experimental

The bronze samples were made from SnO_2, WO_3, and W powders (Johnson and Matthey Specpure grade) by mixing equivalent weights according to $xSnO_2 + (1 - 2/3x)\,WO_3 + 2/3x\,W$ in a rotary mixer for several days and sealing in silica ampules in vacuo of $< 10^{-5}$ Torr. The ampules were heated at 700, 850, or 1000°C for times in the range 1–3 weeks and then air cooled. Before opening, each ampoule was carefully inspected for signs of discoloration, segregation or vapour deposition.

X-ray phase analysis was achieved by means of 11.4 cm Debye–Scherrer and Guinier powder cameras and Weissenberg goniometers. Nickel-filtered $CuK\alpha$ radiation was used throughout.

Differential thermal analyses were performed on 50–100 mg samples in platinum crucibles using a Stanton 650 analyser with Al_2O_3 as the reference. A dry argon atmosphere flowing at 100 cc min^{-1} was used to prevent oxidation with heating rates of 5 and 12° per min. After each DTA run the samples were examined by X-rays and by elution with dilute hydrochloric acid. The elution technique was found to be a sensitive way to detect the tungstate phase by the appearance of a blue colloid in the solution.

The hydrogen reductions were performed on a quartz spiral balance in a silica apparatus incorporated into a high vacuum system. In a typical reduction experiment about one gram of material was degassed overnight at 300°C before hydrogen was admitted and the temperature raised to that required in the range 600–800°C. To keep the water vapour pressure low and hence minimize any reactions between the products of the reaction two large surface area cold fingers were incorporated into the apparatus close to the sample.

Results and Discussion

The utility of the hydrogen reduction kinetic experiments for analyses is shown by the results in Table I where it can be seen that for x above 0.07 in Sn_xWO_3 close agreement between mix composition and product composition results. These results justify the commonly adopted procedure of taking the bronze composition from the initial weighings

TABLE I

SOME ANALYTICAL DATA FROM THE HYDROGEN
REDUCTION METHOD

Mixture Composition	Reduction Temperature (°C)	Experimental composition
$Sn_{0.01}WO_3$	850	$Sn_{0.04}WO_3$
$Sn_{0.07}WO_3$	850	$Sn_{0.08}WO_3$
$Sn_{0.10}WO_3$	800	$Sn_{0.10}WO_3$
$Sn_{0.18}WO_3$	700	$Sn_{0.178}WO_3$
$Sn_{0.25}WO_3$	850	$Sn_{0.227}WO_3$
$Sn_{0.30}WO_3$	750	$Sn_{0.293}WO_3$

as long as the mixing procedure is efficient. The errors at very low tin contents may arise from either inhomogeneities in mixing or too short a reduction time.

Tin Bronze Equilibria at 1000°C

At the outset all preparations were made at 1000°C with a 1 week heating cycle, and in all cases when $0.6 > x > 0.5$ gross contamination of the silica ampule occurred but crystals of a tetragonal bronze of the (12×3)[1] type were found. Above $x = 0.6$ all experiments failed as the tubes cracked and the contents oxidised. It can be seen in Table II that only when $x < 0.2$ at 1000°C are the preparations clean and stable. After the X-ray and microscopic examination, each sample was leached with dilute HCl. The tetragonal bronze crystals were obviously inert but the brown discoloration on the silica ampules reacted easily to give a deep blue colloidal suspension which faded on standing over 12 hr and small yellow-white flakes of WO_3 were collected. Thus the blue colour was some form of tungsten-blue usually obtained when a soluble tungstate is reduced in acid solution. This gave rise to the speculation that this discoloration contains some form of partially soluble ionic tungstate. At the time no tungstates of tin were known, and so mixtures of $SnO + WO_3$ and $SnO_2 + WO_3 + W + Sn$ with stoichiometries $SnWO_4$ and $Sn(WO_4)_2$ were heated in vacuo at this temperature. While the $Sn(WO_4)_2$ preparation showed little reaction,

[1] This notation has been described in an earlier paper on the europium bronzes, *J. Solid State Chem.* **10**, 128 (1974).

