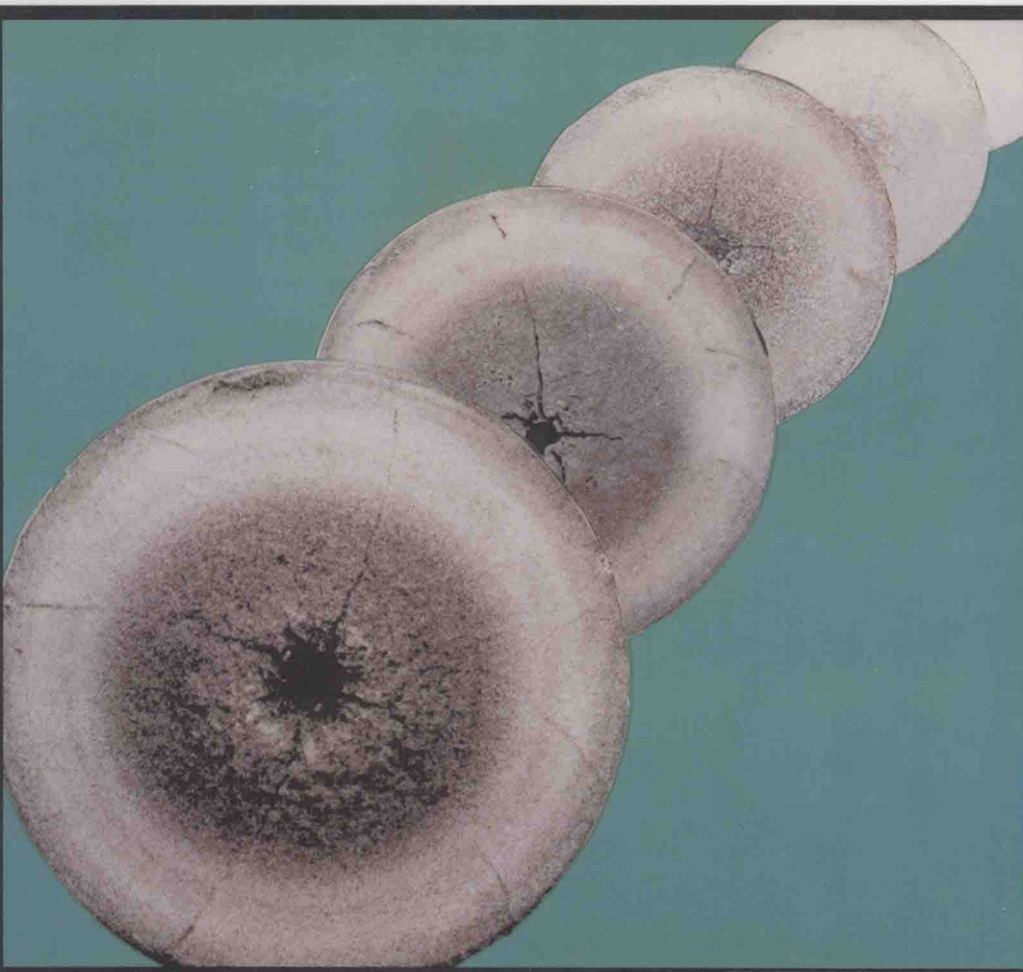
ADVANCES IN CERAMICS • VOLUME 27

FABRICATION AND PROPERTIES OF LITHIUM CERAMICS II

Edited by
Glenn W. Hollenberg
Ian J. Hastings



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The American Ceramic Society, Inc.
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Proceedings of the Second International Symposium on the Fabrication and Properties of Lithium Ceramics, held at the 91st Annual Meeting of the American Ceramic Society in Indianapolis, IN, April 23–27, 1989.

On the cover: A cross section of an Li_2O pellet (2.4 cm diameter) irradiated in the EBR-II reactor where it developed a large temperature gradient with the center approaching 1000 °C. The center annulus, as well as the variation in coloration along the thermal gradient, developed during irradiation. The results demonstrate the viability of this material for applications in the severe fusion blanket environment. (See paper of O. D. Slagle and G. W. Hollenberg.)

