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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	Angstrom		μm	micrometer
°C	degree Celsius		min	minute
g	gram		mol	mole
h	hour		nm	nanometer
kg/cm²	kilogram per square centimeter		pct	percent
$/lb	dollar per pound		wt	weight
lb	pound			

HEXAGONAL PHASE TRANSFORMATION IN THE ENGINEERED SCAVENGER COMPOUND LITHIUM TITANATE

By W. K. Collins,[1] W. D. Riley,[2] and B. W. Jong[3]

ABSTRACT

Engineered scavenger compounds (ESC's) developed by the U.S. Bureau of Mines are a novel class of compounds that selectively can recover a desired element from a solid or molten alloy. Lithium titanate ($Li_2Ti_3O_7$ or $Li_2O \cdot 3TiO_2$) is used as an ESC to recover lithium (Li) from aluminum-lithium (Al-Li) alloys. X-ray diffraction measurements have shown that $Li_2Ti_3O_7$ undergoes a phase change during scavenging from an orthorhombic structure to a hexagonal structure. This change is due to the incorporation of lithium in the matrix of the material and the effect of temperature. Although both phases are metastable, the hexagonal phase that forms during the scavenging of lithium from Al-Li alloys appears to be the more stable phase. Recovering lithium from the ESC by electrodeposition does not cause the structure to revert to the orthorhombic phase. The orthorhombic and the hexagonal structures of $Li_2Ti_3O_7$ have similar scavenging capacities for lithium. This report proposes a new mechanism for the phase transformation.

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INTRODUCTION

The U.S. Bureau of Mines has developed a process to recover both aluminum and lithium from the currently unrecyclable aluminum-lithium (Al-Li) scrap. This development is part of the Bureau's mission to conserve materials for which supplies are limited and to find substitutes for materials that come from insecure sources or are environmentally hazardous.

The development, introduction, and use of Al-Li alloys for aircraft structural components has created a serious problem for the aluminum scrap recycling industry. More than 300,000 lb of Al-Li alloys were produced during 1990, and production is predicted to increase to more than 9 million lb by the year 2000 (3).[4] Recycled aluminum scrap from aircraft is used as feed for the secondary aluminum casting industry (14). The addition of Al-Li scrap to conventional melts creates some very serious problems for the secondary aluminum caster, such as:

1. Reducing the fluidity of the melt;
2. Creating excessive dross and skim;
3. Increasing porosity of the casting;
4. Reducing elongation;
5. Modifying the microstructure of conventional alloys;
6. Increasing the number of inclusions (13);
7. Causing both a health and possibly an environmental hazard (7).

However, there is also an economic incentive for recycling Al-Li alloys. Lithium metal for alloying costs about the same as the aluminum alloy (approximately \$26.00/lb) (2, 13).

This report describes the phase change that occurs in the engineered scavenger compound (ESC) lithium titanate ($Li_2Ti_3O_7$) when lithium is scavenged from Al-Li alloy scrap. ESC's have a channel or tunnel structure that can accommodate ions of a particular size and valence. For example, $Li_2Ti_3O_7$ has a structure that can, preferentially, accommodate metal ions with small ionic radii and low valences, such as the lithium cation (Li^+) with an ionic radius of 0.068 nm (9, 12). Figure 1 shows the pseudobinary phase diagram Li_2O-TiO_2 from 50 to 100 mol pct TiO_2. The figure shows that the hexagonal phase is the more stable of the two phases, but occurs only over a small range of composition and temperatures. When the ESC scavenges lithium, Li^+ is first taken up into the open framework of the crystal lattice and then moves into the tunnel position (12). The addition of Li^+ into the crystal

structure stresses the structure. The stress by, and movement of the Li^+; the resulting flow of electrons in the structure; and the application of heat trigger the transformation of $Li_2Ti_3O_7$ from the orthorhombic phase to the hexagonal phase.

Bureau experiments using $Li_2Ti_3O_7$ as an ESC indicate that this phase change was caused primarily by incorporating Li^+ into the matrix of the material, and by applying heat. Bureau work found that the orthorhombic to hexagonal phase change occurred in less than 30 min when Li^+ was loaded into the $Li_2Ti_3O_7$ at 600° C. Table 1 shows the experimental results of the scavenging trials. Table 2 shows the time and temperature required to cause transformation of the orthorhombic phase $Li_2Ti_3O_7$ to the hexagonal phase when the compound was heated in air without Li^+ insertion. Furnace tests indicate that it took an excess of 24 h at 600° C for transformation to the hexagonal phase to occur. The orthorhombic to hexagonal phase transformation only occurred when the temperature was above 500° C; below this the phase transformation did not occur.

