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Mechanical alloying of an immiscible α-Fe$_2$O$_3$-SnO$_2$ ceramic

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A solid solution of about 6 mol % SnO$_2$ in α-Fe$_2$O$_3$ has been prepared by mechanical alloying of α-Fe$_2$O$_3$ and SnO$_2$ powder blends. This result demonstrates that high energy ball milling can be used to prepare metastable oxide solid solutions with an extended range of compositions in the immiscible ceramic oxide system. X-ray diffraction and Mössbauer spectroscopy investigations show that mechanical milling of α-Fe$_2$O$_3$ amd SnO$_2$ involves alloying on an atomic scale and that true solid solution formation occurs. We suggest that the high defect concentration and the chemical enthalpy of Fe^{3+}-O^{2-}-Sn^{4+} interfaces between nanostructured α-Fe$_2$O$_3$ and SnO$_2$ regions may serve as a driving force for the formation of a solid solution in the immiscible ceramic system. [S0163-1829(97)01402-1]

It has been demonstrated in a variety of systems that mechanical alloying of elemental powder blends allows alloys, which are far from equilibrium, to be synthesized.[1] In particular, much attention of late has been given to the formation of metastable solid solutions in immiscible alloy systems.[2] For example, in the Fe-Cu system,[3] supersaturated bcc solid solutions up to about 30 at. % Cu and fcc solid solutions up to about 60 at. % Fe were obtained by mechanical alloying, whereas the equilibrium mutual solid solubility is less than 0.1 at. % below 873 K.[4] In this work, the mechanical alloying in an immiscible *ceramic oxide system* has been investigated. A binary α-Fe$_2$O$_3$-SnO$_2$ ceramic system was chosen as a model since the solubility of SnO$_2$ in α-Fe$_2$O$_3$ is less than 1 mol % below 1073 K,[5,6] and the system is of interest in the gas sensor industry.[6,7] We have examined the alloying process in a 93.6 mol % α-Fe$_2$O$_3$/SnO$_2$ ceramic system by x-ray diffraction and Mössbauer spectroscopy which is amenable to probing the local environments of both the iron and tin ions in materials by ^{57}Co and ^{119}Sn sources.

Samples of α-Fe$_2$O$_3$-SnO$_2$ were prepared by mixing powders of hematite (α-Fe$_2$O$_3$)(99.9% purity; particle size $\approx$10 μm) and cassiterite (SnO$_2$) (99.9% purity; particle size $\approx$10 μm) with a nominal composition of 6.4 mol % SnO$_2$. The milling was carried out in an open container (i.e., the valves on the lid are open during milling) using a planetary ball mill (Fritsch Pulverisette 5), with tungsten carbide (WC) vials and balls.[8] Thus air was constantly available to the oxide powders during milling. The milling intensity was 200 rotations per minute, and a ball-to-powder weight ratio of 20:1 was chosen. The milling was interrupted after selected times to take out small amounts of powder for analysis. The composition of the sample milled for 110 h was examined by scanning electron microscopy with an energy-dispersive x-ray analysis facility. It was found that the tungsten contamination, originating from the abrasion of the vials and balls was less than 2 at. %. X-ray diffraction measurements were performed on a Philips PW-3710 diffractometer with Cu K_α radiation in the 2θ range of $20°$–$80°$ in steps of $0.02°$. The average grain size of the hematite phase was determined from the broadening of the six strongest diffraction peaks using the Scherrer method. Mössbauer spectroscopy was performed with a conventional constant-acceleration spectrometer in transmission geometry with sources of about 25 mCi ^{57}Co in a Rh matrix and 5 mCi ^{119}Sn in BaSnO$_3$. All isomer shifts are given relative to that of α-Fe at room temperature. A closed-cycle helium cryostate was used for low-temperature measurements.

