Rebuttal Letter

**Spark Plasma Sintering Apparatus used for the Formation of Strontium Titanate Bicrystals**

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We thank the reviewers for their detailed and constructive comments. In the following, we address each comment in the necessary detail and outline the revisions applied to the originally submitted manuscript.

**Editorial Comments**

All editorial changes were applied as requested. Additions to the discussion were made to address the significance of the experimental work with respect to alternative methods. These additions can be found on page 8 of the revised manuscript and are outlined using MS-Word Track Corrections.

**Reviewer #1:**

**1. Introduction. Some of the literature of Joining using SPS should be included. For example some interesting results were reported in the case of SiC and C/SiC composites.**

We appreciate the comment by the referee and agree that specific mentioning of SPS as a joining technique will strengthen the manuscript. We have added the following text to the introduction of the revised manuscript on pages 1-2:

“This technique also leads to the successful formation of composite structures from various materials, including silicon nitride/silicon carbide, zirconium boride/silicon carbide, or silicon carbide, while no additional sintering aids are required.[2-5](#_ENREF_2) The synthesis of such composite structures had been challenging in the past by using conventional hot-pressing. While application of a high uniaxial pressure and fast heating rates via the SPS technique enhances consolidation of powders and composites, the phenomenon causing this enhanced densification debated in the literature.”

**2. In the experimental micron is written as um instead of µm.**

We have fixed these typos in the revised version of the manuscript.

**3. It is not clear how the temperature was probed. Modelling and experimental work (Grasso et al.) suggest significant gradients developed in the punch/die/sample assembly.**

We appreciate this important comment by the referee. In this study, the temperature was probed using a k-type thermocouple that was inserted into the graphite die and is in contact with the sample. We have clarified this aspect of the experimental setup in section 2.8 of the experimental procedure.

The referee is correct that previous studies (including Grasso et al.) have indeed observed temperature gradients within SPS samples. Consistent with these studies, a difference in bonding behavior from the edge of the bicrystal, which exhibits non-bonding, to the center of the bicrystal, which exhibits successful bonding, was observed in our SPS experiments. Also, similar to the experiments reported here, changes in bonding behavior from the edge to the center of a sample were previously observed during bicrystal formation using hot pressing techniques (M. Dupeux*, Journal of Crystal Growth*, 66 (1984) 169-178.). We have clarified this aspect in the first paragraph of the results section.

**4. In table 1 the average and peaks currant and voltages should be given. In figure 1, is there any current flowing across the sample? Are the sample electrochemically reduced during the process affection their conductivity? Is there any color change of the sample induced by the processing?**

For all experiments, a pulsed bias of 4 V and direct current of 550 A were applied to the sample with a 12-2 second pulse sequence. This detail was added to section 2.11 of the experimental procedure as well as in the caption of Table 1.

We have indeed observed a processing induced color change of the sample as considered by the referee. When the STO bicrystal sample is removed from the SPS instrument, it shows grey-black color. After the post-annealing process, STO returns to its off-white color. This color change indicates, as expected, STO reduces during processing, and re-oxidizes due to post annealing (see also reference 11 of the revised manuscript). We have added appropriate language to sections 2.13 and 2.14 of the revised manuscript.

The referee’s question whether any current flows through the sample is critical, though a definite answer can not be provided at this stage. During the reported experiments, current is most likely *not* flowing across the sample as undoped STO is considered a dielectric material with a dielectric breakdown strength of 8e(6) V/m. The voltage output for the SPS apparatus is 4 V with a field strength of approximately 4e(3) V/m for the sample size. While STO is reduced during the SPS process at an oxygen partial pressure of 2e(-6) atm and a temperature of 800˚C, the conductivity of STO is roughly 1e(-4) to 1e(-5) ohm-cm-1 (Balachandran, U., and N. G. Eror. *Journal of Solid State Chemistry* 39.3 (1981): 351-359.). Conductivity of graphite used in SPS instruments is 1e(3) ohm-cm-1 (Mersen, High Strength Graphite for Sintering). We, therefore, conclude current is most likely flowing through the graphite die rather than the STO sample.

