Mechanochemical activation of mixtures of wolframite (FeWO$_4$) with carbon, studied by ^{57}Fe Mössbauer spectroscopy

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Abstract

The effect of mechanochemical activation (high-energy grinding) on mixtures of natural FeWO$_4$ with two forms of carbon has been investigated by X-ray powder diffraction and Mössbauer spectroscopy. The crystallinity of the mechanically activated mixtures, which have previously been found to exhibit enhanced reactivity as precursors for carbothermal production of tungsten carbide, is shown by X-ray powder diffraction to decrease on grinding, but without detectable formation of new crystalline phases. Mössbauer spectroscopy shows that the grinding process is accompanied by the appearance of an unexpected new singlet resonance, attributed to the formation of dilute Fe—C regions. The Mössbauer spectra also show that mechanochemical activation under the present conditions results in progressive oxidation of the Fe^{2+} in the wolframite to Fe^{3+}; this oxidation is more marked in wolframite ground in the absence of carbon, suggesting that the latter exerts an oxygen-scavenging effect on the system. Similar results are obtained irrespective of whether the carbon source is activated carbon or graphite. The crystallization of iron tungsten carbides on subsequent heating of the ground mixtures in argon suggests that the regions identified by Mössbauer spectroscopy as containing iron–carbon interactions may also be associated with tungsten.
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Keywords: Milling; Powders-solid state reaction; Carbon; Mössbauer spectroscopy; FeWO$_4$

1. Introduction

Tungsten carbide (WC) is an extremely hard material of technical importance as an abrasive and a significant constituent of hard metals. WC is typically prepared by the energy-intensive direct reaction at 1400–1600 °C of tungsten with carbon under a reducing atmosphere.[1] One of the sources of metallic tungsten is the mineral wolframite (FeWO$_4$), the smelting of which is also an energy-intensive process. Although direct carbothermal reduction of wolframite should be useful for reducing the energy requirement for its smelting, only slight reaction has been reported at temperatures of about 1200 °C.[2] Mechanochemical activation (high-energy grinding) is an attractive method for increasing the reactivity of solid mixtures, and has previously been found to assist

the synthesis of tungsten carbide from mixtures of elemental tungsten and activated graphite[3,4] and of scheelite (CaWO$_4$) with graphite at about 1200 °C,[5] although the precise mechanism of the mechanochemical process is unknown.

Although carbothermal reduction of wolframite with coal is reported to result in the formation of little WC,[2] mechanochemical activation of wolframite with graphite[6] or activated carbon[7] has been found to facilitate the transformation of the reaction mixture to predominantly WC when heated in Ar at 1100 °C. Mechanochemical activation of these reaction mixtures was found to broaden the XRD peaks of the wolframite and decrease their intensity. However, because of the decreased crystallinity of reaction precursors activated in this way, XRD techniques are unable to provide information about the mechanism by which mechanochemical treatment facilitates the subsequent carbothermal formation of new intermediates or products,[6,7] and provide no information about the role or fate of the Fe component during grinding.

There are several mechanisms by which mechanochemical activation may facilitate the present carbothermal reaction of wolframite. The most obvious mechanism, consistent with the changes observed in the X-ray diffractograms of the precursors, involves the reduction of grain size (cominution) of the reactant mixture, resulting in a greater degree of intergrain contact and homogeneity of the resulting precursor. The increased surface area and exposure of new crystal faces will also facilitate subsequent solid–gas interactions occurring in the carbothermal process. Another possible mechanism involves mechanochemically induced surface reactions between the components of the mixture. This interesting possibility cannot be explored by XRD; such mechanistic details on the molecular level must be obtained by a spectroscopic technique such as ^{57}Fe Mössbauer spectroscopy, which, unlike XRD, is independent of the degree of long-range crystallographic order in the sample.

The present communication reports a Mössbauer study of the effects of mechanochemical activation on the Fe in mixtures of natural wolframite with both activated carbon and graphite, the use of the latter being suggested by the ready availability of spent graphite electrodes from heavy industrial processes and the desirability of re-using these waste products. The Mössbauer results were analysed for evidence of chemical changes in the iron-containing component of the samples arising from their mechanochemical treatment.