Figure 1 shows the x-ray-diffraction patterns of the 6.4 mol % α-Fe$_2$O$_3$-SnO$_2$ samples after different milling times. The pattern of the sample after 2 h milling shows the presence of highly crystalline α-Fe$_2$O$_3$ and SnO$_2$ phases. After increasing the milling time to 19 h, the diffraction peaks of the SnO$_2$ and α-Fe$_2$O$_3$ phases broaden significantly. Upon increasing the milling time, the intensities for the SnO$_2$ phase are further reduced and after a milling time longer than 42 h are hardly observable, indicating the formation of a Fe-Sn-O phase with a structure similar to hematite. Two new peaks located at $2\theta\approx30°$ and $48°$ are observed in the sample after 110 h milling, and are attributed to the WC contamination. The average grain size and the lattice parameters of the hematite phase are shown in Fig. 2 as a function of the milling time. Initially, the milling process reduces the grain size of the α-Fe$_2$O$_3$ powder from 10 μm down to about 8 nm in the
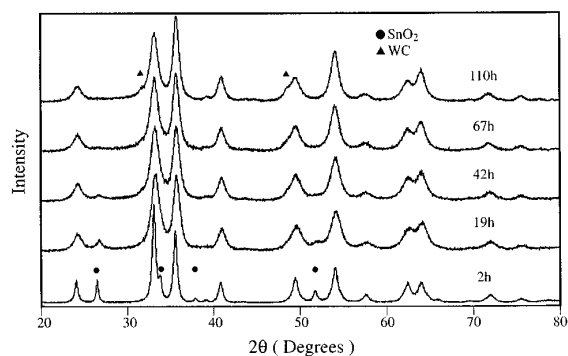
FIG. 1. X-ray powder-diffraction patterns for the 6.4 mol % α-Fe_2O_3-SnO_2 samples after different milling times.

sample milled for 19 h. The grain size is not further reduced by extended milling while the c axis of the hexagonal corundum cell becomes elongated. This result suggests that alloying between α-Fe_2O_3 and SnO_2 powders takes place since the c value is known to increase with increasing tin content in the hematite phase.[6] The milling process initially increases the values of the a lattice parameter, but, after further milling, the value of a becomes virtually constant. The detection of a single phase with the corundum structure in the sample milled for 110 h lmay not be taken as definite evidence for a formation of a homogeneous solid solution on the atomic scale, since for example, an amorphous tin oxide may be formed, the Bragg peaks may become invisible due to line broadening because of small grain sizes of SnO_2, or a coherent structure may be formed between α-Fe_2O_3 and SnO_2 regions. Therefore, we employed both ^{119}Sn and ^{57}Fe Mössbauer spectroscopy to monitor the alloying process in the α-Fe_2O_3-SnO_2 system during milling.

Figure 3 shows the ^{57}Fe Mössbauer spectra obtained at 20 K for the 6.4 mol % α-Fe_2O_3-SnO_2 samples after different milling times. After milling for 2 h, the spectrum is identical to that of hematite with a low Morin transition temperature and has been fitted with two sextets, corresponding to the spins in the hematite phase existing in both antiferromagnetic and weak ferromagnetic states.[9] After 19 h, the spectrum consists of an asymmetrically broadened sextet. Spectra for samples after milling times longer than 19 h are similar. Since the possible influence of superparamagnetic relaxation at 20 K can be considered negligible, the broadening can be attributed to the presence of tin ions in the hematite phase, indicating that the diffusion of tin ions into α-Fe_2O_3 occurs after a milling time of 19 h. From previous work[6,10–12] on samples with a low tin content, it is known that Sn^{4+} ions

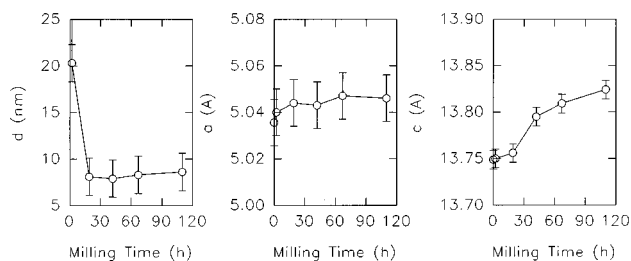FIG. 2. Average grain size and lattice parameters of the hematite phase for the 6.4 mol % α-Fe_2O_3-SnO_2 samples versus milling times. The lines are guides to the eye.
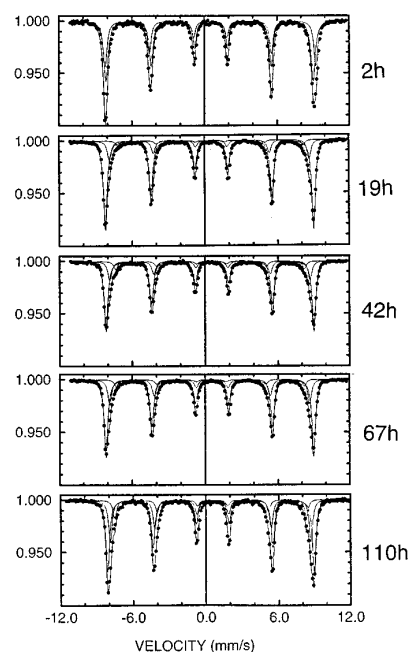