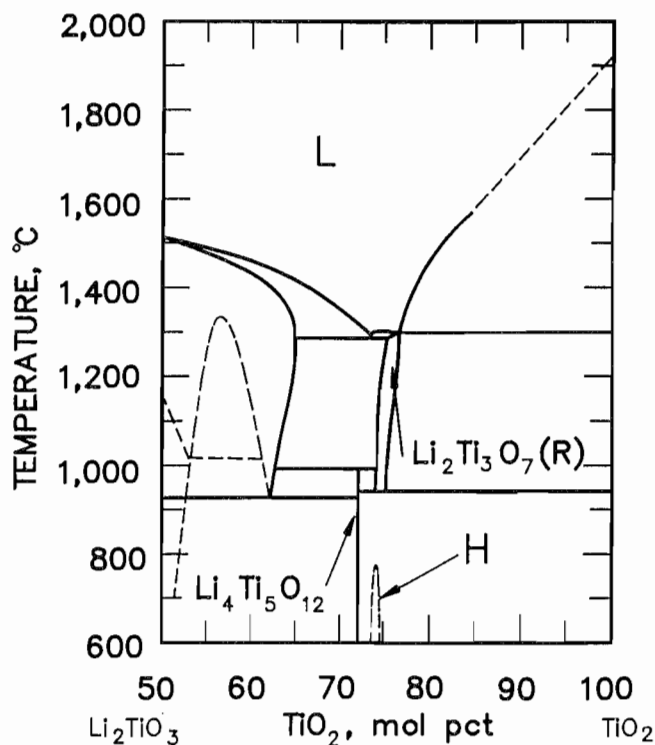Figure 1.—Pseudobinary phase of Li_2O-TiO_2 from 50 to 100 mol pct TiO_2 (11). L = liquid; R = orthorhombic phase; H = hexagonal phase.

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[4]Italic numbers in parentheses refer to items in the list of references at the end of this report.

Table 1.—Orthorhombic to hexagonal phase conversion and experimental results of the $Li_2Ti_3O_7$ scavenging trials

Test[1]	Time, h	Temp, °C	$Li_2Ti_3O_7$/ Al-Li, wt ratio	Hexagonal phase[2] present	Lithium[3] removed, pct
1 ..	0.5	400	1	Not detected ..	81.4
2 ..	.5	600	1	Primary	82.1
3 ..	2	400	1	Not detected ..	51.4
4 ..	2	600	1	Primary	80.0
	2	600	1	.. do.........	86.4
5 ..	.5	400	2	Not detected ..	55.0
6 ..	.5	600	2	Minor	45.0
7 ..	2	400	2	Not detected ..	70.0
8 ..	2	600	2	Primary	80.7
	2	600	2	.. do.........	82.6
9 ..	1.25	500	1.5	Not detected ..	72.1

[1]Tests 4 and 8 were repeated.

[2]Phase compositions: primary—40 to 100 pct; secondary—20 to 60 pct; minor—5 to 30 pct; trace—1 to 10 pct; B. D. trace—<1 pct.

[3]Scrap Al-Li alloy lithium content: 1.45 pct.

Table 2.—Heat treatment of $Li_2Ti_3O_7$ to examine phase changes in air

Time, h	Crystal structure and color
400° C:	
24	Orthorhombic, white.
48	Do.
72	Do.
500° C:	
24	Do.
48	Do.
72	Do.
600° C:	
24	Do.
48	Orthorhombic and hexagonal, white.
72	Test canceled.

EXPERIMENTAL PROCEDURES

STARTING MATERIALS

The ESC $Li_2Ti_3O_7$ was prepared from lithium carbonate (Li_2CO_3) and either anatase or rutile (TiO_2) using a 3-to-1 mol ratio. The compounds used were high-quality reagent grade chemicals. The two components were blended in a rotary mill for a minimum of 2 h to ensure proper mixing. The mixture was placed in a Coors[5] porcelain crucible glazed on the inside, and was prefired at 900° C in air for 2 h. This prefiring converted the Li_2CO_3 to Li_2O. During the conversion from Li_2CO_3 to Li_2O the carbonate became a liquid and coated the TiO_2 particles. The mixture was then immediately placed in another furnace preheated to 1,100° C and held at temperature for a minimum of 15 h in air. Upon cooling, the newly formed $Li_2Ti_3O_7$ was ground to a fine powder. A second firing was done at 1,100° C for 24 h to ensure complete reaction of the components. X-ray powder diffraction analysis of the final sample showed that the major product was the orthorhombic phase of $Li_2Ti_3O_7$ accompanied by a trace of TiO_2. Figure 2 shows the X-ray diffraction patterns of the orthorhombic $Li_2Ti_3O_7$.

ELECTROCHEMICAL CELL

Electrochemical tests were carried out in a molten salt electrolytic scavenger cell. The cylindrical, 316 alloy stainless steel (SS) cell measured 3 in. in diam and 9.5 in

high. Two 1- by 2-in porous SS basket electrodes were used to hold the ESC and Al-Li scrap. A protective atmosphere of argon gas was used to prevent oxidation of the aluminum.