2. Experimental

The natural wolframite used in this study was supplied from the ore-dressing plant in Bayan-Ulgii, Western Mongolia. Its chemical composition (wt.%) is 71.85% WO_3, 20.36% Fe_2O_3, 5.46% MnO_2, 1.2% CaO, 1.1% SiO_2. Its XRD pattern shows it to consist predominantly of crystalline $FeWO_4$ (JCPDS file no. 71-2391), with trace impurities of quartz (SiO_2, JCPDS file no. 33-1161), $CaWO_4$ (scheelite, JCPDS file no. 41-1431) and $MnWO_4$ (huebnerite, JCPDS file no. 74-1497), consistent with the chemical analysis. The particle size of the starting material was >10 μm, based on SEM micrographs. The two carbon sources were graphite from spent electrodes obtained from the thermal power station in Ulaanbaatar, Mongolia, containing 99.5% carbon, and activated carbon from Denka Co., Tokyo, Japan (powder grade, >99.9% carbon). The graphite was pre-milled to tabular particles of 50 μm size, and the activated carbon was used in its as-received state, with an average particle size of 35 nm and a BET surface area of 68 $m^2\,g^{-1}$.

Mixtures were prepared according to the stoichiometry of the reaction:

$$FeWO_4 + 5C \rightarrow Fe + WC + 4CO \tag{1}$$
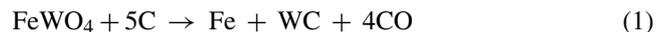
Aliquots of the mixtures were ground in a Fritsch Pulverisette 5 planetary ball mill using a 250 ml zirconia jar and zirconia milling media in the weight ratio powder: balls 1:50. Grinding times of up to 6 h were used. After grinding, the
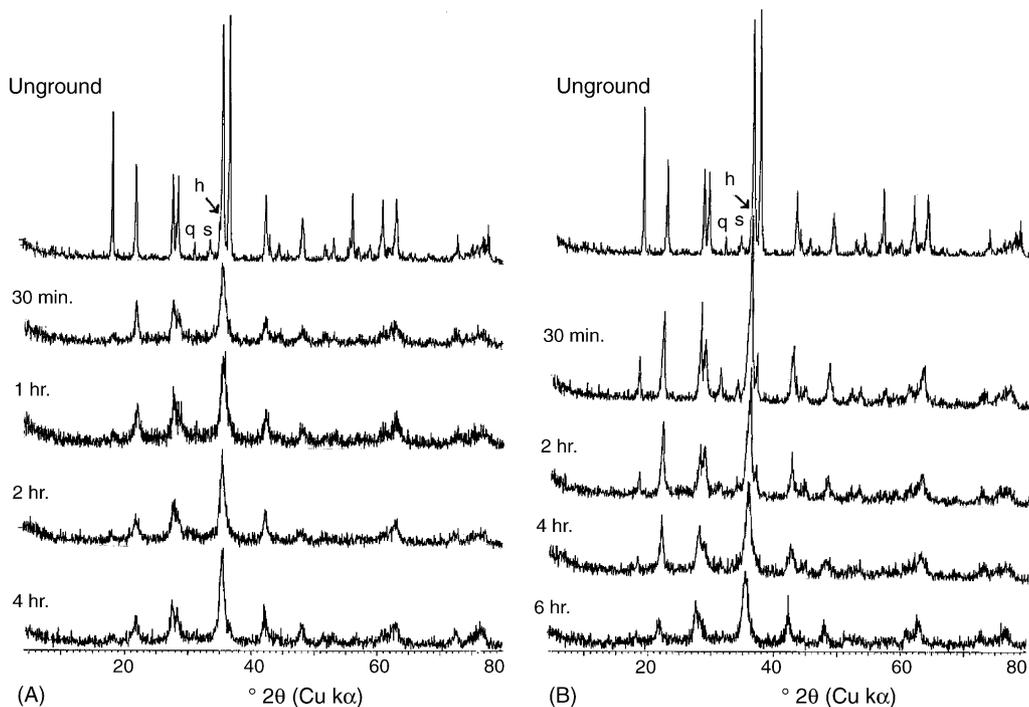

Fig. 1. X-ray powder diffractograms of wolframite ground for various times in the presence of: (A) graphite and (B) activated carbon. Key: q, quartz (JCPDS file no. 33-1161); s, scheelite (JCPDS file no. 41-1431); h, huebnerite (JCPDS file no. 74-1497). The unmarked peaks correspond to wolframite (JCPDS file no. 71-2391).