FIG. 3. ^{57}Fe Mössbauer spectra obtained at 20 K for the 6.4 mol % α-Fe_2O_3-SnO_2 samples after different milling times.

incorporated into α-Fe_2O_3 are expected to occupy cation positions. The Mössbauer spectra showed no evidence for Fe^{2+} and Sn^{2+} ions in samples studied here and we associate charge balance with the creation of cationic vacancies. In general, the hyperfine field can be analyzed in terms of different environments of the iron atoms arising from near-neighbor interactions. This is complex in the α-Fe_2O_3-SnO_2 system. There exist at least three different near-neighbor interactions: Fe^{3+}-Fe^{3+}, Fe^{3+}-Sn^{4+}, and Fe^{3+}-$\square$ ($\square$: cation vacancy). The ^{57}Fe Mössbauer spectra should be fitted using a distribution of hyperfine fields corresponding to various environments of the iron ions in the samples. For simplicity, they were fitted in two ways: one using two sextets and the other three sextets. In the former the first sextet with a hyperfine field of 53 T and a narrow linewidth is attributed to iron ions in environments similar to those of the pure hematite phase. The second sextet with a hyperfine field of 50 T and a broadened linewidth is attributed to the average of the rest. The spectra fitted with three subspectra (I, II, and III components) showed average magnetic hyperfine fields of about 53, 51, and 48.5 T, respectively. The isomer shifts for three sextets are about 0.45 mm/s. The magnetic hyperfine fields and the isomer shifts are characteristics of Fe^{3+} in all samples studied. The relative areas of three components as a function of milling time are shown in Fig. 4. It is clear that the diffusion of tin ions into α-Fe_2O_3 occurs after 19 h milling. Upon further milling, additional diffusion is observed from the increase of relative areas for both II and III components at the expense of component I. The relative areas of three subspectra obtained for the sample milled for 110 h appear to be similar with the relative probabilities for the (13Fe, 0Sn), (12Fe, 1Sn), and (11Fe, 2Sn) configurations calculated on the basis of random substitution taking into account cation vacancies for a sample with a 6 mol % SnO_2 in α-Fe_2O_3, respectively. A cation vacancy is assumed as a nonmagnetic metal ion such as a tin ion.
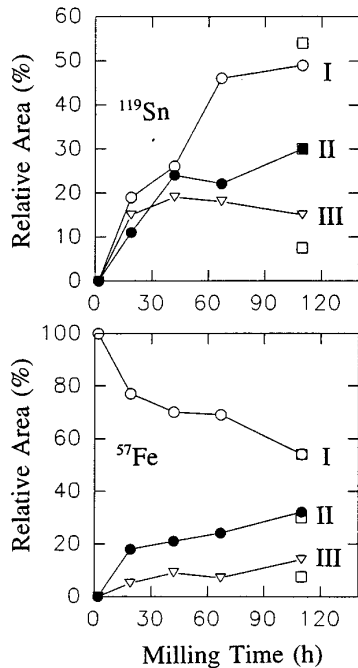
FIG. 4. Relative areas of three fitting components obtained from the ^{119}Sn and ^{57}Fe Mössbauer spectra for the 6.4 mol % α-Fe_2O_3-SnO_2 samples versus milling time. The definitions of the I (open circles), II (solid circles), and III (triangles) components in both ^{119}Sn and ^{57}Fe Mössbauer measurements and the relative probabilities (open squares) for the three atomic configurations are given in the text. The lines are guides to the eye.

FIG. 5. ^{119}Sn Mössbauer spectra obtained at 20 K for the 6.4 mol % α-Fe_2O_3-SnO_2 samples after different milling times.

To further investigate the alloying process during milling, ^{119}Sn Mössbauer spectra for the same samples were also recorded at 20 K, as shown in Fig. 5. After milling for 2 h, the spectrum is identical to that of diamagnetic Sn^{4+} ions in SnO_2 phase with an isomer shift, $\delta = 0.14$ mm/s, a quadrupole splitting, $\Delta E_Q = 0.57$ mm/s and a linewidth, $\Gamma = 1.1$ mm/s. After 19 h, the spectrum shows a significant resonant absorption in the velocity range from -8 to 8 mm/s as well as at a velocity close to zero. The former is attributed to a broadened sextet caused by a hyperfine field distribution, which strongly implies the diffusion of tin ions into the magnetically ordered α-Fe_2O_3 phase. The latter is due to the SnO_2 phase. Upon increasing the milling time, the relative area of the broadened sextet increases at the expense of the area of the central peak. After 100 h of milling the spectrum is dominated by the broadened sextet with a small central peak.

