EVOLUTION OF THE GRAIN BOUNDARY CHARACTER DISTRIBUTION IN STRONTIUM TITANATE DURING GRAIN GROWTH

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ABSTRACT

Previous experimental results have shown the grain boundary plane distribution (GBPD) for a given material to be anisotropic and approximately inversely correlated to the anisotropic grain boundary energy distribution. The goal of the present work is to quantify how the anisotropic GBPD evolves during processing. Interrupted grain growth experiments were performed to observe the evolution of the grain boundary plane distribution, $\lambda(\mathbf{n})$, during grain growth in $SrTiO_3$. The GBPD was determined at three time intervals, in which the average grain diameter increased by nearly a factor of ten. In each case, the distribution of grain boundary planes is anisotropic and similar to that of a previously measured $SrTiO_3$ sample, which showed an approximate inversely correlation to the grain boundary energy anisotropy. Because variations in the GBPD during the different time steps are within experimental uncertainties, it was concluded that $\lambda(\mathbf{n})$ is statistically-self similar during grain growth.

INTRODUCTION

Five parameters are required to characterize grain boundaries in polycrystalline solids: three can be associated with the lattice misorientation of adjacent crystallites and two with the orientation of the boundary plane[1]. Using electron backscattered diffraction (EBSD) mapping in an SEM, it is possible to measure four of the five parameters from a single section plane. The fifth parameter, the inclination of the boundary with respect to the section plane, can be determined either by serial sectioning[2,3] or by stereological analysis.[4,5] The five parameter grain boundary character distribution (GBCD), $\lambda(\Delta g, \mathbf{n})$, describes the relative areas of boundary types in units of multiples of a random distribution (MRD) as a function of these five parameters.

It is also possible to define $\lambda(\mathbf{n})$, the misorientation-averaged grain boundary plane distribution (GBPD). This describes the relative areas of grain boundary plane types, independent of misorientation. This distribution can be calculated from the five parameter GBCD. Recent quantitative studies of the GBCD for a wide range of materials including ceramic systems such as MgO[2,6], $SrTiO_3$[7],TiO_2[8], and $MgAl_2O_4$[9] have led to several important observations. First, in all observed cases, $\lambda(\mathbf{n})$ is anisotropic. Second, it was observed that the preferred habit planes for grains in polycrystalline samples correspond to the same low energy, low index planes that dominate external growth forms and equilibrium shapes of isolated crystals of the same phase[8]. Finally, it was observed that the GBPD shows an approximate inverse correlation to the anisotropic distribution of grain boundary energies[6].

Previous experimental work has focused almost entirely on measuring the GBCD for materials in which processing parameters such as mechanical deformation, and annealing or sintering temperatures are fixed. Few experimental results exist addressing the evolution of the GBPD with processing. In liquid-containing ceramic systems, ($SrTiO_3$[10], PMNPT[11]) the GBPD was observed to continually increase in anisotropy with grain growth, increasingly favoring low energy surfaces. It is expected that this result will be different for ceramic systems with no liquid phase present. It is hypothesized that for a powder-processing based ceramic system with no liquid phase present, a random GBPD may initially exist that will evolve during curvature driven grain growth to a steady-state condition in which the GBPD is statistically self-similar for scale invariant microstructures. This GBPD will exhibit an approximately inverse correlation to the grain boundary energy distribution. In this work, a stereological based technique will be employed to measure the GBPD as a function of time, and thereby test this hypothesis in $SrTiO_3$.

EXPERIMENTAL

Interrupted grain growth experiments in which the GBPD was determined at three time intervals during fixed temperature grain growth was performed on a polycrystalline $SrTiO_3$ sample. Aldrich $SrTiO_3$ (< 5 μm, 99 %) powder was dry-ground for approximately ten minutes in an alumina mortar and uniaxially compacted at 1000 psi to form a ½ " diameter pellet. The sample was fired in a Lindberg Blue/M High Temperature furnace in air using the following heating schedule:

i) 10º C/minute to 900º C with a 10 hour dwell
ii) 5º C/minute to 1340º C with a 10 hour dwell
iii) 20º C/minute to 1470º C; furnace cool to room temperature

This sample was used as the reference point "zero-hour" sample. To achieve a surface finish suitable for EBSD measurements, the sample was lapped flat using a Logitech PM5 with a flat cast iron plate and 3 μm alumina slurry. The sample was then polished on the PM5 using 0.02 μm colloidal silica (Buehler Mastermet II) for approximately 30 minutes. Next came a brief, relatively low temperature anneal at 1100º C for one hour to heal any residual surface deformation. A thin carbon-coating was then evaporated on to the sample to eliminate charging effects in the SEM (SPI-Module Carbon Coater).