the $SnWO_4$ tube was badly attacked in the way that the high tin content preparations were, and clearly the contents had been molten at 1000°C. A rather poor X-ray pattern suggested a cubic phase. It was eventually found that only at temperatures around 700°C was the $SnWO_4$ phase not molten and a mainly white product resulted which gave a cubic pattern with $a = 7.29$ Å. At this time the report by Jeitschko (*10*) on the existence of α and β $SnWO_4$ was available and the situation became much clearer; the cubic phase with $a = 7.29$ Å corresponded to the β-tungstate with a melting point of 785°C found by Jeitschko.

Hence it was concluded that at 1000°C the tin bronzes above $x = 0.2$–0.3 are unstable with respect to the β-tungstate and the upper composition limit for these bronzes is in the range 0.2–0.3 at this temperature.

The Existence of a Hexagonal Tin Bronze

In the above work there was no evidence for a phase with hexagonal symmetry. However, a hexagonal tin bronze around $x = 0.2$ prepared at 1000°C in preparations lasting only 24 hr has been reported (*1*). Thus the time factor might be critical, and to test this a series of preparations in the range $x = 0.2$–0.3 were attempted for times ranging from 95 to 440 hr.

The results are shown in Table III, where it can be seen that a hexagonal phase has, in fact, been found to exist, but it is a metastable phase from which the tetragonal (12×3) structure evolves. (Although we shall refer to it here and in Table III as hexagonal, it should be described as pseudohexagonal; the structure is formed by stacking together hexagonal

TABLE II

RESULTS OF Sn_xWO_3 PREPARATIONS AT 1000°C FOR 1 WEEK

x value	Phases found	Observations
0.1	6-type[a] orthorhombic bronze	
0.2	5-type orthorhombic bronze + tetragonal (12×3)	
0.3	Tetragonal (12×3)[a]	Some discoloration of the ampule
0.4	Tetragonal (12×3)	Heavy brown discoloration
0.5	Tetragonal (12×3)	Gross contamination
0.6–1.0	—	Ampoules failed contents oxidized

[a] For significance of this nomenclature see Ref. (*7*).

TABLE III

PHASE ANALYSIS OF Sn_xWO_3 PREPARATIONS AT AT 1000°C FOR VARYING TIMES

Sample	Phases present		
	95 hr	280 hr	440 hr
$Sn_{0.2}WO_3$	Orthorhombic 5-type Hexagonal Tetragonal	Orthorhombic 5-type Tetragonal	Orthorhombic 5-type Tetragonal
$Sn_{0.25}WO_3$	Hexagonal Trace tetragonal	Tetragonal Hexagonal	Tetragonal
$Sn_{0.27}WO_3$	Hexagonal Trace tetragonal	Tetragonal Hexagonal (trace)	Tetragonal
$Sn_{0.30}WO_3$	Hexagonal Tetragonal β-SnWO₄	Tetragonal β-SnWO₄	Tetragonal β-SnWO₄

layers of WO_6 octahedra, but the symmetry of the complete structure is orthorhombic.) At $x = 0.25$ this hexagonal bronze has its maximum stability and takes longer to transform than other compositions. At $x = 0.2$ the equilibrium mixture contains the orthorhombic and tetragonal bronzes, and it is possible that the hexagonal phase is an intermediate in the transition from orthorhombic to tetragonal.

The morphology of this hexagonal (or pseudohexagonal) material was also time-dependent, exhibiting a fine purple-coloured needle habit after 95 hr which developed into colonies of flat hexagonal plates after 280 hr. Single crystal studies of these plates (4) show that their structure is strictly orthorhombic with space group $Fdd2$, and the unit cell, which extends over 36 hexagonal layers of octahedra has dimensions $a = 135.6$ Å (i.e., 3.77×37 Å), $b = 12.87$ (i.e., $(7.43)^{1/2} \times 3$ Å), $c = 7.43$ Å.

