STABLE AND UNSTABLE GRAIN BOUNDARY STRUCTURES IN NANOCRYSTALLINE SiC

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ABSTRACT

Nanocrystalline silicon carbides (SiC) were selected as the candidates for studying superplasticity in covalent materials. Grain boundary analysis plays a key role in understanding the deformation mechanism that is largely depending on the properties of grain boundaries. To achieve this goal, high performance analytical electron microscope with an electron probe as small as 2.5 Å, equipped with electron energy-loss spectroscopy (EELS) facility and EELS "spectrum imaging" function, and high-resolution electron microscopy (HREM), have been employed to investigate the local structure, segregation, composition and chemical bonding of grain boundaries in two material systems: the liquid-phase sintered (LPS) SiC and the hot-isostatic-pressed (HIPed) boron-doped SiC.

The grain boundary characteristics of these two systems are quite different under deformation. In LPS-SiC, the alumina and yttria dopants segregate to grain boundaries to form amorphous films. In one case with relatively higher alumina content, deformation tests did not eliminate the grain boundary films, but the film composition has changed significantly following the crystallization of most of the dopants staying at intergranular pockets. In another case with less alumina, not only the crystallization of pockets occurred during the deformation, but severe vaporization of mainly alumina dopant (perhaps together with carbon) removed the film from grain boundary. This system indicates that although sintering by liquid phases significantly enhanced the diffusion, the grain boundary does not have a chemically stable structure.

On the other hand, amorphous film was not observed in boron-doped SiC, either HIPed or hot-pressed. EELS has found that boron segregated to the grain boundary and carbon has an excess in respect to silicon. In the HIPed sample oxygen was also found at grain boundary. The energy loss near-edge structures (ELNES) analysis discovers that B-C and Si-O bonds were formed at these boundaries. The boron segregants are quite stable against the deformation as well as against the overall composition change. For HIPed SiC doped with boron in a range from 0.3 wt% to 3.0 wt%, boron segregation remained little changed at the same level, one monolayer, and the accompanying carbon excess has similar quantity. Upon annealing and deformation, boron stayed at the same segregation level while oxygen segregants disappeared rapidly. It is not until the final stage of deformation, more than 100% of elongation for 3 hours at 1800 °C, that boron segregants dropped to one third of the initial level when significant amount of cavities already formed in the material. It is clear that boron and carbon formed a rather stable grain boundary structure, in contrast to the situation with alumina-based films.

1. INTRODUCTION

Ceramic superplasticity is a human endeavor to challenge the nature who embedded non-oxide ceramics with extreme hardness and brittleness. To achieve the seemly impossibility, smaller grain size and higher deforming temperature are two essential factors. However, these are conflicting factors since fast diffusion associated with high temperature means rapid grain growth. Therefore it is necessary to strike a balance between them in finding an optimized combination or the best compromise.

The analysis of grain boundary thus plays an essential role in providing key information to understand the deformation mechanisms as well as the high temperature phase equilibria. The segregants reveal grain boundary species and their abundance, the local structure tells the ordering and scale of the atoms involved in the diffusion process, and the chemical bonding give an insight of the grain boundary fundamentals. These information can all be gained by using modern analytical electron microscopy, including scanning electron microscopy (STEM), EELS/ELNES and HREM.

Therefore two nanocrystalline SiC systems, LPS SiC and HIPed B-doped SiC, were investigated for their grain boundary properties. They provide contrasting cases of grain boundary structure and chemistry. Yet superplasticity has been achieved in both systems [1, 2]. They provide a rare playground to compare the interfacial properties.

To undertake this study, a STEM (VG-HB601UX-R2) with an electron probe as small as 2.5 Å, which has been equipped with EELS spectrometer (Gatan 766) and installed with EELS "spectrum imaging" function (CNRS-University Paris-Sud/JST-Nanotube project), and a HREM (Jeol 2010) belonging to JFCC were utilized here.