Orientation maps were recorded using a 60° sample tilt and a 25 kV beam in a Phillips XL40 FEGSEM. Orientation mapping was completed using TSL/OIM software ver. 4.5 (TSL/EDAX). The step size for the orientation mapping was 0.35 μm in the x-direction, using hexagonal gridding. In total, 26 orientation maps were collected, covering an area of 0.57 mm^2. The orientation data were then processed to remove spurious observations. Processing included a grain dilation in which pixels not belonging grains of a defined size are logically re-assigned to accepted grains and orientation averaging, which assigns a single average orientation to each pixel in a grain. For this sample state, single iteration dilation with a minimum grain size of five pixels was used to avoid filling actual pores with false orientation data. A pseudosymmetry correction (45º rotation around [001]) was also employed to correct for a specific mis-indexing problem involving difficult to distinguish orientations. The resultant dataset was comprised of 48,089 grains with an average equivalent area diameter of 2.89 μm. Using a procedure described by Wright and Larsen[12], 120,938 reconstructed grain boundary line segments were extracted. The GBPD was then determined for this sample state using a stereological technique. The stereological technique used in this work was previously described in detail.[4,5] A short summary will be presented here. To measure the "reconstructed" GBPD, in-plane grain geometry on planar sections is approximated by discrete grain boundary segments for which four of the five parameters required to define a macroscopic grain boundary can be determined. The fifth parameter, grain boundary inclination, is then determined probabilistically by building up many observations of grain boundaries with indistinguishable misorientations. The population of grain boundary terminating planes, independent of misorientation, is then plotted as the GBPD, λ(**n**).

Grains in the same sample were grown using the following heating schedule to create the next sample state, referred to as the "one hour" sample:

i) 10º C/minute to 900º C with no dwell
ii) 5º C/minute to 1470º C with a one hour dwell
iii) 5º C/minute to room temperature

The same sample preparation routine was used to collect a dataset of eight orientation maps with a hexagonal grid and 1.0 μm spacing, covering 6.05 mm^2. A similar cleanup procedure using ten pixels as the minimum grain size (two passes of single iteration) yielded a dataset that included 29,200 grains an equivalent area diameter of 11.9 μm. 81,429 reconstructed grain boundary line segments were analyzed and λ(**n**) was determined using the same stereological technique.

The firing cycle below was then used to create the third sample state, which will be referred to as the "three hour" sample.

i) 10º C/minute to 900º C with no dwell
ii) 5º C/minute to 1470º C with a two hour dwell
iii) 5º C/minute to room temperature

For the "three hour" dataset, eight orientation maps on hexagonal grid with 2 μm lateral resolution were collected covering an area of 14.5 mm^2. After cleanup (single pass dilation with 20 pixel minimum, followed by a single pass with a 5 pixel minimum), 25,909 grains, with an equivalent area diameter of 23.2 μm, remained. 77,445 reconstructed grain boundary line segments were used to reconstruct λ(**n**). A schematic representation of the complete thermal processing cycle is illustrated in Fig. 1.