The electrolyte of the cell was molten lithium chloride (LiCl) and potassium chloride (KCl) of the eutectic composition (58 pct LiCl and 42 pct KCl). Its melting point is 360° C. The eutectic salt was loaded into a protective ceramic crucible and placed into the SS electrolytic cell. The cell was then heated by a vertical Lindberg[6] resistance heating furnace to a temperature range of 400° to 600° C. The electrode baskets, one with powdered $Li_2Ti_3O_7$ and the other with Al-Li scrap, were packed in a porous graphite liner. Both electrodes were assembled and attached to the cell cover and then inserted into the molten salt bath. A thermocouple was also part of the cover assembly. The cell was allowed to return to equilibrium temperature, and then the electrodes were connected to activate the scavenger cell. The cell worked by ionic conductivity. Observations of initial trial runs with the cover off revealed that the $Li_2Ti_3O_7$ immediately began to change color from white to dark blue or black as it scavenged lithium from the Al-Li alloy. The color change began at the edge and progressed to the center of the electrode. Temperature, current, and voltage were measured continuously while the cell was in operation.

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[5]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.
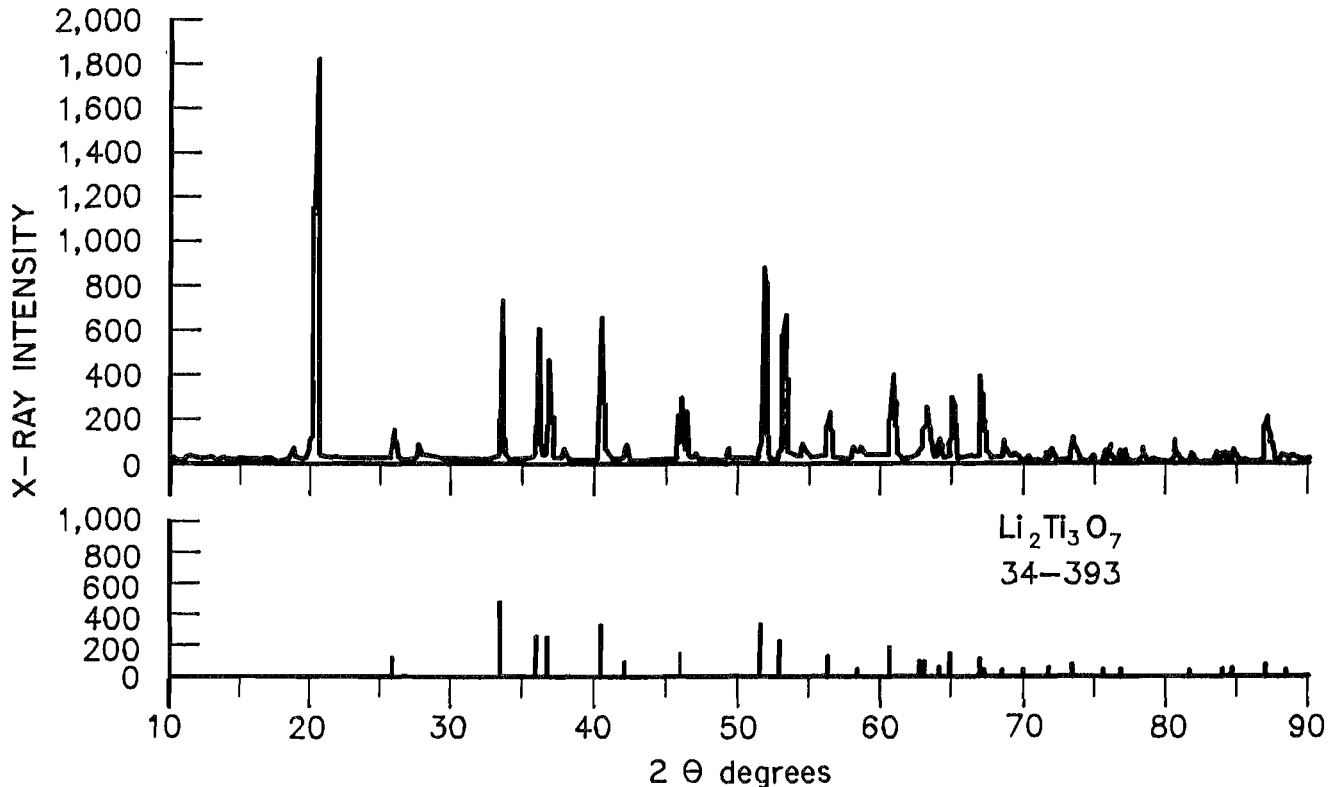
[6]Cited in footnote 5.

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Figure 2.—X-ray diffraction patterns, orthorhombic Li₂Ti₃O₇. Top, Graph is the actual pattern, and the bottom graph is the reference pattern.

