STUDY OF ETCHING PITS IN A LARGE-GRAIN SINGLE CELL BULK NIOBIUM CAVITY *

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Abstract

Performance of SRF cavities are limited by non-linear localized effects. The variation of local material characters between "hot" and "cold" spots is thus of intense interest. Such locations were identified in a BCP-etched large-grain single-cell cavity and removed for examination by high resolution electron microscopy (SEM), electron-back scattering diffraction microscopy (EBSD), optical microscopy, and 3D profilometry. Pits with clearly discernable crystal facets were observed in both "hotspot" and "coldspot" specimens. The pits were found in-grain, at bi-crystal boundaries, and on tri-crystal junctions. They are interpreted as etch pits induced by surface crystal defects (e.g. dislocations). All "coldspots" examined had qualitatively low density of etching pits or very shallow tri-crystal boundary junction. EBSD revealed crystal structure surrounding the pits via crystal phase orientation mapping, while 3D profilometry gave information on the depth and size of the pits. In addition, a survey of the samples by energy dispersive X-ray analysis (EDX) did not show any significant contamination of the samples surface.

INTRODUCTION

This is a follow-on study to understand the circumstances and mechanisms which cause enhanced RF losses of a SRF accelerator cavity in a medium field range from the perspective of surface science. A previous publication [1] has described the manufacturing process and the SRF performance of the Nb large-grain single cell SRF cavity, which exhibited a strong medium field Q-slope. Surface analysis study was undertaken on 12 samples cut from it. The twelve samples were from locations where anomalous heating was detected by thermometry ("hotspots") as well as from locations with negligible overheating ("coldspots"). The study reports recent discovery on these samples.

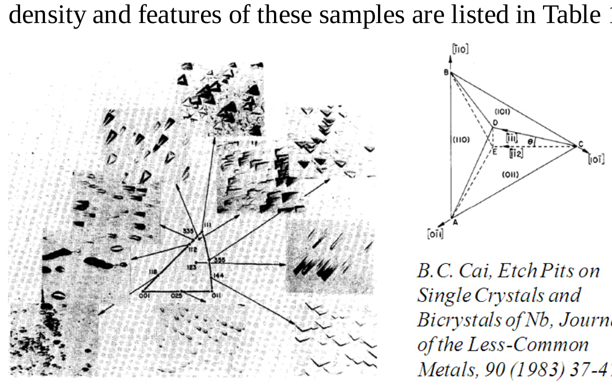
EXPERIMENTAL RESULTS

Twelve 12 mm × 12 mm samples were cut from locations on the cavity (see Ref [1] Fig 2) by careful milling, using water as coolant. For comparison, three coupons were from normal areas (called coldspots zone), eight from hotspots zones and one included the quench location. Optical microscope (*HiRox*™) and scanning electron microscopes were used to observe the sample surface. Other than mechanical scratches attributed to the cutting process, the most obvious features are "pits" along bi-crystal grain boundary, tri-crystal junction, and sometimes in the middle of an ultra flat crystal grain plane. The pits share a similar geometry: they have clear facets. It is known that chemical etching processes [2-4] on crystal defects (such as dislocation, stacking fault, and impurity precipitates) can produce distinct types of preferential etching. Etching pits stem from preferential etching.

Cai reported that the profile of an etching pit directly correlates with the orientation of an exposed crystal surface [2]. It was explained that since various crystal planes have different surface energy, they yield different etching rates. Anisotropic etching rates thus yield the symmetric and facet features of the pits. Figure 1 illustrates how the outmost crystal plane could determine the pit geometry.

Evans' study [3] reported dislocation induced etching pits on large crystal grain Nb materials. His study showed 1) pits have distinct densities on various grains, 2) pits tend to segregate on tri-crystal grain junctions, 3) pits tend to be distributed along a slip path, and 4) pits decorating a slip path can cross grain boundaries. Tetrahedral etching pits were observed on several of the present samples, as predicted by Cai. (See Figure 2).

We examined the correlation of pit density with "hotspots". The densities of pits were counted under optical microscopy at a magnification of 350. Six samples (three are "coldspots" and three are "hotspots") were counted. Each sample was surveyed at 12 evenly distributed sites. Each survey site area was $6*10^5$ µm^2. Pit density was averaged over the 12 surveyed sites. The pit density and features of these samples are listed in Table 1.



B.C. Cai, Etch Pits on Single Crystals and Bicrystals of Nb, Journal of the Less-Common Metals, 90 (1983) 37-47

Figure 1: Geometrical features of tetrahedral etching pits are related to the crystal plane exposed to etchant. Figure taken from Ref [2].

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Table 1: Features observed on samples dissected from the large-grain single cell cavity.