Tin Bronze Equilibrium at 700°C

From the preceding paragraphs it is apparent that work below 780° with long heating periods was necessary to establish the equilibrium relationships in the Sn–W–O system. Thus, all subsequent work was done at 700°C with three weeks heating times. For compositions Sn_xWO_3 with $x = 0.1$ up to 1.0 the data are shown in Table IV. Some interesting features emerge from these results; first the upper limit of tin content is below $x = 0.3$.

TABLE IV

PHASES FOUND IN THE EQUILIBRIA OF Sn_xWO_3 AT 700°C AFTER 3 WEEKS HEATING

x in Sn_xWO_3	Phases present
0.1	6-type orthorhombic
0.2	5-type orthorhombic + tetragonal (12 × 3)
0.3	Tetragonal (12 × 3), trace SnWO₄ + Red crystals
0.4	Same as 0.3
0.5	Same as 0.3
0.6	Same as 0.3
0.7	SnWO₄ + Red crystals + trace tetragonal (12 × 3)
0.8	SnWO₄ + Red crystals
0.9	SnWO₄ + Red crystals + trace Sn
1.0	Red crystals + SnWO₄ + Sn

Second, there is still no evidence for the hexagonal bronze phase, but a hitherto unknown hexagonal nonbronze-like material results at high tin content. This new phase is described below. A third feature is that the tungstate $SnWO_4$ appears from decomposition of this hexagonal material.

A closer examination in the region 0.2–0.3 was made by studying another 24 mixes. Each sample was examined microscopically, by X-rays and by HCl leaching, and from this and all other data the 700°C equilibrium
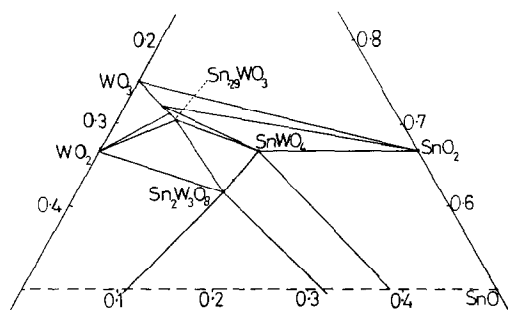
FIG. 1. Parts of the 700°C equilibrium diagram for the Sn–W–O system.

diagram was constructed. This is shown as Fig. 1 in which the complex series of shear plane oxides between WO_3 and WO_2 is omitted for the sake of clarity. In the equilibrium diagram the limiting composition for the Sn_xWO_3 phase has $x = 0.29$. A sample prepared with this composition gave an X-ray powder diagram which could be completely indexed on the tetragonal unit cell $a = 12.090$ Å, and produced a negative blue test. A sample of composition $Sn_{0.3}WO_3$ gave a positive blue test and hence contained a trace of $SnWO_4$. The hydrogen reduction analysis of the residue of the $Sn_{0.3}WO_3$ washed sample produced a value of $Sn_{0.29}WO_3$, and so it is felt that this value is reliable for the upper composition limit of the bronze phase. At this concentration of tin there are many unfilled possible Sn sites but this electron concentration in the band of $0.56e^-$ per W atom appears to be critical.

Figure 2 gives the complete phase boundaries of the tin bronzes at 700°C. Several single- and two-phase regions are shown and the narrow homogeneity range of the (12×3) tetragonal region from $x = 0.21$ to 0.29 is notable. Such a restricted range made subsequent hydrogen reduction kinetic experiments and DTA investigations somewhat restricted too.
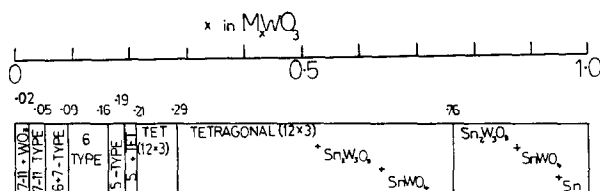
The effect of increasing temperature on these limits was reexamined by heating a number of specimens in the 0.27–0.35 range at 1000° and by making new specimens within this range at 1000°. The limit appears to be insensitive to temperature in this range, but there is a change in the equilibrium with no red hexagonal $Sn_2W_3O_8$ crystals being found.

