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PROPOSED MODEL FOR GRAIN ALIGNMENT IN $YBa_2Cu_3O_{7-x}$ SUPERCONDUCTORS PREPARED BY MELT PROCESSING

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ABSTRACT

PROPOSED MODEL FOR GRAIN ALIGNMENT IN $YBa_2Cu_3O_{7-x}$ (123) SUPERCONDUCTORS PREPARED BY MELT PROCESSING. A model for grain alignment in $YBa_2Cu_3O_{7-x}$ is proposed. The proposed model is based on experimental results that the grain alignment in coarse samples with average grain diameter of 57 μm is higher than that of fine samples with average grain diameter of 1.6 μm which were prepared by melt processing. Other evidence, supported the proposed model, is the difference in microstructure of both samples, i.e. the grain in the fine samples tend to form domain-like structure, while in the coarse sample some large grain randomly oriented in the bulk and some grain aligned on the surface. The alignment of grain in coarse sample is due to capillary mechanism while in the fine samples the alignment could be due to capillary mechanism or sympathetic nucleation.

Key words : Model, Grain alignment, Melt processing, Capillary, Sympathetic nucleation

ABSTRAK

PENGAJUAN MODEL PENJAJARAN BUTIR PADA SUPERKONDUKTOR $YBa_2Cu_3O_{7-x}$ (123) DENGAN PROSES PELEBURAN. Suatu model penjajaran/orientasi butir dalam $YBa_2Cu_3O_{7-x}$ diusulkan. Model didasarkan atas hasil percobaan bahwa penjajaran pada sampel berbutir kasar dengan diameter rata-rata 57 μm lebih tinggi dari sampel berbutir halus dengan diameter rata-rata 1,6 μm. Hal-hal lain yang mendukung model yang diusulkan adalah perbedaan strukturmikro antara kedua sampel, yaitu sampel halus cenderung membentuk stuktur *domain* sedangkan pada sampel kasar beberapa butir besar berorientasi secara acak di dalam *bulk* dan berjajar pada permukaan. Penjajaran butir pada sampel kasar disebabkan oleh mekanisme kapiler sedangkan pada sampel halus penjajaran dapat disebabkan oleh mekanisme kapiler atau pengintian simpatetik.

Kata kunci : Model, Penjajaran butir, Proses peleburan, Kapiler, Pengintian simpatetik

INTRODUCTION

It has been recognized that some grain alignment or textured microstructure occurs in YBCO superconductor prepared by melt processing.

Grain alignment in $YBa_2Cu_3O_{7-x}$ (123) superconductor is very important due to its effect on the electrical and magnetical properties of the samples. W.M. Yang et al. [1] found that the grain alignment of 123 superconductors has some effect on the levitation force. They found that the levitation force values are highly anisotropic depending on the field direction.

The levitation force with magnetic field (H) parallel to c-axis about three times higher than that with H perpendicular to c-axis. High levitation force of bulk superconductors has made it possible for various applications such as flywheel, magnetic levitation transport system etc. [2]. Kausar et al. [3] has explored a technique to achieve high texturing by heated the sample in a temperature gradient of 935-945 ^{o}C. Meanwhile, Zhou et al. using double seeded tehcnique in SmBCO added to the top and bottom of the sample and resulted in grain orientation on both surfaces [4].

So far, no comprehensive model has been proposed that includes the effect of particle size on the grain alignment development during isothermal melt processing. The development of grain alignment in bulk superconductors produced by liquid phase sintering during isothermal melt processing is not well understood.

A mechanism of grain alignment in thin films has been described by Thompson [5]. He proposed the orientation of crystals that form through homogeneous nucleation in bulk amorphous film should be random. However, heterogeneous nucleation at the surface may lead to preferential orientation with specific planes parallel to the surface. Bateman and Jin [6,7] proposed that the orientation in melt processed 123 occurs by sympathetic nucleation. Sympathetic nucleation (first proposed to describe the solidification in metal alloys) is the nucleation of a precipitate crystal at the interface boundary of another crystal of the same phase [8]. This model is almost the same as the one proposed by Thompson as describe above, but occurs in the presence of liquid phase.

Rodriguez et al.[9] using hot stage microscope observed that 123 phase appear in the liquid region near the Y_2BaCuO_5 (211) phase but the 123 nucleation is not necessarily adjacent the 211 crystals. This support previous work of Hojaji [10] who observed a gradient in Y concentration as a function of distance from 211 crystallites.

Grain alignment may depend to some degree on the processing technique, but for all melt processing methods that do not involve translation of a hot zone the basic mechanism shoud be the same. In this paper a model for grain alignment in bulk melt processed 123 is proposed based on the experimental observations and or data from literature.

EXPERIMENTAL METHOD

Two powders with different grain size were prepared. One powder has average grain size of 57 μm which labelled as coarse and the other powder has average grain size of 1.6 μm which labelled as fine. Both powders were then pressed to form bars and then melt processed at the same condition as follows.