Sample	#of grains	Loc.	Pits dens. (#/mm^2)	Etch-pits feature
1	2	Hotspot	34.2	
2	1	Hotspot	29.1	Quench site
3	3	Hotspot		
4	3	Hotspot		
5	3	Hotspot	61.7	a very deep pit on tri-crystal junction; on {110} plane, hi den of elongated etching pits
6	1	Coldspot	6.3	
7	3	Coldspot	19.7	A shallow pit on tri-crystal junction
8	1	Coldspot	17.6	
9	3	Hotspot		a very deep pit on tri-crystal junction
10	1	Hotspot		
11	1	Hotspot		
12	2	Hotspot		

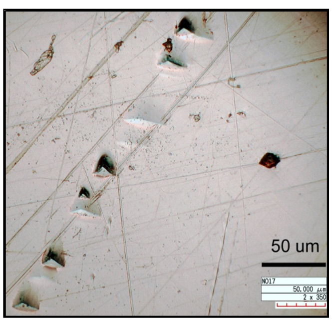


Figure 2: Tetrahedral pits are aligned on a dislocation slip path**.**

The coldspot samples had a lower pit density than that of the hotspot samples. The size of the pits, measured with a 3D profilometer, ranged between 20-80 µm in width and 2-10 µm in depth. It was observed that the etch pits are not uniformly formed on various grains. Figure 3 images were taken from sample 5. On crystal grain "C", there are more elongated pits. This feature is similar to that reported by Evans [3]. The pits appear well aligned.

Other than the tetrahedral pits predicted by Cai [2]. There exist more pits having refined geometry largely deviating from a tetrahedral profile. Figure 4 demonstrated some pits sitting in-grain or on a bi-crystal boundary. They have fascinating crystallite-like features. These features can not be explained by the Cai model.

Dislocation is an inevitable product of plastic deformation. Distribution of dislocation is determined by the space alignment of the crystal grains, which impact the slip system and plastic deforming flow. As a key crystal defect, the dislocation pattern formed during the manufacturing process of the half-cell pressing may affect the etching pit features. Thus, it is necessary to know the crystal grain orientation of the 12 samples. (See Figure 5.)

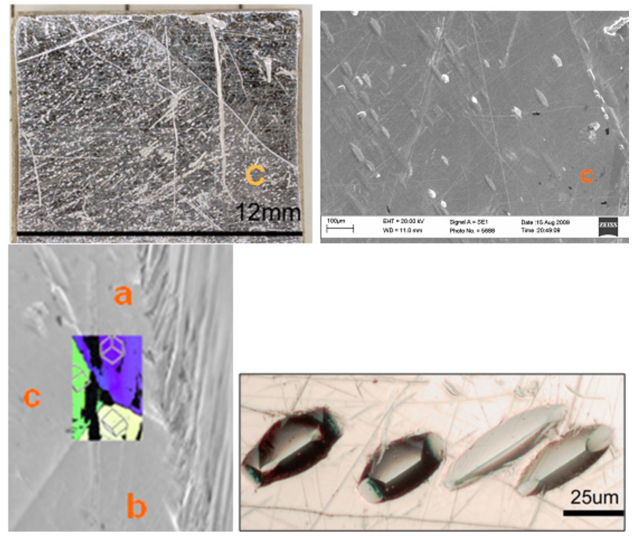


Figure 3: Pits distributed non-uniformly on various crystal grain (sample 5). The reason of forming the elongated profile is unknown.

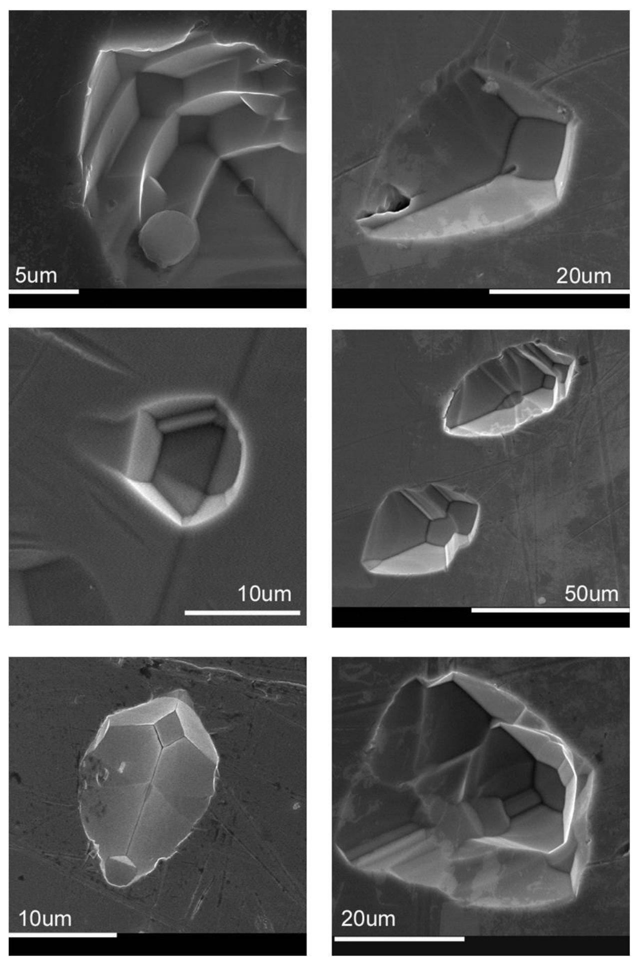
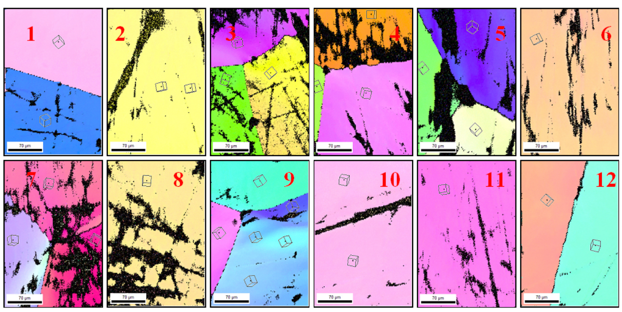


Figure 4: SEM figures of atypical pits which have elaborated symmetrical geometry.

