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Evidence for the Existence of Iron Tungsten Bronzes

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X-ray diffraction, high-resolution electron microscopy, and ^{57}Fe Mössbauer spectroscopy have been used to study the WO_3–Fe system. The results from the diffraction methods can be interpreted either on a scheme involving bronze formation leading to a phase Fe_xWO_3, or on a scheme whereby a reduced tungsten oxide is in equilibrium with $FeWO_4$. The Mössbauer results show, however, that up to $x = 0.0193$ in Fe_xWO_3, a bronze is formed with either an orthorhombic or tetragonal structure, while above $x = 0.0193$ the phases are $FeWO_4$ and reduced tungsten oxides. The Fe_xWO_3 bronze contains a few isolated (102) crystallographic shear planes, which implies a very slight deviation from the ratio WO_3. Reaction of Fe with WO_3 or $FeWO_4$ with WO_3 and W at 950°C under vacuum leads to the bronze phase.

Introduction

Nontransition metals generally form bronze-type compounds by incorporation into tungsten trioxide with no apparent change in the host WO_3 stoichiometry. In this process the WO_3 structure changes progressively to higher symmetry as metal ions are incorporated into cage and tunnel sites. In general, relatively high values of x in M_xWO_3 can be achieved, depending upon the oxidation state of the metal M. It is notable, however, that when bronze formation is attempted between tungsten oxide and transition metals the situation is more complicated. Very small limiting values of x seem to occur for Co, Ni (*1*), Eu (*2*), and V (*3*) and there are uncertainties as to whether the guest metal is in a bronze type of site formed by the corner sharing WO_6 octahedra or whether it substitutes on a tungsten octahedral site. For others, Ti (*4*) and Zr (*5*), much greater reaction takes place, with extensive *CS* phase formation in one case (*4*) and perovskite bronze formation in the other (*5*).

Iron is an element that has not been reported to form bronzes and it was therefore deemed worthwhile to search for bronze phases in the system Fe–WO_3 and to use the techniques of Mössbauer spectroscopy, high-resolution electron microscopy, and X-ray diffraction to study chemical behavior and phase relationships. Since the completion of this work, our attention has been drawn to a doctoral thesis from Bordeaux (*6*) that contains some comparable data on an Fe_xWO_3 phase. Although single-crystal data were obtained in this work, no conclusion could be reached concerning the position of the Fe in the material.

In the work reported below we have been able to show, by a combination of X-ray diffraction, electron microscopy, and Mössbauer spectroscopy, that Fe_xWO_3 is in fact a bronze with iron in sites probably similar to those of Na in the cubic sodium bronzes. The results show that iron bronzes can be made by the reaction of Fe with WO_3 and also from $FeWO_4 + WO_3 + W$, but the upper limit of x in Fe_xWO_3 is very small. The electron microscopy shows that only isolated and infrequent *CS* planes occur in the bronzes so that δ in $Fe_xWO_{3-\delta}$ is exceedingly small.

Experimental

Two preparative methods were used. First, $FeWO_4 + WO_3 + W$ in calculated amounts were heated in sealed evacuated silica tubes at temperatures in the range 850–1050°C. The $FeWO_4$ was made by reacting Fe_2O_3, WO_3, and W at 930°C in a sealed quartz tube for 3 weeks according to the equation

$$3Fe_2O_3 + W + 5WO_3 \rightarrow 6FeWO_4.$$

The WO_3 was obtained from two sources: In most experiments Koch–Light's WO_3 (>99.9 %) was used but in a few experiments spec-pure WO_3 from Johnson–Matthey was used.