STRUCTURE OF $Li_2Ti_3O_7$

Lithium titanate is a transition metal known for its open crystal structure that can accommodate cations over a wide range of stoichiometry (8). Its crystal structure is orthorhombic and similar to that found in the mineral ramsdellite (MnO_2) (1). Because of this similarity, $Li_2Ti_3O_7$ is also referred to as ramsdellite. The open framework structure is made up of multiples of octahedral oxides (MO_6) forming chains sharing corners and edges. This octahedral linking forms tunnels parallel to the c-axis (8). Figure 3 shows the cross section of the orthorhombic unit cell (11). Figure 4 shows a perspective view of the orthorhombic structure illustrating the tunnels and octahedra (8). Figure 5 shows the orthorhombic structure viewed along the [001] direction. Oxygen and titanium atoms are drawn to size, and the tunnels are shown with possible lithium sites indicated by "Li" (8).

Lithium titanate has two distinct means of scavenging Li^+. They are—

1. The crystal lattice contains vacancies that can be filled with Li^+. The lattice has too few titanium ions to completely fill the octahedral sites (4).

2. Lithium cations can fill the tunnel sites created by the joining of the MO_6 octahedrons (4).

The $Li_2Ti_3O_7$ made at the Bureau's Albany Research Center was a very fine polycrystalline structure. Selected area diffraction patterns taken on a Phillips CM12[7] transmission
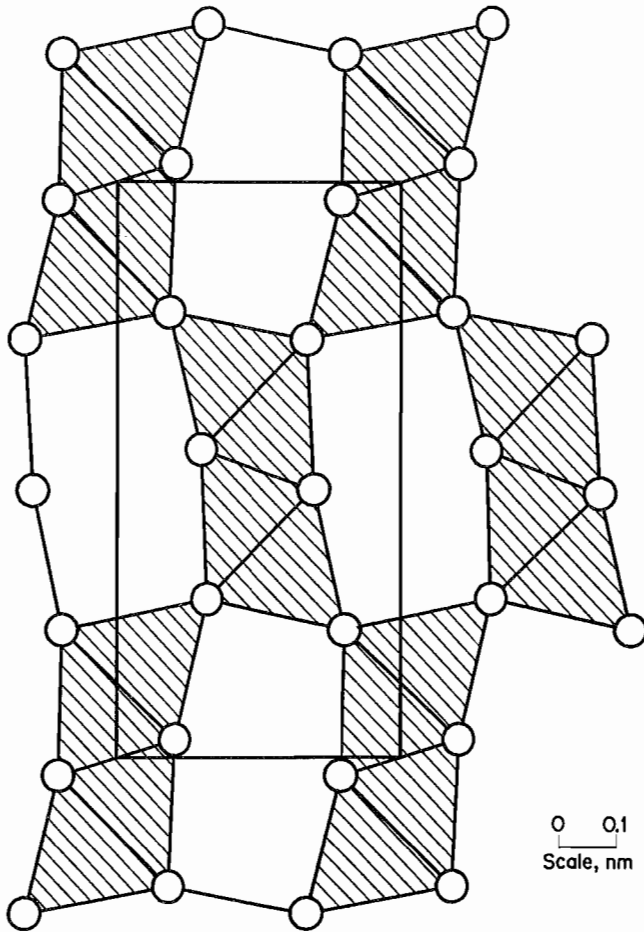
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[7]Cited in footnote 5.

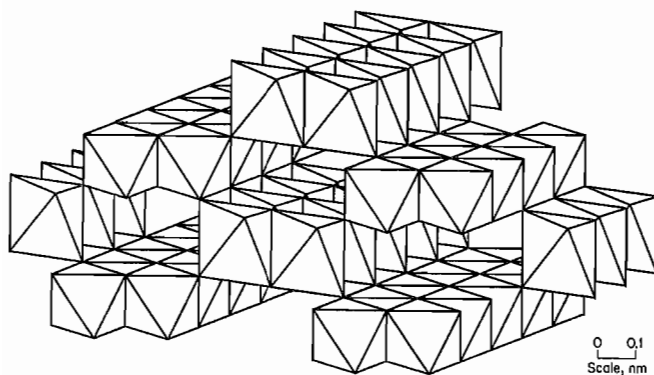Figure 3.—Cross section of orthorhombic unit cell (12).