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Preface

Continued research on the fabrication and properties of lithium ceramics allowed this second symposium to be undertaken. This volume of Advances in Ceramics is almost one-third larger than the book from the first symposium, which is indicative of the stable progress and growth in this field of technology. This forum for communicating research on the fabrication and properties of lithium ceramics is unique among the array of meetings available worldwide to scientists. The book continues the focus on features of lithium ceramics which are necessary to support such applications as fusion blankets; but still contains too much detailed ceramic essence to be diffused into the normal spectrum of fusion technology.

As editors, the most enjoyable facet of this symposium series is the international flavor of the event. The research on lithium ceramics is distributed throughout the world, with authors from Japan, Australia, Canada, United States, Belgium, Italy, France, and Germany. This widespread research on lithium ceramics is far more unified than expected. We certainly appreciate the extra effort that is required of our global friends in contributing to the volume.

As originators of the symposium series, through the American Ceramic Society's Nuclear Division, we are again gratified by the response. Even before this publication could be issued, "grass-roots" support for another symposium is evident. We propose to continue the series as long as the technological evolution of lithium ceramics continues.

Glenn W. Hollenberg
Battelle Pacific Northwest Laboratories

Ian J. Hastings
Atomic Energy of Canada Ltd.
Chalk River Nuclear Laboratories

Dedication

We dedicate this volume of Advances in Ceramics to

Dr. Theodore C. Reuther
U.S. Department of Energy
Germantown, MD, USA

on the occasion of his retirement, 1990. Dr. Reuther has fostered the development of lithium ceramics for use in fusion energy during the past decade and his leadership will be missed. His influence has extended beyond the territorial boundaries of the United States and he is in no small part responsible for the international character of this technical initiative.

Glenn W. Hollenberg   Ian J. Hastings

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Section I
Fabrication of Lithium Ceramics

Aluminum Doped Lithium Orthosilicate as a Breeder Material

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The preparation of solid solutions in the lithium orthosilicate-eucryptite system of the type $Li_{4-3x}Al_xSiO_4$, is described. It can be shown by thermogravimetric investigations and DTA measurements that the desired solid solutions are obtained by calcination at temperatures above 500°C. With Al^{3+}-ion doping, the α-γ transformation is not as structured as in pure lithium orthosilicate. Tritium release is better at temperatures around 300°C than that for pure lithium orthosilicate. Excellent tritium release makes this modified material comparable with lithium metazirconate and more attractive as long-lived activation products are not included in the solid breeder.

Introduction

Major properties of breeder materials for use in fusion reactors are the tritium release and the lithium atom density. Further, it is desirable, above all with a view to acceptance by the public, to use only low-activation materials in components exposed to fusion generating neutrons or materials which contain short-lived activation products.

Of the lithium-bearing double oxides, lithium metazirconate (Li_2ZrO_3)[1] and lithium orthosilicate (Li_4SiO_4)[2] exhibit the most favorable tritium release behavior. However, in the temperature range below 350°C lithium metazirconate offers advantages over lithium orthosilicate in tritium release kinetics. The lithium atom density is clearly highest in the lithium orthosilicate. The activation products originating from lithium metazirconate are troublesome, especially ^{93}Zr which has a half life of 1.5×10^6 years. The silicates and aluminates of lithium do not produce long-lived activation products.

These simple considerations of the advantages and disadvantages of the two breeder materials with the highest rates of tritium release give rise to arguing whether it would not be possible to compensate the disadvantages of lithium orthosilicate by doping.[3] This promises some success, not the least because lithium diffusion in lithium orthosilicate is known to be capable of clear enhancement by doping with aluminium[4] or phosphorus.[5,6]

First results of measurements of the tritium release after neutron irradiation have partly confirmed this reasoning.[7] Although the mechanism of release has not yet been clarified, these experimental results show nevertheless that doping with aluminum in the lithium orthosilicate-eucryptite ($LiAlSiO_4$) quasi-binary system results in a substantial improvement of tritium release. Relying on these positive interim results, we have continued the investigations into the compounds of the type $Li_{4-3x}Al_xSiO_4$.

Preparation of Al^{3+}-doped Lithium Orthosilicate

Lithium orthosilicate is best prepared by the reaction of the SiO_2 and LiOH in alcohol.[3,8,9] Al^{3+}-doped lithium orthosilicate can likewise be produced according to this procedure.[8] To prepare Li_4SiO_4, amorphous SiO_2 (Degussa "Aerosil") and LiOH are suspended in methanol and the suspension is boiled at reflux with permanent stirring. A milky suspension is formed which consists of a compound with lithium, silicon, and organic constituents.