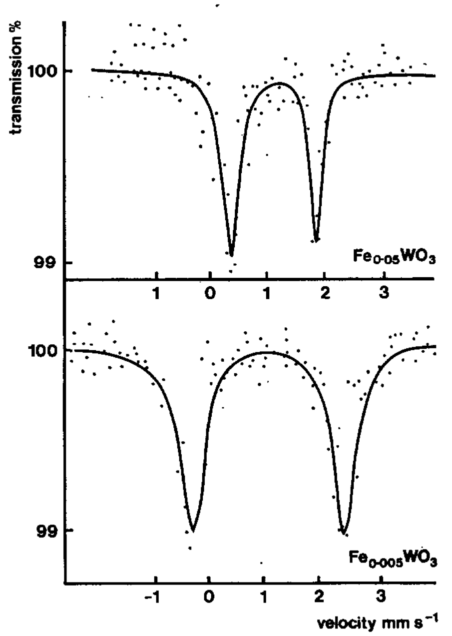

FIG. 1. Mössbauer spectra taken at 300°K of (a) $Fe_{0.005}WO_3$ and (b) "$Fe_{0.05}WO_3$."

A second route to the bronzes lay in mixing ^{57}Fe powder with WO_3 in a rotary mixer for 24 hr, and then sealing in a vacuum $<10^{-5}$ Torr in silica tubes. The tubes were heated in the range 950–1050°C for 3 weeks with intermittent shaking. This method produced crystalline samples which were examined without any further treatment after heating.

Each sample was examined by X-rays using a Hägg–Guinier focusing camera with strictly monochromatized Cu$K\alpha_1$ radiation. Mössbauer spectra were obtained using an NSEC spectrometer following methods previously described (*2*). All isomer shifts are quoted relative to Fe foil taken as zero. Typical spectra are illustrated in Fig. 1. Electron microscopy was carried out using a JEM 100B electron microscope fitted with a goniometer stage and operated at 100 kV. Suitable samples were prepared by crushing crystals in an agate mortar, dispersing the fragments in *n*-butanol, and allowing a drop of the resultant suspension to dry on perforated carbon films. High-resolution electron micrographs were taken of some fragments, using the techniques described by Iijima (*7*) and Allpress and Sanders (*8*); otherwise, low-resolution diffraction contrast images were used to identify the defect structure of the crystals under examination.

Results and Discussion

Table I contains the experimental data for the samples examined. One notable feature is the agreement between the techniques with respect to the upper limit of Fe in the tungsten oxide before $FeWO_4$ and reduced oxides become apparent in the phase analysis. This upper limit is judged to be about $x = 0.0193$ in Fe_xWO_3, and in the range 0–0.0193, the symmetry of the structure changes from monoclinic to tetragonal. The position and role of Fe in the compounds can be inferred only when the results obtained from all three techniques are used.

X-ray results for compositions in the range $x = 0.0018$ to 0.04 are not in a continuous sequence and a few anomalous results were found which suggests that equilibrium is difficult to achieve in some cases despite the

TABLE I

Experimental Data for Fe_xWO_3 Preparations and $FeWO_4$[a]

	Mössbauer				
Sample	T (°K)	δ (mm s^{-1})[b]	Δ (mm s^{-1})	X-ray	Electron microscopy
$Fe_{0.0018}WO_3$	300	1.16(1)	2.87(1)	Monoclinic + orthorhombic "WO_3"	Disordered (102) *CS* planes becoming more ordered as the value of x increases
$Fe_{0.005}WO_3$	300	1.15(4)	2.80(8)	Monoclinic + orthorhombic "WO_3"	
$Fe_{0.008}WO_3$	—	—	—	Monoclinic + orthorhombic "WO_3" + $FeWO_4$	
$Fe_{0.0102}WO_3$	300	1.16(1)	2.88(5)	Orthorhombic + tetragonal "WO_3"	
$Fe_{0.0193}WO_3$	300	1.16(2)	2.87(4)	Orthorhombic + tetragonal "WO_3"	
$Fe_{0.02}WO_3$	—	—	—	$FeWO_4$ + orthorhombic "WO_3"	—
$Fe_{0.03}WO_3$	—	—	—	$FeWO_4$ + tetragonal "WO_3"	—
$Fe_{0.04}WO_3$	—	—	—	$FeWO_4$ + orthorhombic + tetragonal "WO_3"	—
$Fe_{0.05}WO_3$	300	1.08(3)	1.46(3)	Strong $FeWO_4$ + tetragonal "WO_3"	—
$Fe_{0.08}WO_3$	300	1.14(1)	1.55(2)	$FeWO_4$ + tetragonal "WO_3"	—
$Fe_{0.10}WO_3$	300	1.16(3)	1.50(1)	$FeWO_4$ + tetragonal "WO_3"	—
$Fe_{0.20}WO_3$	300	1.01(1)	1.31(1)	$FeWO_4$ + tetragonal "WO_3"	—
	4.2	1.27(1)	1.90(2)		
$FeWO_4$		1.14(1)	1.51(1)	$a = 4.721$ Å, $b = 5.706$ Å, $c = 4.961$ Å	