Although a Sn^{4+} itself is nonmagnetic, its nucleus can sense a nonvanishing magnetic hyperfine field by the effect of a supertransferred hyperfine interaction (STHI) with the magnetically ordered Fe^{3+} ions in the α-Fe_2O_3 phase. The mechanism giving rise to the magnetic hyperfine field is fairly similar to that for the superexchange interaction.[13,14] When a diamagnetic cation ^{119}Sn substitutes a magnetic ion Fe^{3+} in the lattice of a magnetic oxide, α-Fe_2O_3, the spin densities from the magnetic ions permeate the oxide ions surrounding the diamagnetic cation and are further supertransferred to the outer s orbital of the diamagnetic cation ion. The spin-polarized (spin-unbalanced) s electrons contact the nucleus of the diamagnetic ion giving rise to the Fermi contact magnetic field. The hyperfine field can be observed as magnetic splitting in the ^{119}Sn Mössbauer spectrum. The
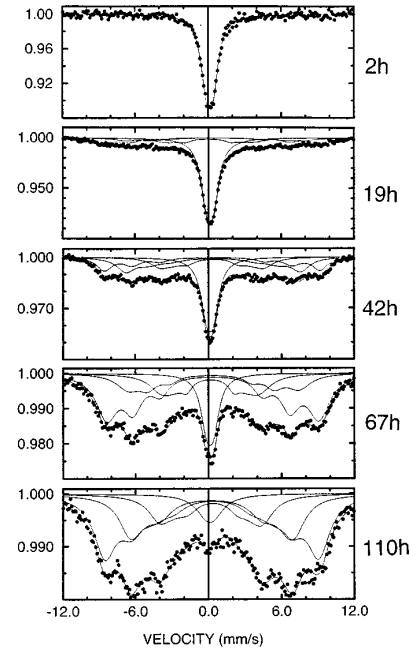
crucial point of the STHI is that significant spin transfer only occurs to such diamagnetic cations that are bound through anions to magnetically ordered cations. If we assume a chain of ions, for example, -Fe^{3+}-O^{2-}-Sn_1^{4+}-O^{2-}-Sn_2^{4+}-, spin transfer from the Fe^{3+} ion to Sn_2^{4+} ion is by far smaller than that to the Sn_1^{4+} ion. The magnetic hyperfine field of the tin ion in tin doped α-Fe_2O_3 samples (tin concentration <1 at. %) has been found to be about 13 T at 80 K,[10–12] in which most of the tin ions located in the α-Fe_2O_3 lattice are surrounded by iron ions. The magnetic hyperfine fields of tin ions decrease by replacement of some near-neighbor Fe^{3+} ions with diamagnetic tin ions or cation vacancies.[6] Magnetic splitting for such tin ions strongly bound to the surface of α-Fe_2O_3 can be observed and has been found to be less than about 7 T.[15]

It follows that the broadened sextet in the ^{119}Sn spectra of the samples after a milling time exceeding 2 h should be fitted by a magnetic hyperfine field distribution, corresponding to different local environments of tin ions in α-Fe_2O_3. Three magnetic sextets were used to fit the broadened resonant sextet in ^{119}Sn Mössbauer spectra, following the proceeding adapted for treatments in the ^{57}Fe Mössbauer spectra. The average hyperfine fields of the three sextets (I, II, and III components) are found to be about 13, 10, and 6 T, respectively. The relative areas for different components as a function of milling time are also shown in Fig. 4. They may be related to the Sn^{4+} ions in the α-Fe_2O_3 lattice having zero, one, and two tin neighbor ions, respectively. The tin ions strongly bound to the surfaces of α-Fe_2O_3 particles could also contribute to the III component. The isomer shifts for the three sextets are about 0.1 mm/ which implies that the tin ions in the α-Fe_2O_3 lattice for all samples take the valence state of Sn^{4+}. [Sn^{2+} and metallic tin are easily characterized in the ^{119}Sn Mössbauer spectra by high positive isomer shifts with respect to SnO_2 ($\sim$2–4 mm/s).[16]] After a milling time of 19 h, the percentage of both I and II components reaches about 30% of total tin ions in the material and