Table 1
Mössbauer parameters of unground wolframite ($FeWO_4$) and of mixtures with graphite and activated carbon, ground for varying times

Sample	Grinding time (h)	CS Fe^{2+} (mm s^{-1})[a]	QS Fe^{2+} (mm s^{-1})	CS Fe^{3+} (mm s^{-1})[a]	QS Fe^{3+} (mm s^{-1})	CS Fe—C (mm s^{-1})[a]	Fe^{3+} (%)	Fe—C (%)
FeWO$_4$	0	1.13	1.54	0.29	0.62	–	12	–
	4.0	1.10	1.95	0.40	0.99	–	43	–
FeWO$_4$ + graphite	0.5	1.14	1.62	0.40	1.03	0.02	10	8
	2.0	1.14	1.64	0.37	1.03	0.04	12	6
	4.0	1.15	1.66	0.35	0.99	0.08	23	9
	6.0	1.15	1.61	0.37	0.96	0.06	44	8
FeWO$_4$ + activated C	0.5	1.15	1.67	0.37	1.03	0.05	11	11
	1.0	1.14	1.66	0.36	0.98	0.04	26	8
	2.0	1.14	1.61	0.35	0.98	0.06	40	7
	4.0	1.15	1.65	0.36	0.95	0.02	34	8

Notes: (1) Estimated errors are as follows: CS Fe^{2+} (±0.01 mm s^{-1}), QS Fe^{2+} (±0.01 mm s^{-1}), CS Fe^{3+} (±0.03 mm s^{-1}), QS Fe^{3+} (±0.05 mm s^{-1}). (2) The minimum detection limit for the Fe—C singlet is approximately 4%, and the estimated errors in the relative areas of the Fe^{3+} and Fe—C components are 4% and 3% respectively.

[a] Centre shift (CS) values quoted with respect to the centre-point of natural α-Fe metal.

samples were examined by X-ray powder diffractometry (Philips PW 1700 diffractometer with graphite monochromator and Co Kα radiation). Their Mössbauer spectra were acquired at room temperature (293 K) by mounting the samples in Plexiglass holders such that 1.7 mg Fe cm^{-2} was presented to the beam, which is the ideal absorber thickness based on the chemical composition.[8] The spectra were recorded in transmission mode using a constant acceleration Mössbauer spectrometer with a nominal 50 mCi ^{57}Co source in a 6 μm Rh matrix. The velocity scale was calibrated relative to 25-μm α-Fe foil using the positions certified for the (former) NBS standard reference material no. 1541. Line widths of 0.28 mm s^{-1} were obtained at room temperature for the outer lines of the α-Fe spectrum. The spectra were fitted to Lorentzian lineshapes using the commercially available fitting program NORMOS written by R.A. Brand (distributed by Wissenschaftliche Elektronik GmbH, Germany).

3. Results and discussion

The X-ray powder diffractograms of the unground mixtures and mixtures ground for various periods of time are shown in Fig. 1.

In both the starting mixture containing graphite and that containing activated carbon, grinding has the effect of decreasing the intensity of the FeWO$_4$ reflections, and removes the graphite reflections from the graphite-containing sample. Grinding for longer periods progressively broadens the FeWO$_4$ reflections, but does not completely remove them over the timescale of the present experiments; neither is there any XRD indication of the formation of new crystalline phases as a result of the grinding process.

The Mössbauer spectra of the unground FeWO$_4$ (Fig. 2, top) is dominated by a doublet with parameters consistent with octahedral Fe^{2+}, and is similar to previous data reported in the literature for natural wolframites.[9] A small absorption
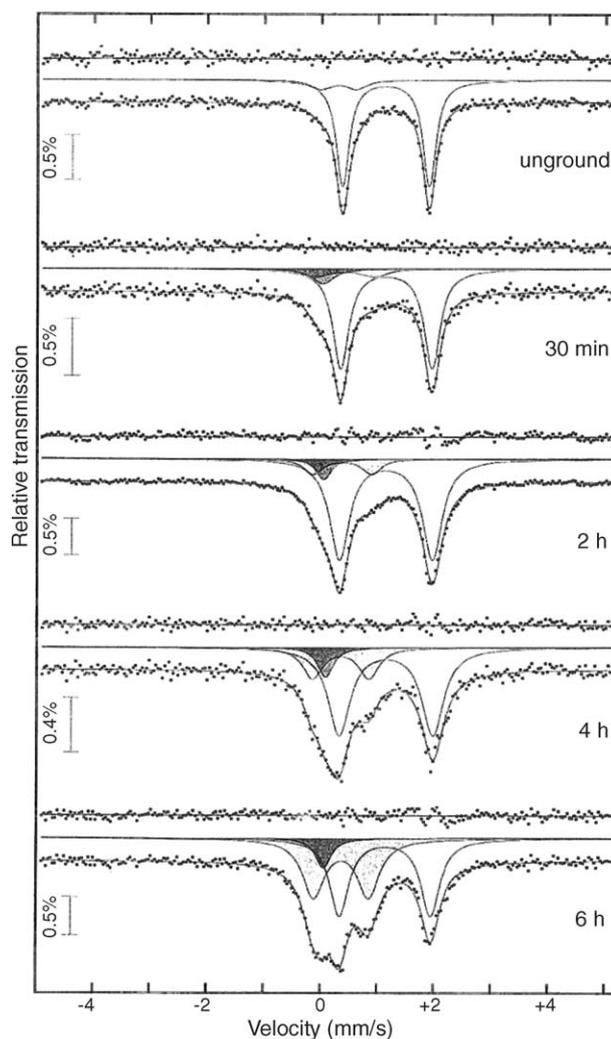