Hexagonal Tungstate $Sn_2W_3O_8$

Originally from the above phase study many red crystals were isolated manually. These were of hexagonal columnar habit, transparent, electrically insulating and inert to acids and dilute alkalis. They did not generate the blue colour with HCl as found when $SnWO_4$ was tested. A hydrogen reduction analysis and tin content analysis gave their composition as $Sn_2W_3O_8$.

The X-ray powder diagram (Table V) was completely indexed on a hexagonal unit cell $a = 7.696$ Å, $c = 18.654$ Å which was confirmed by the single crystal data. The space group from the single crystal examination is $P6_3$ or $P6_{3/m}$. Attempts made to prepare this phase from SnO, WO_3 and W always resulted in a mixture containing $Sn_2W_3O_8$ and $SnWO_4$.

A selected pure sample of the red crystals was examined on the DTA apparatus. On heating in argon a broad peak centred on 1047°C was found, while on cooling there was a small peak at 846°C. The product of this test gave a positive blue test with HCl which confirms the presence of the tungstate and so suggest that $Sn_2W_3O_8$ decomposes to give rise to $SnWO_4$ with some Sn and WO_2 and this mixture results in a positive blue test with HCl.

Considering this information with the earlier work, the probable decomposition of the tetragonal tin bronze goes via the hexagonal $Sn_2W_3O_8$ phase which above 700°C makes way for $SnWO_4$. The structural work on $Sn_2W_3O_8$ shows that it is probably a

FIG. 2. A magnified section of Fig. 1 showing the phase boundaries of the tin tungsten bronzes at 700°C.

TABLE V

X-Ray Powder Data for Hexagonal $Sn_2W_3O_8$

$(\lambda = CuK\alpha_1)$

Intensity[a]	$\sin^2\theta$ (obsd)	$\sin^2\theta$ (calcd)	$h\,k\,l$
S	.0068	.0068	0 0 2
S	.0134	.0134	1 0 0
M	.0151	.0151	1 0 1
VS	.0201	.0202	1 0 2
VW	.0272	.0273	0 0 4
VW	.0288	.0286	1 0 3
M	.0401	.0401	1 1 0
W	.0406	.0406	1 0 4
S	.0535	.0534	2 0 0
S(D)	.0554	.0551	2 0 1
		.0554	1 1 3
S	.0559	.0559	1 0 5
M	.0613	.0614	0 0 6
W	0.673	.0674	1 1 4
VS	.0687	.0687	2 0 3
S	.0745	.0747	1 0 6
VW	.0827	.0827	1 1 5
S	.0935	.0935	2 1 0
M	.0959	.0960	2 0 5
W	.0968	.0969	1 0 7
M	.1003	.1003	2 1 2
W	.1013	.1015	1 1 6
S	.1091	.1091	0 0 8

[a] VS = very strong; S = strong; M = medium; W = weak; VW = very weak; (D) = diffuse.

structure containing elements of the bronze structure based on WO_6 octahedra and also layers of WO_4 tetrahedra which constitute the tungstate phase.

Differential Thermal Analysis of the Tetragonal Sn_xWO_3 phase

Only single phase samples in the $x = 0.21$–0.29 range were examined under argon up to $900°C$. On heating, two endothermic effects were observed with only one exothermic peak on cooling. These are shown in Fig. 3 which also contains the peaks present in the investigation of a mixed bronze $Sn_{0.57}Eu_{0.50}WO_3$. Several other tetragonal (12×3) bronzes were examined from the Pb_xWO_3, Na_xWO_3 and Eu_xWO_3 systems, but none gave any thermal effects; the effect was confined to tin or tin-containing bronzes. The data are summarized
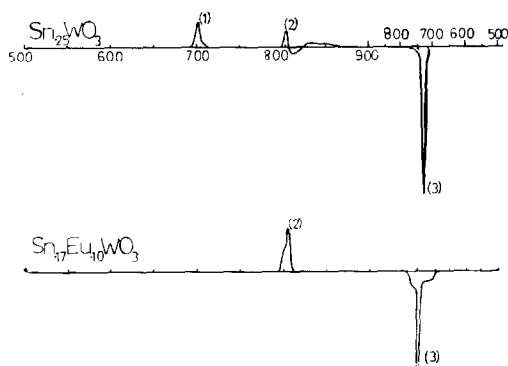

Fig. 3. Typical DTA curves for tetragonal bronzes containing tin.

in Table VI. Thus a possible explanation must be sought in the structure of the tin bronzes and in particular in the occupancy of the tin sites in these materials.