2. RESULTS

2.1 Liquid-phase sintered SiC with alumina-based grain boundary film

In nanocrystalline SiC fabricated by LPS [3], alumina, yttria and calcia were added into the materials facilitate the sintering at lower temperatures. Materials with two dopant compositions were analyzed, one with 7 wt% Al_2O_3, 2 wt% of Y_2O_3 and 1 wt% of CaO (hereafter AYC SiC), the other with 9 wt% of YAG ($3Y_2O_3 \cdot 5Al_2O_3$) (hereafter YAG SiC). The AYC sample were deformed in both tension and compression at 1725 °C with strain rate of 2×10^{-4}/s and at 1750 °C with 1×10^{-4}/s, respectively. Both tests reached deformation of more than 40%. The YAG sample was deformed only in tension at 1725 °C with 2×10^{-4}/s and reached 50% elongation.

Amorphous grain boundary films were found in all three AYC SiC samples, the as-sintered and the deformed alike (Fig. 1). All three dopants segregated to those amorphous films, as revealed by spectrum of a grain boundary as shown in Fig. 2. After both deformation tests, those films remain at grain boundary, but their chemical compositions have been altered [4]. While calcium remains unchanged, both oxygen content and its variation from film to film have decreased at grain boundaries. The oxygen change signifies that the grain boundary films have been narrowed and they became more uniform in thickness [5, 6]. However, aluminum content increased more than twice and triple times in the tensile and compressed samples. It is found that such unexpected change of aluminum content is related with the crystallization process of intergranular pockets where most of the dopants stay. The YAG phase in the pockets needed less aluminum so that the excessive dopants went to grain boundary films.

The spatially-resolved ELNES analysis involving spectrum separation [7, 8] gives further

information about chemical bonding within amorphous films. A typical spectrum for grain boundary film including ELNES of both $Al\text{-}L_{2,3}$ and $Si\text{-}L_{2,3}$ edges was shown in Fig. 3 together with a spectrum from SiC matrix. It can be seen that Si ELNES is not much different from SiC and it has no sign of Si-O bonds, therefore its signal is mainly from the surface layers of the two grains that confined the amorphous film. In contrary, twin peaks in Al ELNES not only exhibit the amorphous film is made of Al oxide as we have already known from the film composition, they also reveal that Al-O bonding took the forms of both tetrahedral $Al\text{-}O_4$ and octahedral $Al\text{-}O_6$, just as in the case of YAG structure [9].

In YAG SiC sample the dopant initially also segregated to grain boundary films [10]. However, severe vaporization of alumina dopants occurred during the deformation process and the crystallization of pocket phases. Aluminum disappeared from the grain boundary as well as from the pockets. In the latter silicon replaced them in the structure and this implies that some carbon were also gone. In grain boundary the amorphous films have disappeared together with Al, as observed by HREM (not shown) and by the absence of oxygen too (Fig. 4). This is another evidence that the amorphous films are sustained by alumina-based films. This is the origin of the unstable behavior of such films since alumina is not a good network builder for amorphous structure.

2.2 HIPed SiC with boron-segregation and without grain boundary film

For the other nanocrystalline SiC system, HIPed with boron and carbon addition, amorphous film was not observed by HREM (Fig. 5). EELS analysis found not only boron segregated to grain boundary but carbon also has correspondingly an excess there in respect to silicon [11]. Oxygen was also found to segregated to grain boundary, as shown in Fig. 6. ELNES analysis discovered that B-C and Si-O bonds were formed at these boundaries, as shown in Fig. 7 by a comparison of Si ELNES between the HIPed SiC and the oxygen-free hot-pressed SiC [12].

Moreover, the chemical width of such amorphous film-free grain boundary still reaches more than 1 nm, as revealed by the chemical profiles obtained from EELS profiling technique. In Fig. 8 a same grain boundary was scanned with different probe sizes, 2.5 Å and 5 Å respectively. The bigger probe was useful to reveal oxygen signals at grain boundary. The surprisingly large chemical width, in contrast to the absence of film at grain boundary, is mainly due to the surface modification of SiC structure, which has been exposed twice by ELNES in both SiC systems (Figs. 3 and 7).

The boron segregants are quite stable against the deformation as well as the bulk doping level change. For boron doping ranging from 0.3 wt% to 3.0 wt%, boron segregation remained little changed at the same level, which is about one monolayer, and the accompanying carbon excess has always similar quantity. The excessive boron formed B_4C grains, while graphite layers were frequently found in triple-grain junctions where they shield empty or amorphous spaces in most cases [13].