Figure 4.—Orthorhombic phase showing tunnels and arrangement of the octahedra (8).
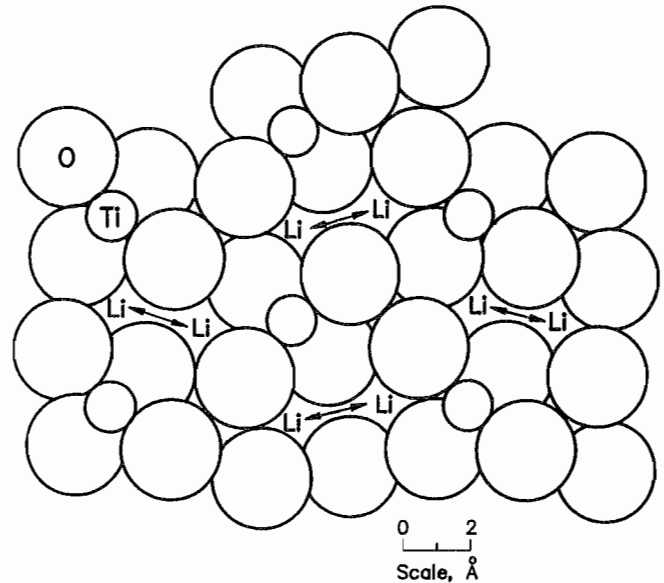

Figure 5.—Orthorhombic phase viewed along the [001] direction with the oxygen and titanium ions drawn to scale. Lithium atoms are not shown, but their positions in the tunnels are indicated with "LI" (8).

electron microscope (TEM) showed ring patterns that are characteristic of extremely fine polycrystalline materials. X-ray diffraction of the crystals confirmed the composition to be the orthorhombic phase of $Li_2Ti_3O_7$.

Upon placing the $Li_2Ti_3O_7$ into the molten salt cell and starting the scavenging cycle, $Li_2Ti_3O_7$ would change color from white to black. The color of the $Li_2Ti_3O_7$ did not change back to white (or light gray) when the compound was unloaded as reported in the earlier research. This was the first indication that something different had happened. X-ray powder diffraction found that the orthorhombic phase had transformed to the hexagonal phase. Figure 6 shows the X-ray diffraction pattern of the hexagonal $Li_2Ti_3O_7$. Figure 7 shows the cross section of the hexagonal phase (8). Note the four tunnel sites. The amount of phase change depended on the amount of lithium scavenged during the experiment, as well as the temperature and duration of the operation. TEM examination of partially scavenged $Li_2Ti_3O_7$ observed both the orthorhombic and hexagonal crystal structures. Figure 8 reveals both the original orthorhombic structure with octahedrons and the newly formed hexagonal crystals. These crystals are large compared with the other crystal examples examined, and
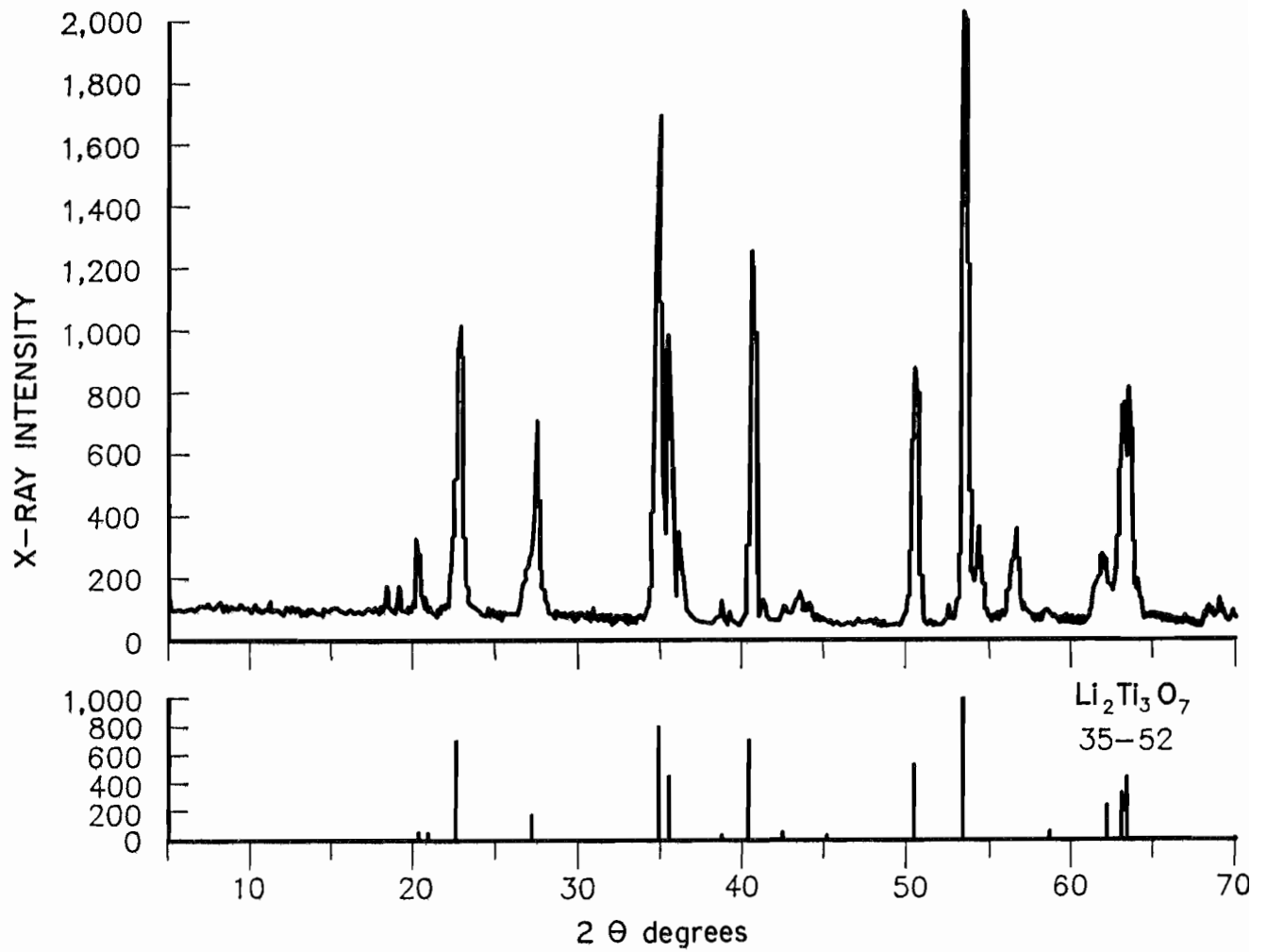
Figure 6.—X-ray diffraction patterns, hexagonal $Li_2Ti_3O_7$. Top, Graph is the actual pattern, and the bottom graph is the reference pattern.
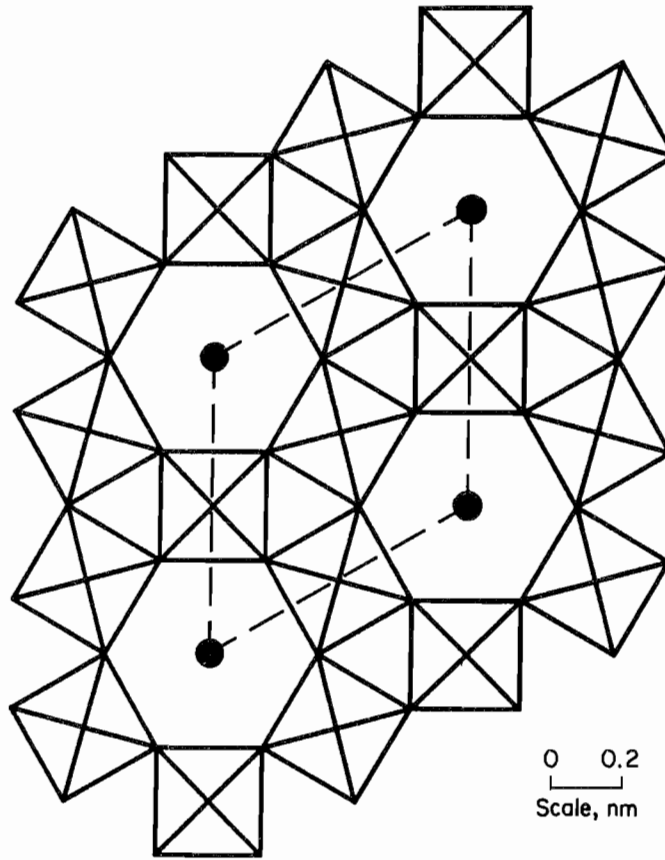
Figure 7.—Hexagonal unit cell crystal structure (8).

