Electrical Field Effects in Flash Sintering and Spark Plasma Sintering: Grain Growth Rate in Hyper-Stoichiometric UO_2

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Highlights

- $UO_{2.16}$ processed in SPS can develop asymmetric microstructures
- The direction of the electric field plays a role in controlling the local stoichiometry
- The results contribute to understanding the behavior of oxides in SPS and Flash Sintering

1. Introduction

Electric Field Assisted Sintering Techniques such as SPS and Flash Sintering rely on the application of an electrical current that causes rapid Joule heating. Often a faster densification kinetic is reported compared to conventional processing. Object of discussion is whether the current has merely a thermal effect or if additional effects caused by the current of electrical field are present. The evaluation of the role of the current/field is complicated by the difficulties in measuring the real sample temperature, particularly in the case of rapid transients and possible local concentrations.

Recent observations of grain growth kinetics of oxides annealed under the application of an electric field (as in Flash Sintering conditions) have shown the development of asymmetry microstructure and rate of grain growth dependent on the polarity of the electrode. Experiments on Spark Plasma Sintering of hyper-stoichiometric UO_2 have shown that also during SPS (at lower voltage compared to Flash Sintering and with the current flowing predominantly through the graphite dies), the microstructure of initially homogeneous $UO_{2.16}$ show a memory of the direction of the electrical field during sintering. The local stoichiometry is also affected by the application of an external electrical field.

In this talk we will review some early experiments on Flash Sintering of oxides, recent literature data and present the authors' data on Flash Sintering and SPS experiments of non-stoichiometric oxides.

2. Methods

Flash-Sintering experiments were conducted in a custom made furnace by suspending a green dog-bone shaped sample in a vertical tubular furnace by the mean of two platinum electrodes in air atmosphere [1] and the Spark Plasma Sintering tests were performed with a SPS installed in a glovebox to allow safe handling of radioactive materials [2].

3. Results and discussion

During Spark Plasma Sintering, hyperstoichiometric UO_2 is gradually reduced to $UO_{2.00}$. One of the reasons is the presence of the graphite die that contributes to create a strongly reductive environment. However also the electrical current can play a significant role in the reduction of UO_{2+x} to $UO_{2.00.}$ Whereas pellet sintered at high temperature or for long times (1600°C no dwell or 1000°C, 1h) are homogeneously reduced, pellets sintered at low temperatures or short times show a gradient in the oxidation state. The oxidation state depends on the direction of the field. The electric field influences also the grain growth rate by controlling the redistribution of the oxygen interstitials. An example of the grain size variation in an asymmetric UO_2 microstructure that was developed after sintering at 1200°C for 5 minutes is shown in Fig. 1. [3]

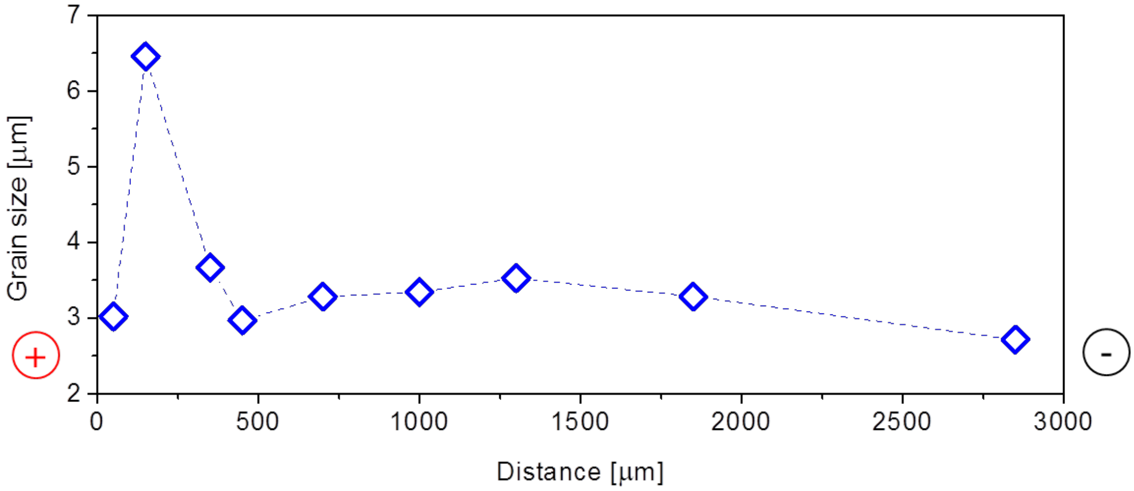

Fig. 1. Grain size as a function of the distance from the positive punch. Starting powder $UO_{2.16}$ sintered for 5 minutes in SPS at 1200°C. [Adapted from Ref. 3]

4. Conclusions

Two electrode methods (as in Flash Sintering configuration) have shown that in metal oxides, the field can influence the defect chemistry, which in turn governs the diffusion kinetics. Similar effects were also observed at lower fields, in SPS of uranium oxide. In UO_2 it is well known that small deviations from stoichiometry result in very large variation in the diffusion coefficient of the cation. The microstructure can thus show a memory of the local oxidation state during sintering.

Although those experiments are far from giving a definitive answer, they can contribute to a better understanding of the behavior of ceramics in field assisted sintering conditions.

References

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Keywords
Flash Sintering, Spark Plasma Sintering, Stoichiometry, Microstructural Gradients