Fig. 2. Room-temperature Mössbauer spectra of unground wolframite compared to spectra of samples ground for various times in the presence of graphite. The fitted doublet shaded light grey is assigned to Fe^{3+}, the singlet shaded dark grey is assigned to Fe—C and the unshaded doublet is assigned to Fe^{2+}. The residual spectrum is shown above each set of subspectra.

feature at low velocity indicates the presence of an additional component, which is assigned to octahedral Fe^{3+}, based on its centre shift.[10]

As the graphite-containing mixture is ground for increasing lengths of time (Fig. 2), the low-velocity component increases. The enhanced absorption at low velocity is dominated by a Fe^{3+} doublet, but also indicates the appearance of absorption with a relatively low isomer shift (Fig. 2). This was fitted to a singlet, which is assigned to a dilute Fe–C phase. Previous Mössbauer studies of iron with dilute interstitial C have shown the presence of a dominant singlet, assigned to iron atoms with no carbon next-nearest neighbour (see[11] and references therein). The isomer shift of the singlet in our spectra is consistent with the mean isomer shift of the Fe–C spectra reported in the literature.

The integrated area of the Fe–C singlet reaches a maximum value after 30 min of grinding, and thereafter remains essentially unchanged (Fig. 4 and Table 1). By comparison, the area of the Fe^{3+} doublet increases progressively during grinding, due to the ongoing process of oxidation of the new surfaces freshly exposed as the particles are progressively reduced in size. A very similar result is found for mixtures containing activated carbon (Table 1), suggesting that the mechanochemical reactivity is essentially independent of the initial form of the carbon used. Wolframite ground in the absence of carbon shows a greater abundance of Fe^{3+} compared to samples ground for the same amount of time in the presence of either graphite or activated carbon (Fig. 3), indicating a greater degree of oxidation in the absence of carbon. This could be related to a buffering of the system when carbon is present, where the excess oxygen is consumed in the reaction $C + O_2 \rightarrow CO_2$. Notably there is no evidence for the Fe–C singlet in the spectrum of the carbon-free sample, providing further support for the observation that Fe–C forms during grinding in the presence of carbon.

Changes in the occupation of the various iron sites in mixtures of wolframite–graphite and wolframite-activated carbon are shown in Fig. 4 as a function of grinding time. Grinding with either graphite or activated carbon leads to the formation of a significant content of Fe–C interactions. The absence of crystalline iron carbides in the XRD patterns of these samples suggests that the Fe–C entities must be present
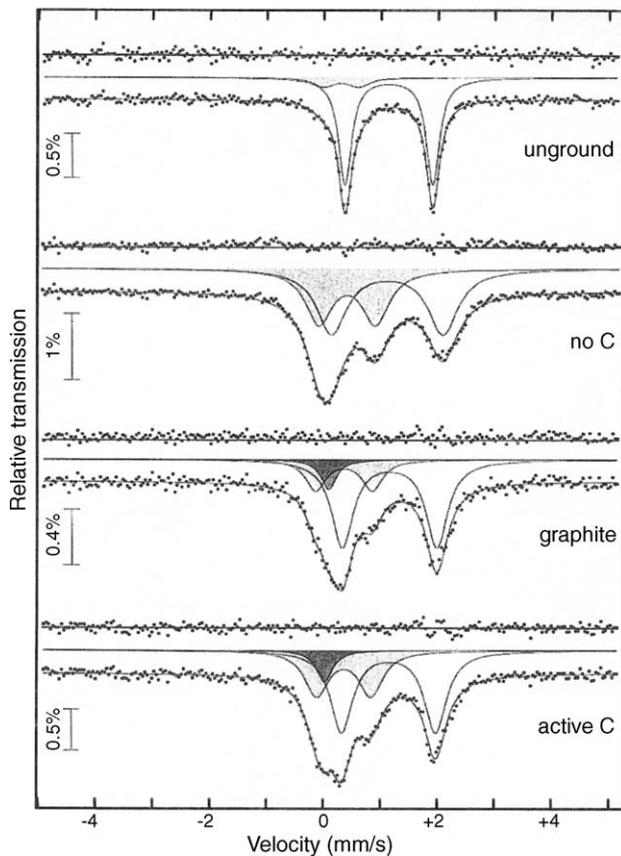