are thought to come from the middle of the crucible where they would have had time to grow as they were the last to cool.

The hexagonal phase was first reported by Mikkelsen in 1979 (*11*). Earlier research indicated that the ortho-rhombic structure transforms irreversibly to the hexagonal phase. This transformation takes place during lithium loading of the orthorhombic phase, or can be caused by heating above 500° C (*4, 8*). The phase diagram (fig. 1) indicates that to change the hexagonal phase back to the orthorhombic, the hexagonal phase must be synthesized at temperatures greater than 940° C. This places the material in the $Li_2Ti_3O_7$ orthorhombic phase region of the pseudobinary phase diagram. Hardeman and Fray, and Liebert reported rapid phase changes during Li^+ loading in the orthorhombic crystal, but these changes were to the spinel phase ($Li_4Ti_5O_{12}$) (*5, 8*). The unit cells of both orthorhombic and hexagonal crystal structures were com-pared. The hexagonal cell was very rodlike with a c di-mension seven times longer than that of the longest

dimension in the orthorhombic. Figures 3 and 7 show the two unit cells and include the MO_6 octahedrons that make up the substructure of the unit cell. Both structures are open and have tunnels. Crystal imperfections (metallur-gists know these as dislocations) can cause blockage of a tunnel, affecting its length and how much lithium can be inserted. Table 3 shows the unit cell dimensions.