Upon annealing and deformation at high temperatures, boron stayed at the same segregation level while oxygen segregants were disappearing quickly. Only until the end of deformation after 3 hours at 1800 °C that reached more than 100% elongation, that boron segregants dropped to one third of the initial amount at grain boundary when significant amount of cavities have already been formed by the deformation.

3. CONCLUSIONS

These two nanocrystalline SiC systems demonstrate that, at one hand, amorphous grain boundary films do not have a chemically stable structure although the liquid phases significantly enhanced diffusion to promote deformation and on the other hand, boron and carbon formed a rather stable grain boundary structure against both the high temperature deformation and the chemical variation while the amorphous film was absent. These outstandingly contrasted results proved the prediction by the force-balance model that in SiC the grain boundary should not have amorphous film in equilibrium situation [14].

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Fig. 1   HREM image of grain boundaries with amorphous films in a AYC SiC sample.
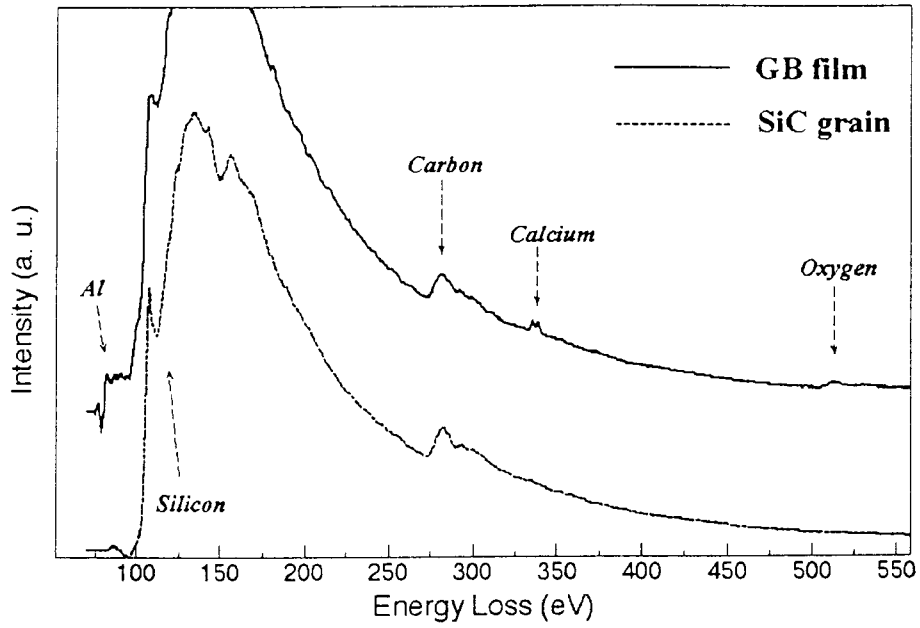
Fig. 2   EELS spectrum of a grain boundary film and SiC grain in as-sintered AYC SiC.
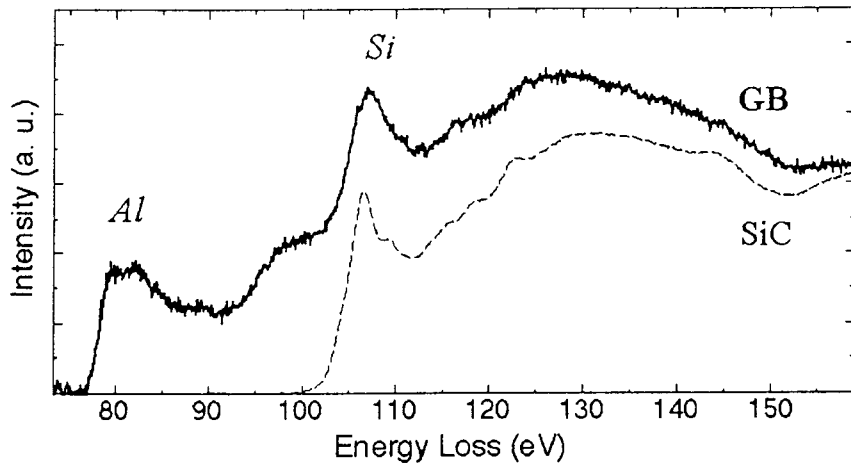