[a] Figures in parentheses are standard deviations in the last significant figure.

[b] Relative to Fe foil.

long heating times employed. As a group, however, the films could be described as containing only WO_3 or $WO_3 + FeWO_4$. On films with no $FeWO_4$ lines identified, i.e., $x = 0.0018$, 0.005, 0.01, and 0.0193, the "WO_3" is always a mixture of the monoclinic and orthorhombic or orthorhombic and tetragonal forms. On the films with $FeWO_4$ present, i.e., $x = 0.019$, 0.02, 0.03, 0.04, and anomalously 0.008, the "WO_3" is again either orthorhombic, orthorhombic and tetragonal, or tetragonal. There was no defined equilibrium between $FeWO_4$ and a particular form of WO_3 except at the highest $FeWO_4$ content, where the tetragonal WO_3 predominates.

The changes observed in the WO_3 symmetry, passing from monoclinic to tetragonal, are associated with increasing temperature and are usually considered to be stabilized to room temperature by adding small amounts of "impurities." However, recent studies of binary tungsten oxides heated under vacuum have shown that these high temperature phases can be retained at room temperature under slightly reducing conditions (*9*). An electron microscope and X-ray study of the V_xWO_3 system (*3*) also revealed that orthorhombic WO_3 could be stabilized to room temperature when the oxide was slightly reduced. The common feature of both these results is that a slight degree of reduction and the associated presence of disordered (102) *CS* planes seems able to stabilize these high symmetry forms to room temperature. This is discussed in detail by Ekström and Tilley (*3*) and will not be reiterated here, except to stress that the symmetry changes seen by X-rays cannot be definitely linked to Fe as a dopant in the WO_3 structure.

Accepting this, all the results are in agreement with the suggestion that only very small amounts of Fe enter the WO_3. In all cases where $FeWO_4$ can be identified, apart from one anomalous film, the results are in accord with a reaction scheme

$$x\mathrm{Fe} + \mathrm{WO_3} \rightarrow x\mathrm{FeWO_4} + \mathrm{W}_{1-x}\mathrm{O}_{3-4x}. \quad (1)$$

In fact, from X-ray data alone it would be difficult to discount scheme (1) as being responsible for all the observations. The degree of reduction of the $W_{1-x}O_{3-4x}$ residue is hard to estimate from the X-ray work but is in accordance with the scheme proposed in Eq. (1), in that no greatly reduced oxides such as $W_{18}O_{49}$ were observed to form.