Table 3.—Unit cell dimensions of the orthorhombic and hexagonal $Li_2Ti_3O_7$ structures

Crystal structure and axis	Cell dimension, nm
Orthorhombic:	
a	0.50182
b	.95523
c	.29455
Hexagonal:	
a	.878
c	6.986

Source: Mikkelsen (*10*)

Scale, μm

0   500

Figure 8.—TEM micrograph, orthorhombic and hexagonal phase. The octahedra are clearly visible. The dark shapes are possible hexagonal crystals viewed along the "c" direction.

HEXAGONAL PHASE TRANSFORMATION TEMPERATURE AND TIME, HEATING IN AIR

The $Li_2Ti_3O_7$ was heated in a muffle oven for up to 72 h at 400°, 500°, and 600° C to determine the time and minimum temperature at which the crystal change from orthorhombic to hexagonal occurred. Nine samples of $Li_2Ti_3O_7$ were heated in nickel crucibles in a muffle oven. One sample at each temperature was removed after 24 h, the second sample after 48 h, and the third sample after 72 h.

X-ray powder diffraction was performed on each sample to determine if any phase change had occurred. Phase change was detected in the 600° C 48-h sample. The other, lower temperature samples exhibited no phase change. The results of the heating experiments are shown in table 2.

EVALUATION OF PHASE CHANGE

The phase change from orthorhombic to hexagonal occurred rapidly during scavenging at 600° C. This rapid change only occurred during insertion of the Li^+ into the crystal structure. In the absence of Li^+, the phase change was slow and barely detected after 24 h at 600° C. The mechanism for this change was the Li^+ first filling the open positions in the crystal, stressing the crystal (12). This phase change mechanism for $Li_2Ti_3O_7$ is not reported in earlier research. Lithium titanate's MO_6 octahedral substructure is deficient in titanium cations. These openings, or crystal vacancies, make ideal insertion positions for Li^+ (4). Hardeman and Fray reported an increase (distortion) of 0.0002 nm in the lattice parameter of reacted to unreacted orthorhombic $Li_2TI_3O_7$, from 0.8356 nm to 0.8354 nm (5-6). This indicates that the orthorhombic phase was stressed by the inclusion of lithium into the crystal structure, resulting in the transformation from an orthorhombic to a hexagonal form.

Very little information is available on the hexagonal phase, and the conversion was not expected by Bureau researchers. Temperature was the only reported mechanism for phase change from orthorhombic to hexagonal $Li_2Ti_3O_7$. Hardeman and Fray reported a phase change in their research, but to the spinel $Li_4Ti_5O_{12}$ and rutile TiO_2 phases (5). This was the expected phase change.

The conditions in this experiment differed from those used by other researchers. The Bureau process used anatase instead of rutile to form $Li_2Ti_3O_7$. The Bureau made $Li_2Ti_3O_7$ in larger quantities than had other researchers. Scavenging was done by the Bureau with a powdered titanate held in a basket. Most of the other reported work done on molten salt battery systems used single pressed pellets. Liebert pressed the powder into pellets using 3,500 kg/cm² pressure for 1 min (8). Slight stoichiometric chemical differences may affect the transformation product. These slight differences may be enough to cause the orthorhombic to transform to the hexagonal instead of the

spinel phase. The Bureau electrolytic cell was run at 400° to 600° C. Hardeman and Fray ran their cell at various temperatures that ranged from 427° C to that of molten Al-Li alloy (750° C) (5). Liebert's cell temperature was about 500° C or less (8). Bureau research found that transformation did not occur below 500° C. Except where noted, Bureau cycle time for lithium scavenging was 30 min to 2 h. Hardeman and Fray's times were much longer, up to 10 h per cycle. Lithium cation incorporation into the structure at 600° C was enough to trigger the phase change from orthorhombic to hexagonal. Bureau work observed a one-way color change of the $Li_2Ti_3O_7$ crystal from white to black. Other researchers reported that the $Li_2Ti_3O_7$ became lighter when lithium was unloaded. Table 4 lists the results of the scavenging experiments at 600° C. The hexagonal phase became the primary phase present within 30 min. A trace of the next more stable spinel phase $Li_4Ti_5O_{12}$ was also detected by X-ray diffraction. Figure 9 shows the TEM micrograph with the results of the complete phase transformation from orthorhombic to hexagonal. Note that the crystal size is very small. The coarse grain structure in the micrograph is the applied conductive carbon coating.