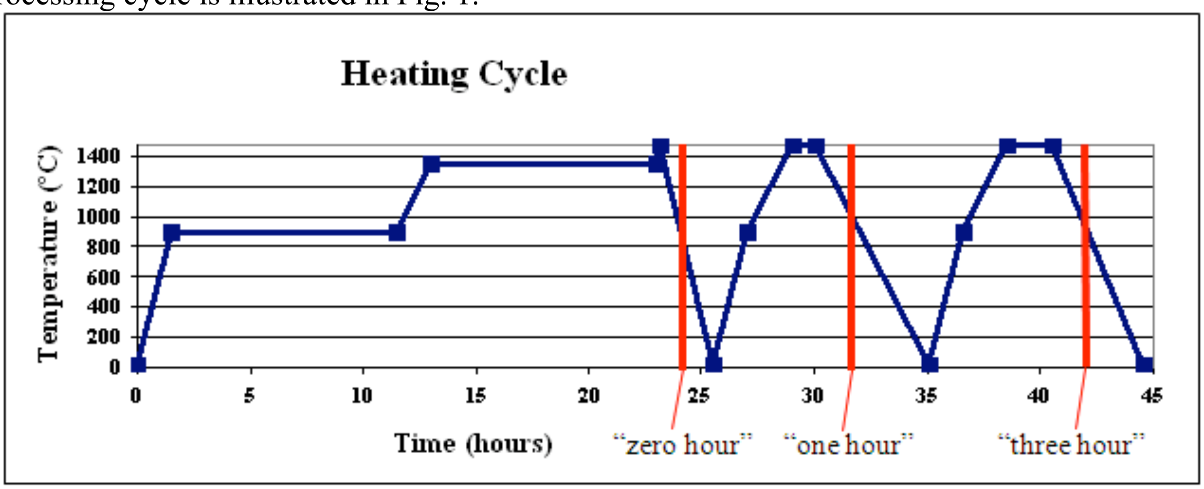

Figure 1. A schematic of the thermal cycle experienced by the $SrTiO_3$ sample used in this study. Markers are placed to denote the "zero hour," "one hour," and "three hour" sample states for which the GBPD was measured.

RESULTS

The [001] inverse pole figure orientation maps shown in Fig. 2 are representative of the three microstructures. The average grain diameter increased by nearly a factor of ten from the "zero hour" state to the "three hour" state. Note that in the initial state, the grain size distribution is bimodal.