**5. It might be useful to add (as inset) a simulated atomic structure to replicate the atomic distribution seen in figure 3.**

We thank the referee for this suggestions, and have added a model atomic structure to Figure 3. This structure model is composed of two single crystals, one in <100> and one in <110> zone axis orientation with a {001} interface plane. Deviations of the experimental imaging data from the projected structure model represent changes of the interface configuration compared to the ideal single-crystal atom positions. A more refined minimum energy structure model would need to be modeled from first principles and is beyond the scope of this publication. Appropriate language was added to the caption of Figure 3.

**6. Is any oxygen reduction appreciated comparing before and after SPS using the techniques described in the paper (see figure 4)?**

As discussed for point 4 above STO is reducedduring SPS processing, and re-oxidized before subsequent TEM characterization. All EELS experiments were carried out on re-oxidized samples so any observed reduction close or within the grain boundary cores is an intrinsic property of the grain boundary rather than the processing conditions.

**7. In the some of the figures the direction of the applied load should be given.**

We thank the referee for this comment, which is addressed in Figure 1. The application of load is perpendicular to the grain boundary of the STO bicrystal.

**8. To support the field currents effect, polarity induced effect should be seen. Is there any field/current effect seen resulting in asymmetric atomic distribution/microstructures?**

We thank the referee for this intriguing comment. In fact, an asymmetric atomic structure should be expected around the grain boundary plane. The focus of this publication, however, is to demonstrate the optimal conditions for creating STO bicrystals with the SPS apparatus. A detailed atomic structure analysis is beyond the scope of this current paper, and requires sub-Ångström spatial resolution imaging conditions coupled with density functional theory. Asymmetry of the atomic structure across a grain boundary is more reliably ascertained from segregation profiles of dopant elements. Such experiments are currently underway.

**Reviewer #2  
1. Why did the authors perform post long-time annealing at 1200C after spark plasma sintering? According to Takehara et al. (J Mater Sci (2014) 49, 3962), SrTiO3 bicrystal can be formed at 1000 degree for 80 h. It is not clear whether the bicrystals were mainly bonded during the SPS process or post annealing process.**

Annealing parameters were selected according to work done by Hutt *et al* (*Zeitschrift fur Metallkunde.* **92** (2), 105-109 (2001)), in which the bicrystals are formed at high vacuum. Annealing parameters in other studies, including Takehara et al., are selected for bicrystals formed in an ambient environment. To ascertain the impact of the post-annealing process on the diffusion bonding in this work, diffusion bond lengths were calculated and found to be 0.27 nm.It is therefore concluded that the post-annealing had limited impact on the diffusion bonding of the bicrystal created in this study. A control experiment for bicrystal bonding with a 45° twist misorientation did not result in sufficient interfacial bonding when carried out using only the post-annealing parameters. An appropriate discussion of the post-annealing and its effect on the diffusion bonding was added to the reviswed manusctipy in section 2.14 of the experimental procedure, and on page 8 within the discussion section.

**2. Is any pressure applied during the post annealing processes?**

No pressure was applied during the post-annealing process. We have clarified the language in section 2.14 when describing the experimental procedure.

**3. The authors showed some numerical data on the fractions of successfully bonded regions and unsuccessful regions. To obtain such statics, how large regions of the grain boundaries were observed and analyzed?**

The referee is correct that sufficient statistical data is required to compare the bonded versus non-bonded interface fractions of as-synthesized bicrystals. In this work, bonded interface fractions were calculated from an average grain boundary length of 1.5±0.4 mm. For clarification, we have amended Table 1 in the revised manuscript accordingly.

**4. What is the bubble like contrast in the Figure 2a?**

Spherical beads observed in Figure 2a represent residual silica from polishing. We have added a clarifying comment to the caption of Figure 2.