Fig. 3   ELNES of a grain boundary film and SiC grain in deformed AYC SiC.
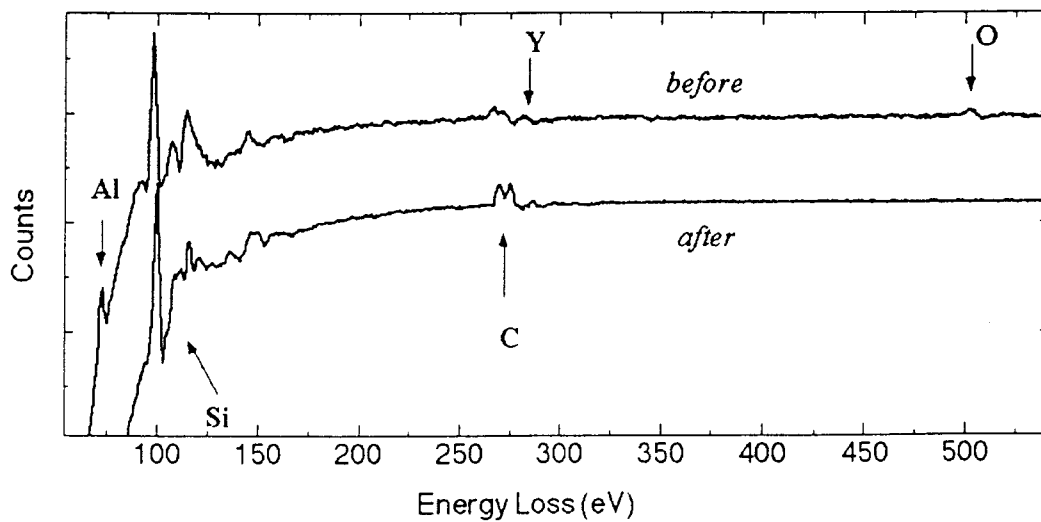

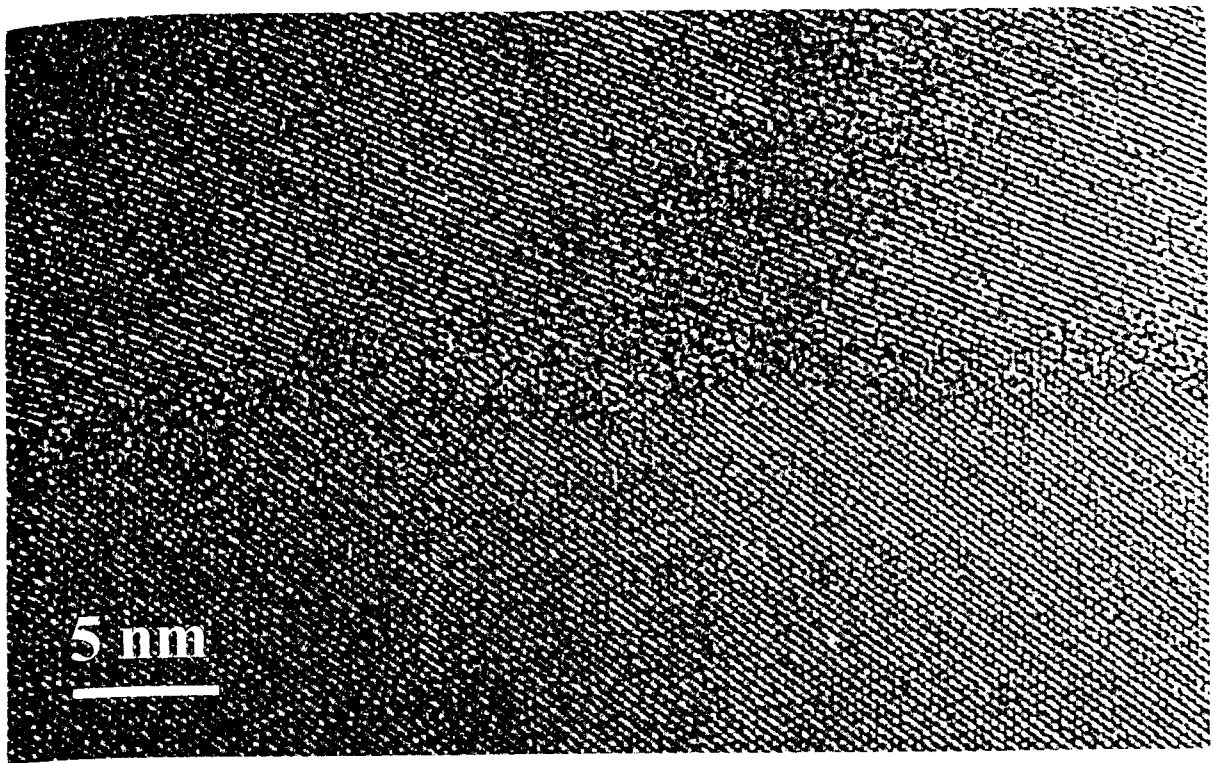Fig. 4   EELS spectrum at grain boundary in YAG SiC before and after deformation.