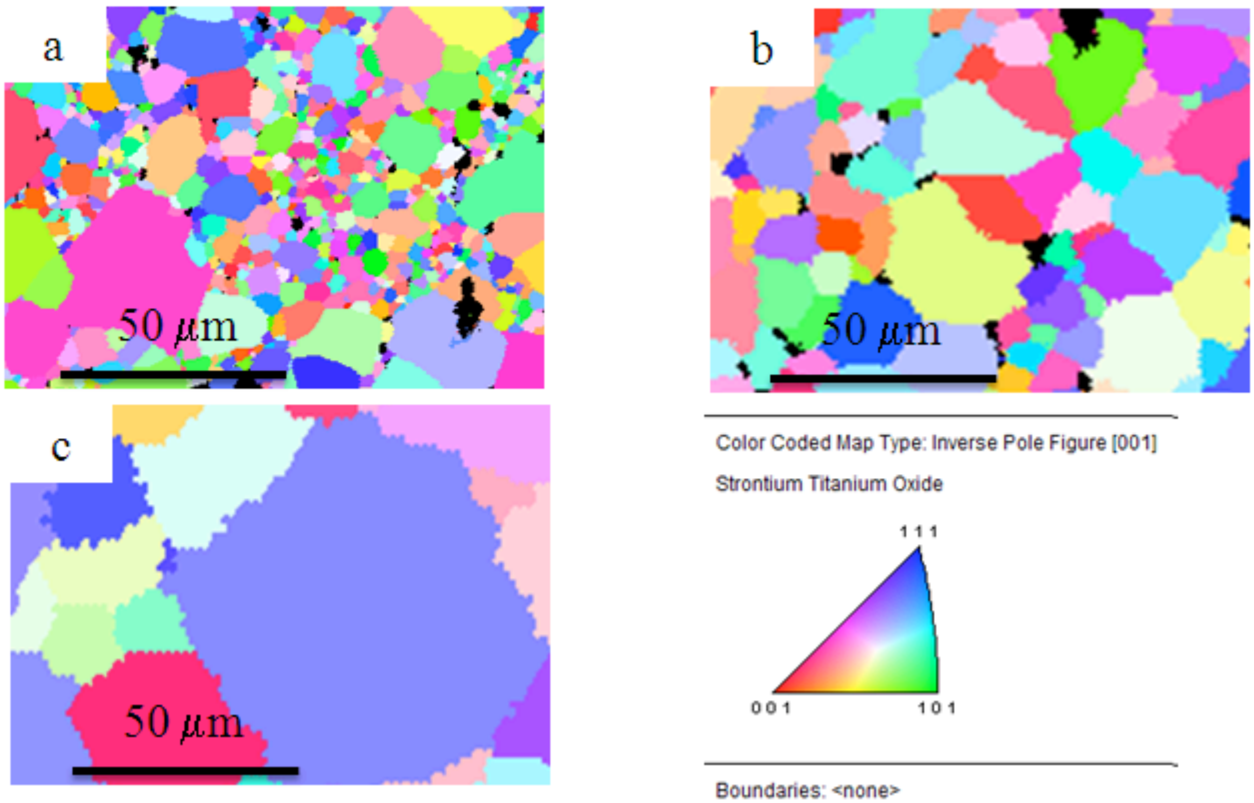

Figure 2. Inverse pole figure orientation maps are plotted for the (a) "zero hour," (b) "one hour," and (c) "three hour" sample states. Grains are colored by orientation according to the scale in the lower right of the figure.

The misorientation-averaged GBPD, $\lambda(\mathbf{n})$, was reconstructed with 10° resolution of the boundary plane parameters for each sample state and the results from each dataset are plotted in Fig. 3 in units of multiples of a random distribution (MRD) on stereographic projections. It is noted that the "zero hour" sample state exhibits anisotropy in $\lambda(\mathbf{n})$ which is similar to that of a previously measured, coarse grained $SrTiO_3$ sample[7]. In fact, a similar anisotropic distribution of grain boundary planes is observed at each time step. In each case, the distribution peaks for {001} type planes, which occur with a frequency of approximately twice that of a random distribution (2 MRD). The average of the maxima of the three distributions is approximately 2.1 MRD.

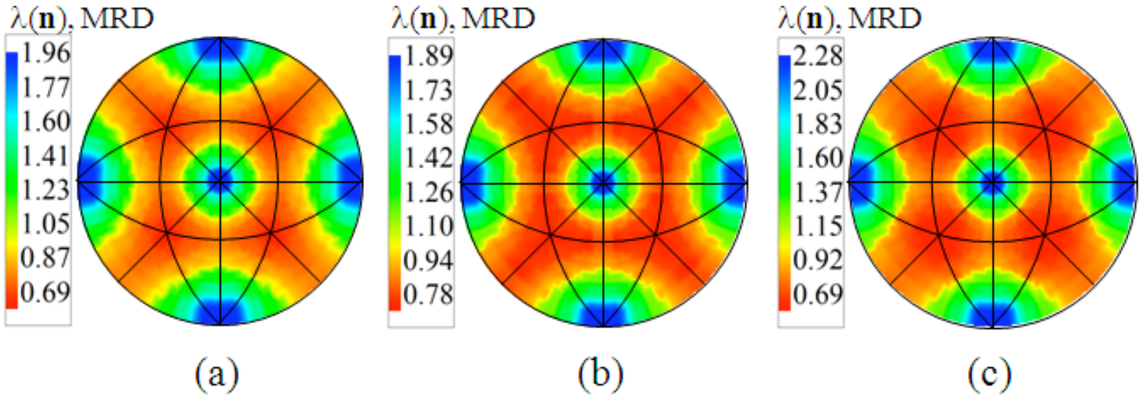

Figure 3. $\lambda(\mathbf{n})$ is plotted in units of multiples of a random distribution (MRD) for the (a) "zero hour," (b) "one hour," and (c) "three hour" sample states. All distributions exhibit a maximum for {001} boundary types. These boundary types occur with a frequency approximately twice that of in a random distribution.

DISCUSSION

It is obvious that the resultant grain boundary plane distributions are not exactly the same. The question is whether or not these differences are representative of differences in the microstructure or if they are simply the result of experimental uncertainties. To address the hypothesis that a steady state, self-similar distribution will develop with grain growth, we must determine to what degree these distributions are the same or different. The maximum values of each distribution vary by approximately 10 % from the average maximum of 2.1 MRD. Using simulations, Saylor[5] showed that the number of reconstructed boundary observations used in the stereological reconstruction of the five parameter grain boundary character distribution can affect the reliability of the result. It is thus necessary to first determine the number of experimental observations required from this sample to achieve reliable and consistent reconstructed GBPDs with variations of 10 % or less. Further, we can also ask, if separate sets of the data, representative of the same material, are used to calculate the GBPD, are the variations less than 10 %. These questions are addressed below.