Electron electron-back scattering diffraction microscopy (EBSD) has been applied to investigate crystal grain orientation via a technique named *orientation index mapping* (OIM). Figure 5 presents the 12 samples' outmost crystal planes in a view of *inverse polar figure* (IPF). For instance, sample 1 is made of two patches of colors. The lower area is blue, which means that the crystal plane facing toward readers is a {111} plane. The upper area is purple, which represents a high index plane with its crystal axis in the middle of <001> and <111>. No correlation of hot/cold spot character with crystal orientation in immediately apparent. Our future work will further explore the relationship between crystal grain orientation and the pit formation mechanism.



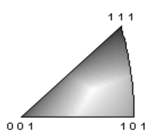


Figure 5: Crystal grain orientation of the 12 samples. Samples 1-6 are at the first row (L to R). Samples 7-12 are at the second row (L-R). Nb [001] IPF color legend.

It was observed that some etching pits are aligned in straight lines. (See Figure 6.) EBSD survey demonstrated that they are in a single crystal grain. Although a similar pattern was observed in deformed and etched NaCl crystallite, it was not reported on Nb material. We speculate they are dislocation induced etching pits. The underlying line then would represent a dislocation slip path.

CONCLUSION

The analysis of the surface topography of samples cut from a large-grain single cell characterized by a strong medium field Q-slope revealed a high density of etching pits. These were found to be distributed both along grain boundaries and within grains, the latter case possibly being related to the presence of lattice defect, such as dislocations, or impurities. Etching pits observed in this study are uncommon to the surface of large-grain BCP-etched cavities. It was noted that all small Nb samples (cut from a flat plane but not a cavity) after a BCP process demonstrated no features of etching pits as reported in this study. And a recent survey of dissected samples from a large grain SRF cavity found only a few shallow pits. It seems the density of pits observed in this study is atypical.

It is worth exploring if the pits were somehow caused by ingot impurities or only determined by crystal lattice defects after deformation, particularly on dislocations. If their origin is better understood, modifications to the process of metallurgy purification, mechanical deformation, or heat treatment might reduce the etch pit density in the final application. Our future work intends to investigate the cause of pit nucleation and explore whether an electro-polishing (EP) process will effectively remove the pits, because EP surface brightening is independent of crystal surface energy.

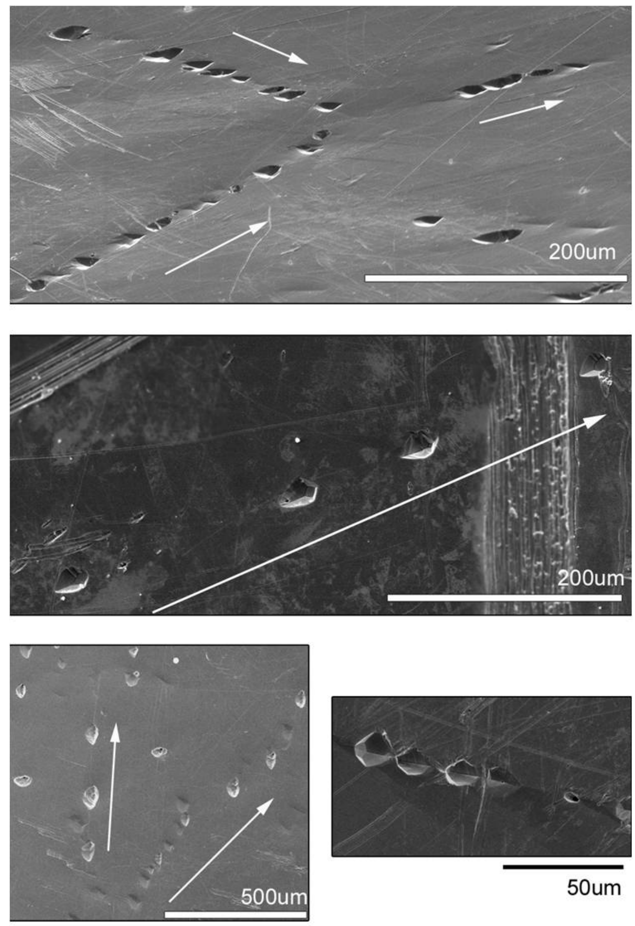


Figure 6: Aligned etch pits on various single crystal grains (selected from different samples). They might embody dislocation slip paths formed during pressing of the half-cell (plastic deformation).

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