Fig. 5   HREM image of a grain boundary in HIPed SiC doped with 1 wt% boron.
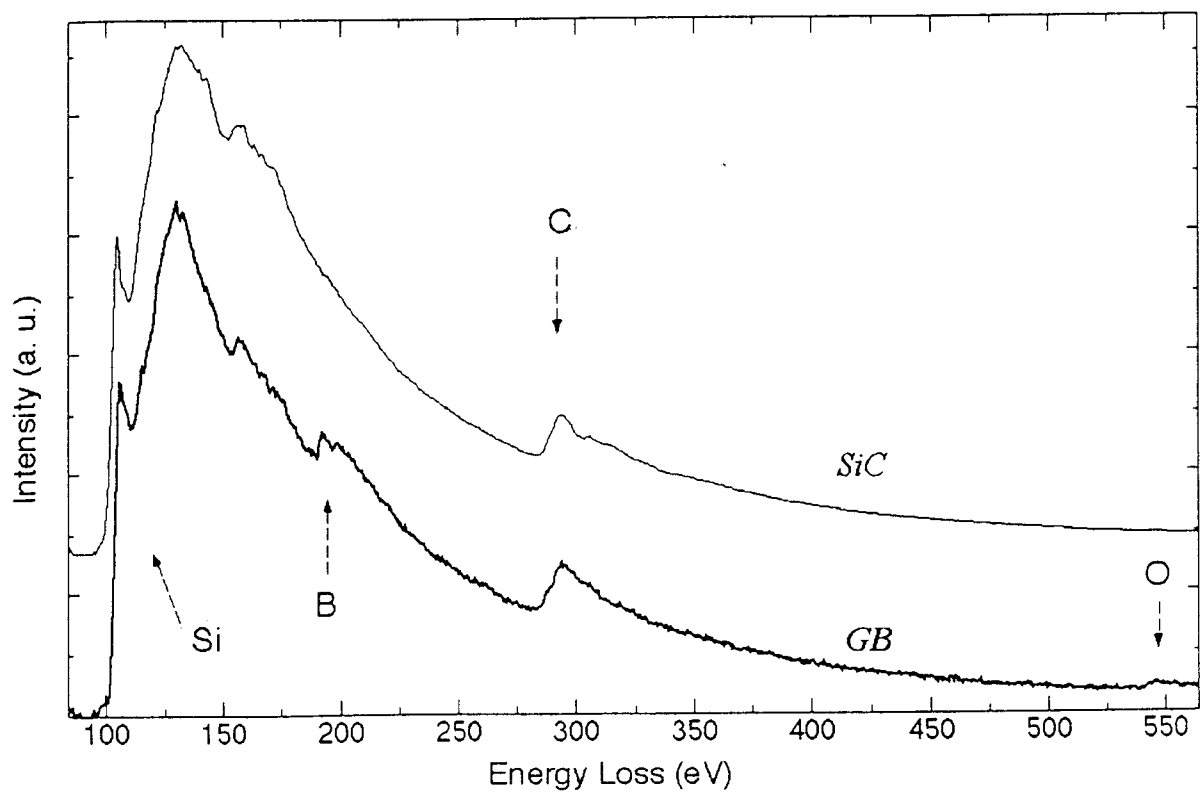