To determine the number of required observations, the GBPD was reconstructed for subsets of the full "three hour" dataset. The first N lines of the reconstructed boundary segment file (where N = 500, 1,000, 2,000, 10,000, 20,000, 50,000, or 75,000) were used to reconstruct $\lambda(\mathbf{n})$. The maximum and minimum values of each distribution, along with the maximum/minimum ratio, are plotted with respect to the number of segments used in Fig. 4. The plot shows that using fewer than 20,000 boundary segments in the reconstruction process results in underestimation of the GBPD anisotropy. For greater than approximately 20,000 segments, the maximum, minimum and maximum/minimum ratio of the distributions are approximately constant. The "zero hour," "one hour," and "three hour" datasets contain at least three times this amount of data. From this result, we can conclude that the reconstructed GBPDs in this experiment should be reliable (with respect to the number of observations) and that any observed differences in $\lambda(\mathbf{n})$ with grain growth are independent of the number of observations used in the stereological reconstruction.

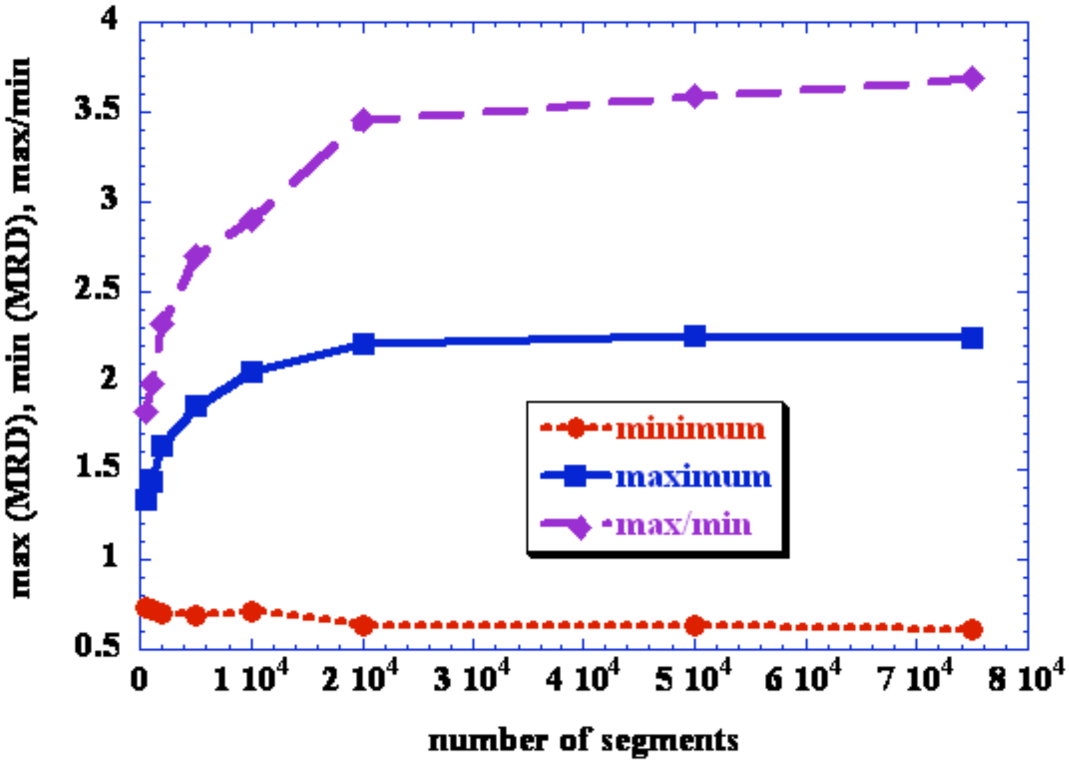

Figure 4. The maximum, minimum, and maximum/minimum ratio (MRD) of the GBPD are plotted with respect to the number of segments used to calculate the GBPD with the stereological technique. Results show the determination of the GBPD to be consistent when greater than 20,000 segments are used.