X-ray structural work has shown that the Sn^{2+} ions take-up asymmetrical positions within the pentagonal tunnels of the WO_3 lattice. The three noncentral sites found for the Sn^{2+} are illustrated in Fig. 4. Sites B and C are identical and are such that the Sn^{2+} is at the apex of a pyramid with four oxygens forming a square base as in SnO. Site D is similar but has the Sn–O pyramid at a different orientation. The population of these sites is determined by the tin content, but the sharpness of X-ray diffraction spots make it unlikely that the Sn^{2+} ions occupy the sites in a random way, and thus the existence of domains in the crystals has been suggested (5). Domains in this case are regions in the crystal where the Sn^{2+} occupies only one of the possible sites. The number and type of domains will depend on the thermal history of the crystals.

The small DTA peaks indicate that small enthalpies are involved, and the known asymmetric filling of the pentagonal tunnel sites suggests that centralization is a possible transition. However, there are two peaks on heating but only one on cooling. Repeated heating and cooling cycles enhance the peaks which was particularly noticeable where peak 1 only appeared on the second heating cycle of a $Sn_{0.23}WO_3$ sample.

An interrupted heating cycle was used to examine an $Sn_{0.25}WO_3$ specimen when it was

TABLE VI

DIFFERENTIAL THERMAL ANALYSIS DATA FOR BRONZES AND RELATED TIN PHASES

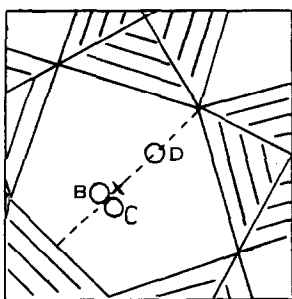| Sample | Atmosphere | Peak Temperature (°C) | |
		(a) Heating	(b) Cooling
WO_3	Air	744	
		902	
$SnWO_4$	N_2	677	
		802	
$Sn_{0.23}WO_3$	N_2	804	723
$Eu_{0.125}WO_3$	N_2	No effects	No effects
$Sn_{0.25}WO_3$	N_2	694	715
		794	
		822	
$Pb_{0.20}WO_3$	N_2	No effects	No effects
$Sn_{0.12}Wu_{0.10}WO_3$	N_2	800	715
$Sn_{0.01}WO_3$	N_2	647	870
		894	
$Sn_2W_3O_8$	N_2	1047	846
		Broad	
$Sn_2W_3O_8$ 2nd cycle	N_2	674	723
		806	644
$Sn_{0.18}Eu_{0.12}WO_3$	N_2	798	711
$Sn_{0.27}WO_3$	N_2	703	715
		798	
		822	

FIG. 4. [001] section through pentagonal tunnel in $Sn_{0.29}WO_3$. O = guest ion site; x = centre of the tunnel.

held at 775°C that is between peaks 1 and 2 at 694 and 794°C, respectively. On cooling no peak corresponding to 3 at 715°C was found, and on reheating to 900°C only peak 2 at 794°C was produced, but when cooled peak 3 was again observed. One explanation of these effects is that on heating the centralization process is two stage with Sn^{2+} from sites B and C going to D and then at higher temperature from D to A the tunnel centre. Thus when held

at 775° the tin does not become centralized and so peak 3 is not apparent.

The cooling rate is sufficiently fast to quench the tin on the D site and so on reheating the first transition at 694°C would not be found. It is not possible to cool fast enough to quench the Sn^{2+} at the centre site A, and randomization occurs over sites B, C, and D on cooling from 900°C. Thus on reheating both the 694 and 794°C endotherms are found.