Equation (1) implies no substitution of iron for tungsten in octahedral sites and further evidence for this line of reasoning comes from the electron microscopy of samples with $x = 0.019$, 0.010, and 0.005. The plates shown in Fig. 2 contain isolated (102) *CS* planes identical to those that arise during the heating of pure WO_3 under vacuum (*10*). Assuming that all reduction is taken up on the *CS* planes, it is a simple matter to calculate the composition of the oxide and to show that the *CS* planes are not present in sufficient density to account for the formation of a phase (Fe, W)-$O_{3-\delta}$ in which all the Fe has substituted onto

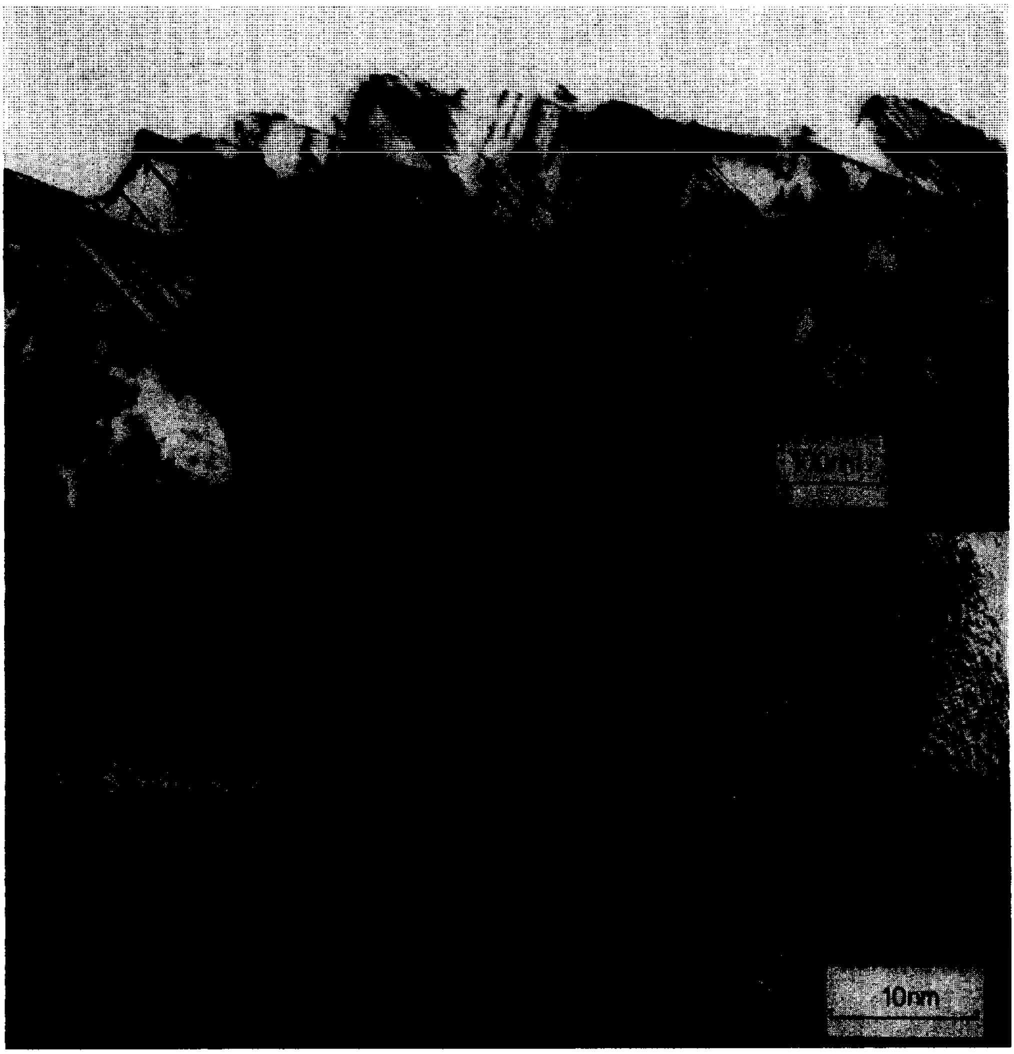

FIG. 2. Electron micrographs of crystal fragments from samples of bulk composition $Fe_{0.019}WO_3$. (a) Low-magnification micrograph showing groups of [102] *CS* planes. (b) High-magnification micrograph showing a few closely spaced [102] *CS* planes in a basically unmodified WO_3 structure.

octahedral sites and stoichiometric balance has been maintained by *CS* formation. On the other hand, the *CS* plane densities do not disagree too greatly, within the uncertainty of the method, with the density of *CS* planes expected in a $W_{1-x}O_{3-4x}$ residue of composition suggested in Eq. (1). Thus, the electron microscopy gives no conclusive evidence that Fe is in fact in the crystals and does not disagree with the scheme given in Eq. (1) nor does it provide evidence for (or against) an Fe_xWO_3 bronze formulation.