To better understand the effects of experimental uncertainty on observed differences in GBPDs from several different samples, we can first quantify the effects of experimental variation on the determination of the GBPD for a given sample state. Again, the GBPD was calculated for subsets of the full "three hour" dataset. For this analysis, however, identical sized subsets of approximately 25,000 grain boundary segments – greater than the previously determined amount required for consistent determination of the GBPD – were used. Results from three subsets are plotted below in Fig. 5. Similar to the results of the grain growth experiment, the GBPDs are similar but not exactly identical, and {001} type boundary planes occur with an average frequency of approximately 2.1 MRD. The resultant GBPDs from individual subsets vary from the average and from the full dataset GBPD (Fig. 3, (c)) by amounts comparable (less than 10%) to the variation in the reconstructed GBPDs from the GBPD evolution experiment. From this result, we conclude that differences in $\lambda(\mathbf{n})$ less than 10 % cannot be separated from experimental uncertainties. As a result, we conclude that $\lambda(\mathbf{n})$, the misorientation-independent grain boundary plane distribution , exhibits steady state behavior in with curvature-driven grain growth in $SrTiO_3$.

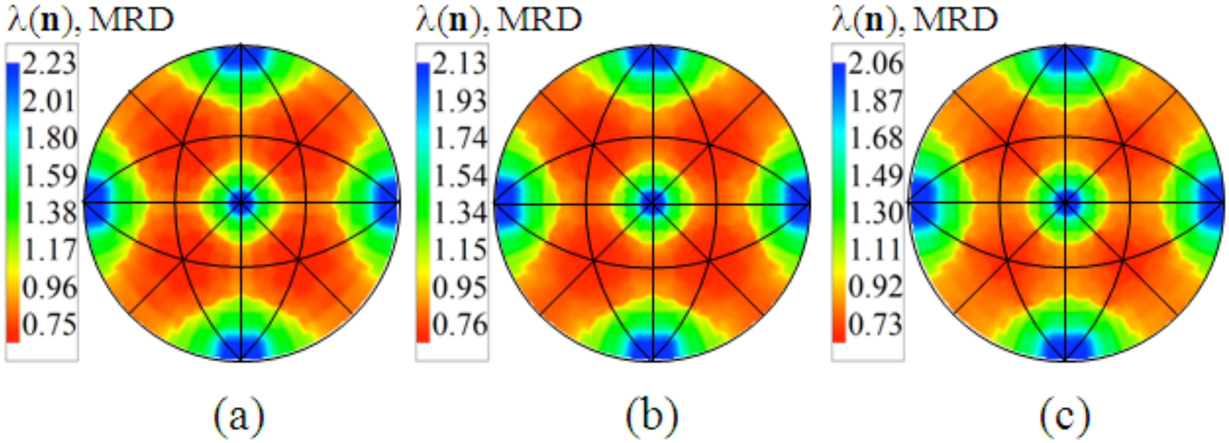

Figure 5. λ(**n**) is plotted for three subsets of the full "three hour" dataset. Each subset contains approximately 25,000 grain boundary segments. Distribution maximas for (a), (b), and (c) differ by less than 10 % of the mean of 2.1 MRD. This deviation is attributable to experimental variation.

The initial portion of the hypothesis was that the GBPD would initially be random, and that is clearly not the case for our earliest sample. It is uncertain how early in the sintering process anisotropy develops in the GBPD. It must be acknowledged that some grain growth has occurred even prior to the "zero hour" sample state. This fact is made clear by the presence of several larger grains and many smaller grains in Fig. 2, (a). It is possible that the simple reorientation of planes that occurs during sintering is enough to create anisotropy in the GBPD. However, it has been concluded that during grain growth in $SrTiO_3$, a statistically self-similar GBPD with approximate inverse correlation to the anisotropic surface energy distribution persists. It is expected that this phenomena will hold true for similar material systems.

SUMMARY

The grain boundary plane distribution, λ(**n**), was found to be the same within experimental uncertainty for $SrTiO_3$ at three time intervals during grain growth in which the average grain diameter increased by nearly a factor of ten. In other words, steady state behavior of λ(**n**) with curvature driven grain growth was observed. At all measured time steps, the anisotropic distribution of grain boundary planes was peaked for {001} type planes, which occurred with a frequency of approximately 2 MRD. It was established that for the current resolution of the five parameter space, at least 20,000 observations should be used for the GBCD stereological reconstruction procedure, and that when comparing different GBCDs, differences of less than 10 % cannot be separated from experimental uncertainties.

ACKNOWLEDGEMENT

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