After this reaction has come to an end, the rest of methanol is distilled off while water is added. From this aqueous suspension a flowable powder can be prepared by spray drying which, after a calcination step at temperatures beyond 500°C, gives lithium orthosilicate. It has already been demonstrated that this procedure is adaptable for technical-scale production.[10]

Solid solutions in the Li_4SiO_4-$LiAlSiO_4$ system are formed on the lithium-rich side by exchange according to the formula

$$3Li^+ \rightarrow Al^{3+}$$

so that a phase composed of

$$Li_{4-3x}Al_xSiO_4$$

is obtained.

The value x describing the solubility of Al^{3+} is, according to Skokan,[7]

$$0 \leq x \leq 0.16 \quad (1100°C)$$

and, according to Jackowska and West,[4]

$$0 \leq x \leq 0.06$$

As already shown, this compound can be prepared by adding an appropriate amount of $Al(OH)_3$ to the initial suspension.[3] However, since it is very difficult to prepare freshly precipitated aluminum hydroxides with an accurately defined water content, substantial difficulties have to be overcome in this procedure when a compound of a defined composition is to be prepared. Therefore, a more favorable variant of the process had to be developed.

The process variant which is currently most favorable is to add aluminum in the form of isopropoxide $(OC_3H_7)_3$ Al to the amorphous SiO_2 and LiOH suspended in methanol. The mixture is allowed to react while boiling at reflux. The reaction taking place is approximately similar to that in which pure lithium orthosilicate is prepared. On account of the low water content in the suspension, only a minor fraction of aluminum isopropoxide is hydrolized which means that it practically does not participate in the reaction. After this reaction has come to an end water is substituted for methanol. As even minor residues of higher-valence alcohols cause noticeable carbon contents, water must be substituted for alcohol until the boiling temperature of 100°C is attained. During this process aluminum isopropoxide is completely hydrolized. $Al(OH)_3$ formed during this process enters into reactions with the other suspended substances. At the same time, the lithium and silicon containing organic phase is partly hydrolized and lithium metasilicate is formed.

Powder can be prepared by spray-drying from the aqueous suspension. Figure 1 shows the typical appearance of the powder particles. Unlike the pure orthosilicate powders, the particles shown in Fig. 1 exhibit a structured surface.

After spray-drying of the suspension the characteristic line of lithium metasilicate can be detected in the X-ray diffraction diagram. As some of the free LiOH reacts with the CO_2 during spray-drying in air, lines of Li_2CO_3 can be detected in addition to the LiOH. There is no indication of an aluminum compound. With this treatment any aluminum hydroxide and aluminum dialuminate formed some should be present in crystallized form, and as the amounts are very low, no information can be provided on the type of aluminum compound occurring.

Figure 2 shows the course of the reaction measured with a thermobalance (1 K/min heating rate). Three reaction stages can be recognized:

Stage 1	20°C–140°C
Stage 2	140°C–450°C
Stage 3	450°C–640°C

The DTA plot recorded in parallel shows that except for stage 1 all stages are exothermic. The exothermic character of stage 2 is evident from Fig. 3 in which

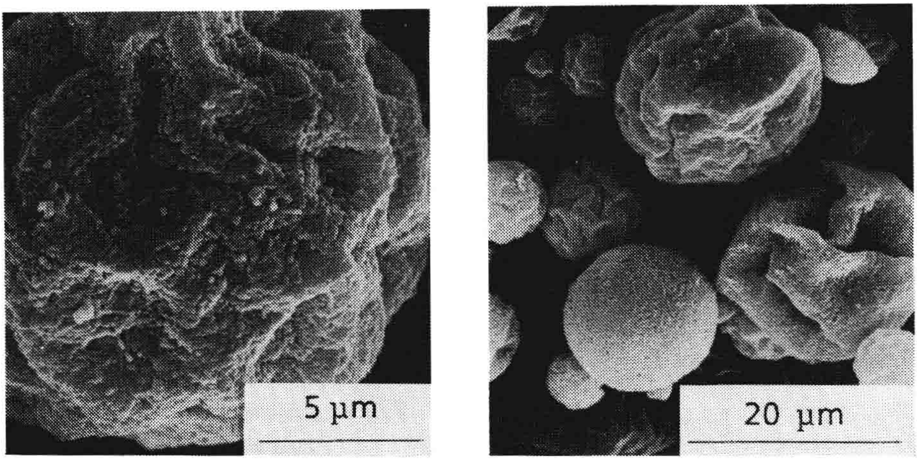

Fig. 1. Appearance of spray dried $Li_{3.7}Al_{0.1}SiO_4$ powder particles.