Fig. 3. Room-temperature Mössbauer spectra of unground wolframite compared to samples ground for 4 h. in the presence of the indicated carbon phases. The fitted peaks are shaded according to the scheme of Fig. 2 and the residual spectrum is shown above each set of subspectra.
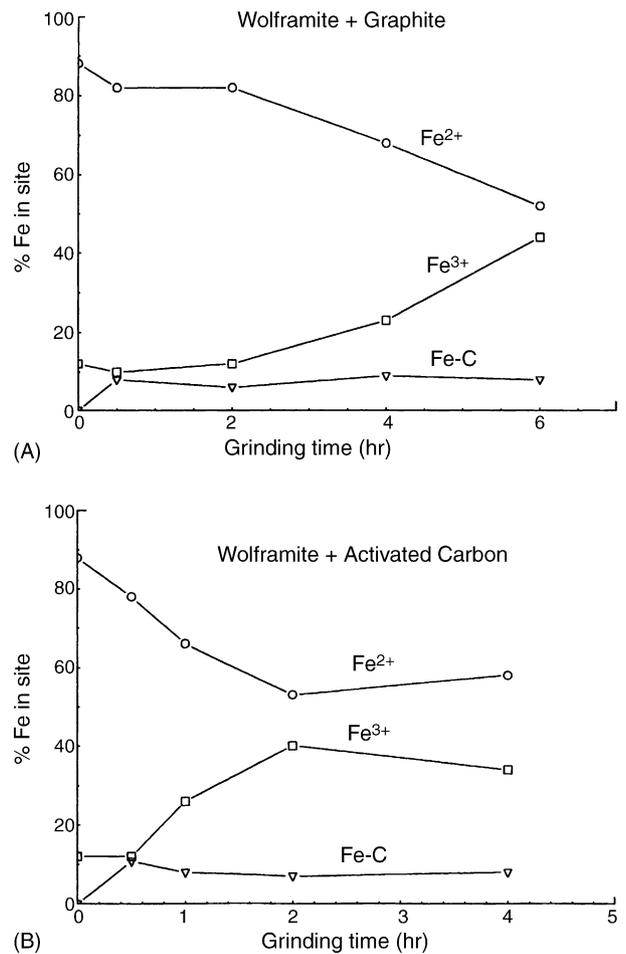

Fig. 4. Partitioning of iron into the various sites identified by Mössbauer spectroscopy, for wolframite ground with graphite and activated carbon, as a function of the grinding time. (A) Graphite and (B) activated carbon.

in the activated samples in an amorphous state, or, if in a crystalline form, in a concentration estimated to be no more than 3–4%. The presence of incipient Fe–C regions in the ground materials is consistent with the subsequent formation of crystalline iron carbide intermediate phases (Fe_6W_6C and Fe_3W_3C) when the activated mixtures are heated in flowing Ar.[6,7] It should be noted that the present results provide no information about the possible association of tungsten with the incipient carbides present in the milled mixtures, since the dilute nature of these species causes them to display a singlet peak more typical of superparamagnetic behaviour rather than a magnetic six-line spectrum of greater diagnostic value. The fact that the carbide phases, which subsequently crystallise are iron tungsten carbides suggests, however, that the incipient Fe–C regions may also be associated with tungsten.

4. Conclusions

1. When mixtures of wolframite ($FeWO_4$) and either graphite or activated carbon are milled under highly energetic conditions, the wolframite X-ray reflections are broadened and decrease in intensity, but no new *crystalline* phases are formed.
2. The behaviour of the iron during mechanochemical activation was monitored by ^{57}Fe Mössbauer spectroscopy, which indicates that during grinding, a singlet peak appears at an early stage of activation. This unexpected peak is attributed to the formation of dilute Fe–C regions and provides evidence of mechanochemically induced chemical interactions between the reactants at a molecular level. The crystallisation of iron tungsten carbide intermediates during subsequent heating of the ground mixtures in flowing Ar suggests that these regions of iron–carbon interaction may also be associated with the tungsten component.
3. Concomitantly with the development of the new Fe–C bonds, progressive oxidation occurs of the Fe^{2+} in the wolframite starting material, as new surfaces are formed by cominution. This oxidation occurs to a greater degree when the grinding is carried out in the absence of carbon, suggesting that the latter exerts a degree of buffering (oxygen scavenging) on the system.
4. These mechanochemically induced reactions are essentially independent of the nature of the carbon used as the starting material.

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