increases following further milling. These results reflect the increase of tin content in α-Fe_2O_3 when the milling time increases. On the other hand, in the sample milled for 19 h the component III reaches a high value about 15% of tin ions, which indicates that the Fe^{3+}-O^{2-}-Sn^{4+} bonds between nanostructured α-Fe_2O_3 and SnO_2 regions may be formed during initial ball milling. After a milling time of 110 h about 93% of the tin ions alloy with α-Fe_2O_3, and about 7% tin ions are in SnO_2. These results demonstrate that the alloying between α-Fe_2O_3 and SnO_2 oxides occurs on an atomic level after 110 h milling. If the sample after 110 h milling consisted of a mixture of small pure SnO_2 and α-Fe_2O_3 particles, then no magnetic field on the diamagnetic tin ions would be observed. Room-temperature ^{119}Sn Mössbauer spectra of the 6.4 mol % α-Fe_2O_3-SnO_2 samples after different milling times showed the magnetic hyperfine field distributions of the broadened sextets to be similar in trend to those observed at 20 K. The ratio of the resonant absorption area of the spectrum at room temperature to that at 20 K is in the range of 0.6–0.7 in all samples. This means that the tin ions in the samples have high effective Debye temperatures. This indicates that tin ions are situated in α-Fe_2O_3 lattice rather than weakly bound on the surfaces of small α-Fe_2O_3 particles. If all the tin ions in the sample milled for 110 h were in a monolayer on the surfaces of small α-Fe_2O_3 particles, hyperfine magnetic fields of such tin ions could be induced by the STHI. However, the hyperfine magnetic fields would then be smaller than 7 T.[15] Because the magnetic hyperfine fields for most tin ions in the sample milled for 110 h are larger than 7 T, it can be concluded that in the sample after 110 h milling, alloying between α-Fe_2O_3 and SnO_2 oxides occurs on an atomic level to form a α-Fe_2O_3-SnO_2 solid solution containing about 6 mol % SnO_2.

In the equilibrium state, the solubility of SnO_2 in α-Fe_2O_3 is very small, <1 mol % below 1073 K.[5,6] However, after a milling time exceeding 2 h, the average grain size of the α-Fe_2O_3 particles is rapidly reduced and found to be about 8 nm in the sample after 19 h. After extended milling, the grain size is saturated. For such nanometer-sized particles, structures of the surface of particles and interfaces between particles will be expected to be highly defective and defects, e.g., cation vacancies. The cation vacancy concen-

tration could be substantially high in α-Fe_2O_3-SnO_2 solid solutions due to the charge compensation, e.g., it can be about 1% of total cation positions for the sample with 6 mol % SnO_2 in α-Fe_2O_3 assuming $4Fe^{3+} \rightarrow 3Sn^{4+} + \square$. Thus, these regions may act as fast diffusion pathways having low activation energies.[17] Furthermore, the oxygen lattice in both α-Fe_2O_3 and SnO_2 phases is hexagonally close-packed so that the oxygen lattices would easily form a coherent structure between α-Fe_2O_3 and SnO_2 regions, as indicated in the sample milled for 19 h. The chemical enthalpy of the Fe^{3+}-O^{2-}-Sn^{4+} interfaces between α-Fe_2O_3 and SnO_2 regions can enhance the free energy of a mixture of nanostructured α-Fe_2O_3 and SnO_2 composites above that of the related solid solution thus providing a driving force for the diffusion of Sn^{4+} in α-Fe_2O_3. (Note that the anions have much lower mobility than cations in these oxide ceramics with a close-packed oxygen lattice[18]). The importance of the interface chemical enthalpy for alloy formation by mechanical alloying has also been suggested in immiscible alloy systems.[2] Further studies of the mechanical alloying process in the α-Fe_2O_3-SnO_2 system with a wide range of compositions are in progress.

In conclusion, the alloying process of the 6.4 mol % α-Fe_2O_3-SnO_2 system during high-energy ball milling has been studied by x-ray diffraction and Mössbauer spectroscopy. Initially the milling process reduces the grain sizes of both α-Fe_2O_3 and SnO_2 oxides powders. After 19 h milling, some Fe^{3+}-O^{2-}-Sn^{4+} interfaces between nanostructured α-Fe_2O_3 and SnO_2 regions are formed and consequently diffusion of tin ions into the α-Fe_2O_3 phase occurrs. When the milling time increases, tin ions diffuse further into the phase. After 110 h of milling, a solid solution with about 6 mol % SnO_2 is formed. The high defect concentration and the chemical enthalpy of Fe^{3+}-O^{2-}-Sn^{4+} interfaces between nanostructured α-Fe_2O_3 and SnO_2 regions are suggested as the driving force for the formation of a solid solution in the immiscible ceramic system. The results show that high-energy ball milling is able to extend solubility not only in immiscible alloy systems, but also in the immiscible ceramic oxide system.

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