The Mössbauer data were the most important in providing evidence for the existence of an iron-bearing tungsten bronze of very limited composition range. The isomer shift δ for the bronze is identical to that for $FeWO_4$ but the quadrupole splitting Δ is almost twice as large in the bronze phase. Thus, the change from bronze to $FeWO_4$ plus "WO_3" is easy to detect. The value of δ in the bronze phase region $0.0018 < x < 0.0193$ shows that the Fe is present as high-spin Fe(II) and in this respect iron follows the expected behavior for polyvalent elements in being present in the lowest stable oxidation state (*11–13*). The Δ value in the bronzes is high (approximately 2.87 mm sec^{-1}), which shows that Fe is in a site that is only moderately distorted from cubic symmetry, whereas the value of Δ in the stable tungstate $FeWO_4$ is 1.51 mm sec^{-1} which is low for high-spin Fe(II) and probably denotes a highly distorted site for the Fe atoms (*14*). The high symmetry of the Fe sites in the bronzes could indicate that no replacement of W by Fe occurs because WO_6 octahedra in monoclinic WO_3 are known not to be symmetrical and indeed ^{182}W Mössbauer spectroscopy of WO_3 shows considerable line broadening (*15*). However, it is not established whether the linewidth is as great in other forms of WO_3 as the monoclinic form. Thus, this technique establishes that Fe is present in the compound in a form distinct from $FeWO_4$ and, since the *CS* plane density and quadrupole splitting data argue strongly against an $(Fe, W)O_{3-\delta}$ phase, one is forced to conclude that the Fe is present in symmetrical bronze tunnel sites up to $x = 0.0193$. Frequently, a slight asymmetry was detected in the Mössbauer spectra with the low-velocity peak being about 10% more intense than the high-velocity peak. The asymmetry decreased as the temperature decreased.

From the above evidence we conclude that an iron bronze exists containing high-spin Fe(II) in a narrow phase range. The size of Fe^{2+} is such that it can be accommodated either in the square tunnels associated with the cubic bronzes or in the pentagonal tunnels associated with tetragonal bronzes. If pentagonal tunnels were present these would have been resolved in the electron microscope. Figure 2b, which is typical of the defect contrast present, is clearly not associated with elements of the tetragonal bronze structure. This leads one to ask why so little Fe can be incorporated before $FeWO_4$ is preferentially formed. The phase range identified here for the Fe system is narrower than for the analogous cobalt and nickel systems (*1*). Co_xWO_3 exists up to $x = 0.035$ and Ni_xWO_3 up to $x = 0.040$ before each coexists with an oxide W_nO_{3n-2} and the corresponding tungstate. Since Ni and Co are probably present in the divalent state the small differences may merely reflect the greater stability of $FeWO_4$ compared to $CoWO_4$ and $NiWO_4$. The appearance of $FeWO_4$ and a reduced tungsten oxide is in agreement with the 900° equilibrium diagram for the Fe–W–O system described by Schmahl and Dillenberg (*16*).

In conclusion, this work has shown that iron bronzes, analogous to the Ni and Co bronzes, can be prepared from solid-state reactions at 850–1050°C with $0.0018 < x < 0.0193$. They contain iron in relatively undistorted bronze sites as high-spin Fe(II). Above $x = 0.0193$, the orthorhombic or tetragonal bronze coexists with $FeWO_4$ and a reduced tungsten oxide. The bronzes contain isolated *CS* planes that are not directly related to the iron content, but cause some slight degree of reduction.

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