A single crystal structural analysis of the $Sn_{0.12}Eu_{0.10}WO_3$ specimen which will be reported elsewhere shows that there are ions on site A which therefore are probably Eu, with Sn only on site D. It is notable that this sample produces an asymmetric 800°C peak only on heating and one peak cooling. This behaviour was not changed on repeated recycling. The asymmetry of the DTA peak is in accord with this suggested type of phase transition which only involves small displacements and undergoes only slight superheating or supercooling. However, without the aid of

8

Composition	Hydrogen pressure (mmHg)	Activation energy (KJ mole^{-1})
$Sn_{0.04}WO_3$	200	95–6
$Sn_{0.04}WO_3$	100	109
$Sn_{0.09}WO_3$	100	82–4
$Sn_{0.29}WO_3$	100	105
$Sn_{0.29}WO_3$	200	104
$Sn_{0.29}WO_3$	300	120

high temperature single crystal structure determinations it will be difficult to verify this model.

Hydrogen Reduction of Tetragonal Sn Tungsten Bronzes

Detectable reduction in the apparatus used here begins at 600°C at 100 mm Hg pressure. Linear kinetics are observed for much of the process. The course of the reduction follows removal of H_2O with production of a higher bronze up to the limit of $x = 0.29$ together with $SnWO_4$ and residual oxides of tungsten. The final product of this reaction is a mixture of Sn and α-W. The temperature dependence of the reaction rate in the temperature range 600–850° was studied for a few systems and the activation energies are shown in Table VII.

There are too few data to perceive the effect of composition on activation energy, but some comparisons can be made with the data of Dickens and Whittingham (9) who have published the results of a hydrogen reduction study of Na_xWO_3 bronzes in the temperature range 400–600°C and with the reduction of WO_3 (11, 12).

The activation energy for the reduction of WO_3 in a comparable temperature range 670–850°C has been found to be 85.4 kJ mole$^-$ and thus the results obtained here suggest that tin in the lattice generally raises the activation energy. Dickens found that the activation energy varied with sodium content and with structure type with a maximum of 178 kJ mole^{-1} at $Na_{0.9}WO_3$ and dropping through the cubic region to 105 kJ mole^{-1} at $x = 0.35$. Within the tetragonal phase range the value fell from 140 kJ mole^{-1} at $x = 0.35$ to 115 kJ mole^{-1} at $x = 0.12$. The tin bronze values in the range 82–109 kJ mole^{-1} are thus quite comparable.

Acknowledgments

References

1. T. E. GIER, D. C. PEASE, A. W. SLEIGHT, AND T. A. BITHER, *Inorg. Chem.* 7, 1646 (1968).
2. I. J. McCOLM, R. STEADMAN, AND A. HOWE, *J. Solid State Chem.* 2, 555 (1970).
3. R. STEADMAN, R. J. D. TILLEY, AND I. J. McCOLM, *J. Solid State Chem.* 4, 199 (1972).
4. C. DIMBYLOW AND R. STEADMAN, *Mat. Res. Bull.* 7, 841 (1972).
5. R. STEADMAN, *J. Chem. Soc. Dalton* 1972 (1972).
6. I. J. McCOLM, R. STEADMAN, C. DIMBYLOW, AND N. N. GREENWOOD, in preparation.
7. I. J. McCOLM, C. DIMBYLOW, N. N. GREENWOOD, AND C. BARTON, *J. Solid State Chem.*, 10, 128 (1974).
8. W. OERSTERTAG, *Inorg. Chem.* 5, 758 (1966).
9. M. S. WHITTINGHAM AND P. G. DICKENS. *7th Int. Symposium. Reactivity of Solids* (W. Roberts, Ed.).
10. W. JEITSCHKO AND A. W. SLEIGHT, *Acta Cryst.* B28, 3174 (1972).
11. P. BARRET AND L. C. DUFOUR, *Comp. Rend.* 258, 2337 (1964).
12. L. G. AUSTIN, *Ind. Eng. Chem.* 53, 659 (1961).