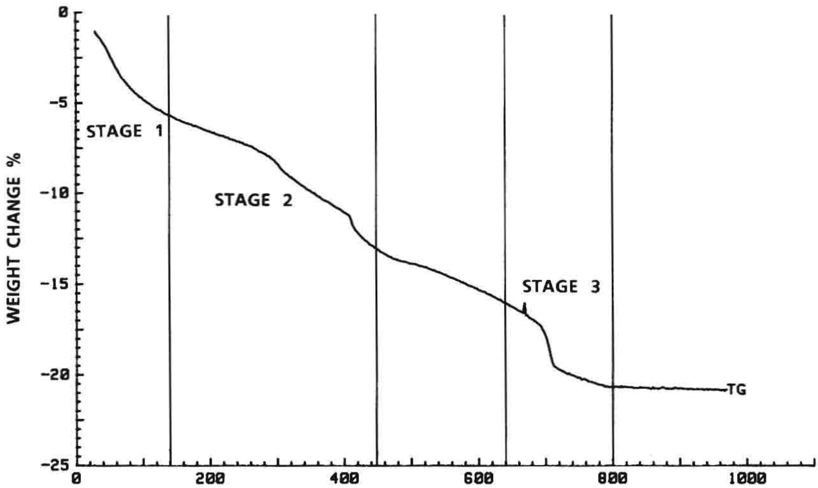

Fig. 2. Formation of $Li_{3.7}Al_{0.1}SiO_4$ from the spray dried initial product. Heating rate 1 K/min; TG = development of weight change.

the same reaction was traced at a higher heating rate (10 K/min). The reaction is thought to proceed as follows:

At stage 1, weakly bound water is released; the quantity released depends essentially on the duration of storage of the product (cf. also Fig. 2).

At stage 2, Li_2SiO_3 reacts with lithium in the form of Li_2CO_3 and LiOH. According to Fig. 3, it seems that this is an exothermic reaction. However, an additional endothermic reaction can be observed to take place towards the end of this stage. During stage 2 an initially non-identified transition phase is formed which subsequently changes into lithium orthosilicate. This transition phase may be the X-phase which was also observed by Flipot, et al.[11] At the end of stage 2, lithium orthosilicate can be detected by X-ray diffraction in addition to residues of lithium metasilicate and the intermediate phase.

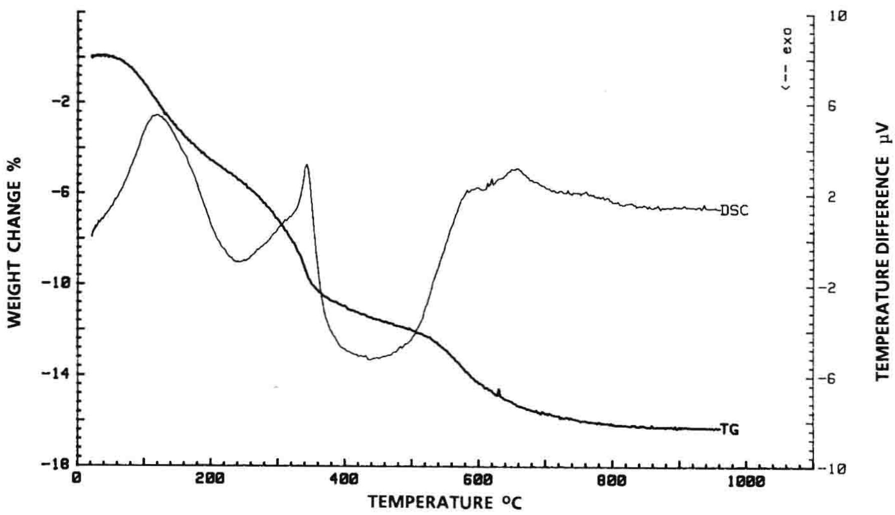

Fig. 3. Formation of $Li_{3.7}Al_{0.1}SiO_4$ from the spray dried initial product. Heating rate 10 K/min; TG = development of weight change; DSC = Differential Scanning Calorimetry.