Table 4.—X-ray-identified phase from X-ray diffraction for $Li_2Ti_3O_7$ after two 0.5-h cycles at 600° C

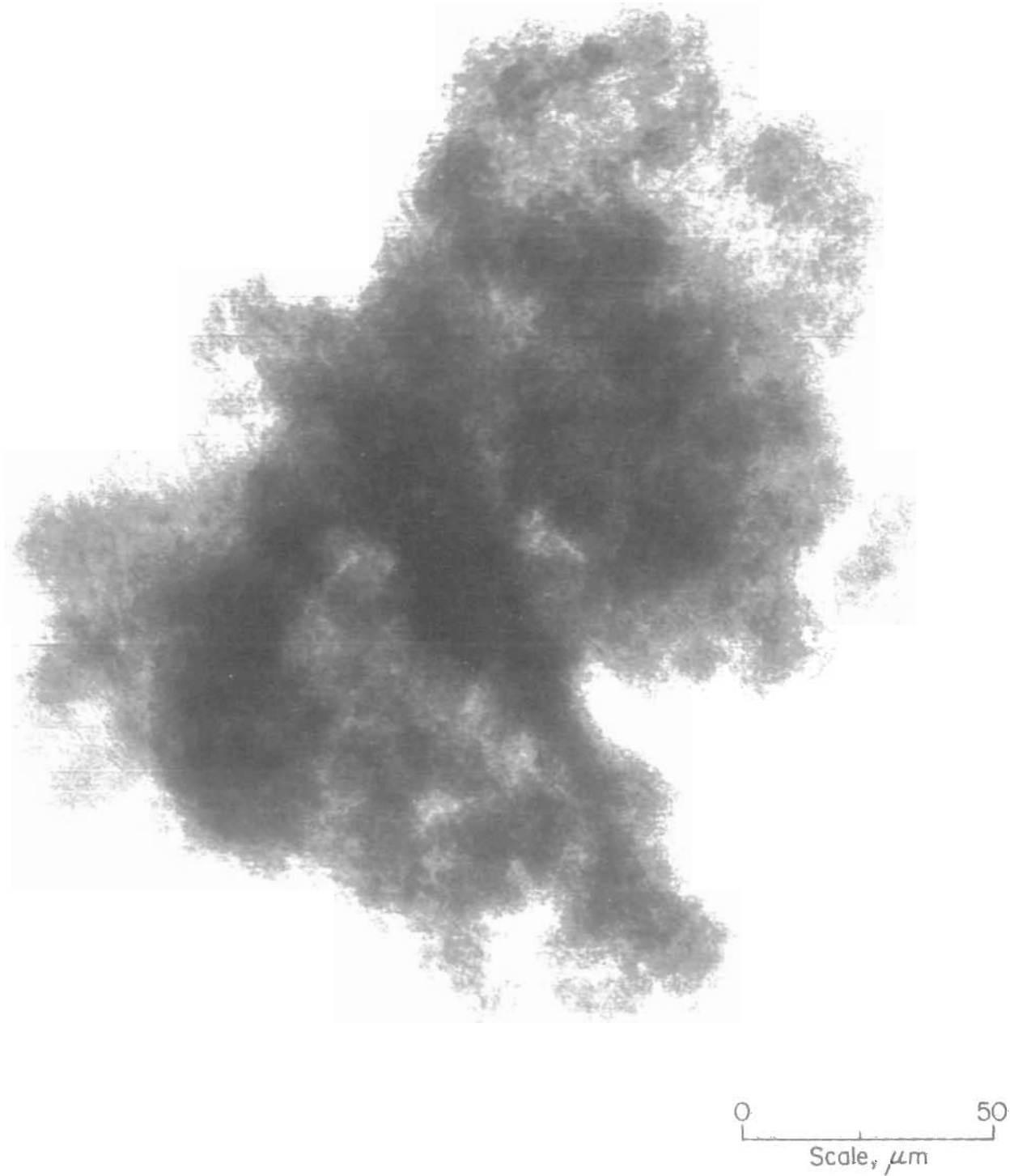| Cycle	
Original:	
Primary phase	Orthorhombic $Li_2Ti_3O_7$.
Trace	TiO_2.
1st cycle	Not available.
2d cycle:	
Primary phase	Hexagonal $Li_2Ti_3O_7$.
Trace	TiO_2, Li_2O-TiO_2.

0 _____ 50

Scale, μm

Figure 9.—TEM micrograph, fine hexagonal crystals formed from the orthorhombic phase during lithium scavenging. The hexagonal shape is barely observable. The coarse grain appearance is the conductive carbon film placed on specimen for viewing in the TEM.

CONCLUSIONS

The mechanism for phase change to the hexagonal crystal structure caused by inserting lithium into orthorhombic $Li_2Ti_3O_7$ is proposed. This mechanism has not been reported previously for lithium titanate. The hexagonal phase forms rapidly from the orthorhombic phase when Li^+ fills the vacancies in the open orthorhombic crystal, stressing the lattice. Crystal lattice vacancies are filled first, then the Li^+ moves into the tunnels. The phase change from orthorhombic to hexagonal does not affect the operation of the scavenger cell. Both crystal structures are open and have tunnel sites. Both crystal structures scavenge lithium from the Al-Li alloys. The crystal changes color from white to black upon scavenging lithium, but does not lighten in color when the lithium is unloaded from the scavenger compound, indicating that some lithium remains in the crystal structure.

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