Fig. 6   EELS spectrum of grain boundary in HIPed SiC with boron and oxygen segregation.
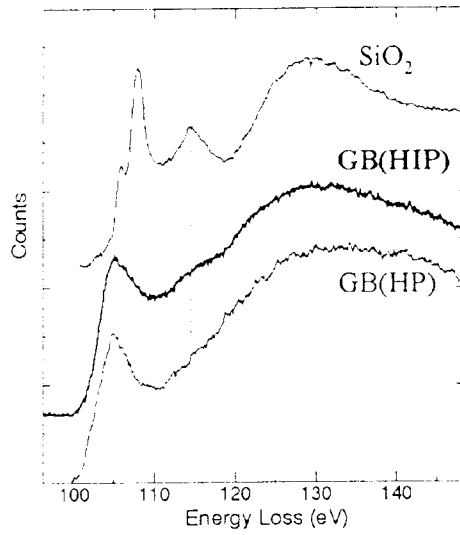
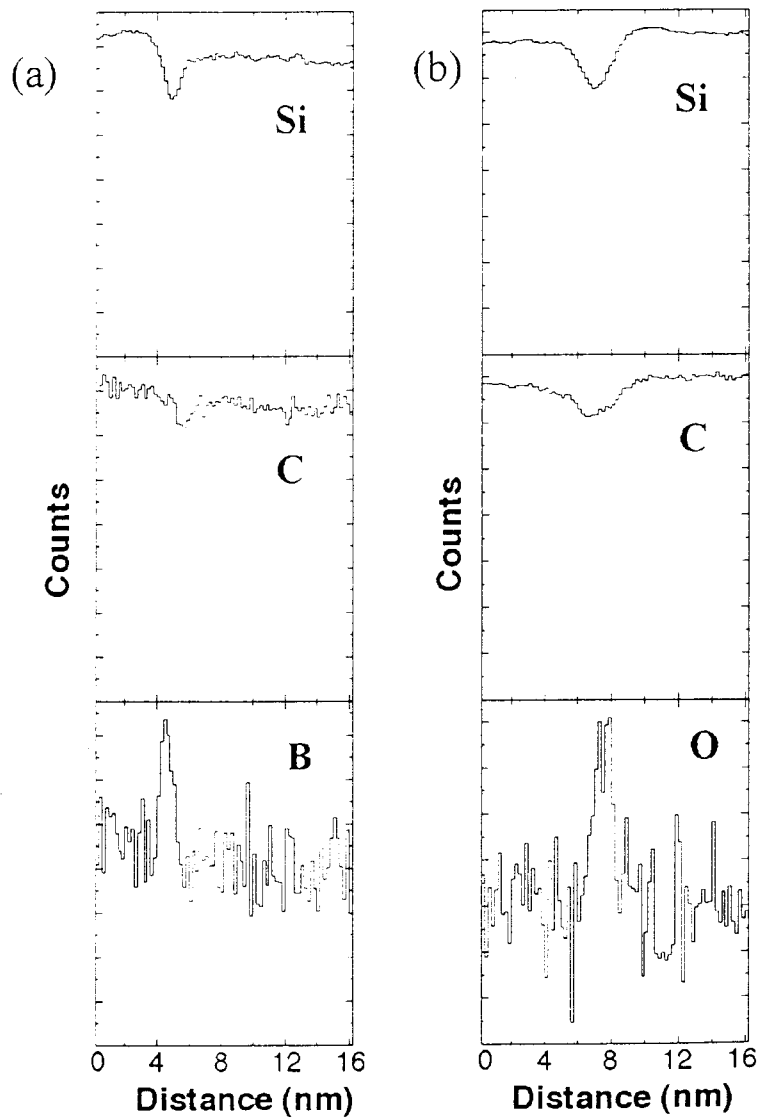Fig. 7   Si ELNES of grain boundary in HIPed SiC and hot-pressed SiC, together with SiO_2.

Fig. 8   Chemical profiles of grain boundary in HIPed SiC with probe size: 2.5Å (a) and 5Å.