Both samples were heated to 1030 °C at the rate of 4 °C/min, held for 2.5 hours and then air quenched. The other samples were heated to 1030 °C, held for 2.5 hours and then cooled to 980 °C at the rate of 2 °C/min and then quenched. The samples were then characterized by X-Ray Diffractometer (XRD) and Scanning Electron Microscope (SEM). The top, side and bottom surface of samples were also characterized with XRD.

The other samples were melt processed at 1030 °C cooled to 980 °C and soaked for 100 hours at 980 °C and naturally cooled to room temperature and characterized by SEM. The difference in mineral composition and microstructural development were then used as the basis to propose a model to explain the development of grain orientation in the sintered samples.

PROPOSED MODEL AND DISCUSSION

Before explaining the hypothesis of texture development in the coarse samples, two important points from experiment must be mentioned first.

During cooling, it was previously speculated that heterogeneous nucleation occurs in which 211 grains act as nucleation sites for 123 formation [11]. However, later observations by some researchers [6,8,12] show that 211 grains dissolve in the liquid and 123 emerges from the solution.

At the peritectic temperature, nucleation is unfavourable. The formation of nuclei is expected when the sample is undercooled as predicted by nucleation theory, with the number of nuclei increasing as the degree of undercooling increases. For this experiment, the annealing temperature is 980 °C, which is 50 °C undercooled. At this temperature, the barium cuprate liquid and 211 phase system are no longer stable. The choice of this temperature is based on previous work [13].

It has been reported in the literature that the grain growth of 123 is more energetic in the a-b direction than in the c-direction [14,15]. If this is the case, then the grain growth will go faster in the a-b plane.

The proposed model for grain alignment is based on the following experimental results. The similarity in phase composition of coarse and fine samples quenched from 1030 °C as shown in Figure 1. Figure 1 shows the XRD pattern of samples melt processed to 1030 °C and then quenched. It can be seen that there is no difference of phase development at 1030 °C for both coarse and fine samples. Both samples contained 211, BaCuO and CuO phases.

The difference in the grain alignment between coarse and fine samples quenched from 980 °C (Figure 2). Figure 2 shows the XRD pattern of sample melt processed to 1030 °C and then cooled to 980 °C and quenched.

It can be seen that there are some differences in phase development between coarse and fine samples.

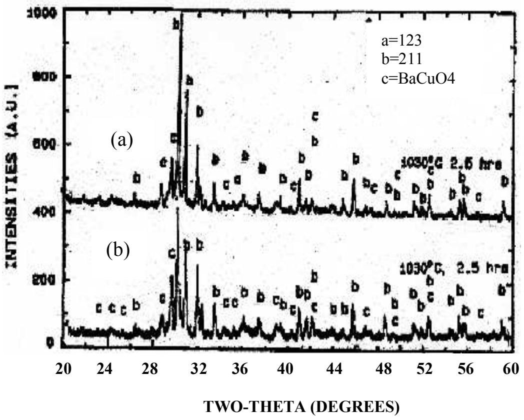

Figure 1. XRD pattern of (a) fine sample and (b) coarse sample quenched from 1030 °C

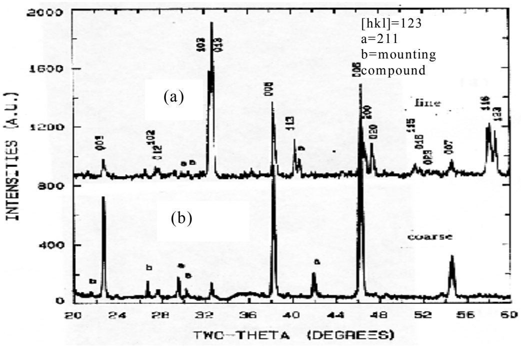

Figure 2. XRD pattern of (a) fine sample and (b) coarse sample quenched from 980 °C

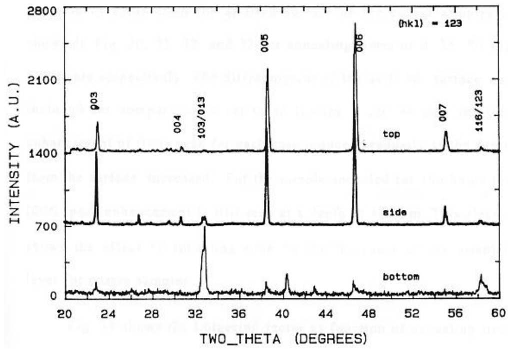

Figure 3. XRD of (a) top, (b) side and c) bottom surface of coarse samples annealed for 100 hours at 980 °C

Both top and side surface of the coarse sample show the same level of orientation (Figure 3). Figure 3 shows the XRD pattern of the top, bottom and side surface of the samples of coarse powder. It can be seen that the top and side surface shows some grain alignment while the bottom surface does not show any alignment.

Green (unfired) sample shows no effect on fired orientation since all 123 has peritectically melted to form 211 and liquid (Figure 4). From Figure 4 it can be seen that although the oriented surface has been removed, the fired sample shows grain alignment on the surface.

The difference in microstructure between coarse and fine samples annealed for 100 hours (Figure 5)

When considering the mechanism responsible for the development of orientation during isothermal melt processing, the two experimental observations must be considered. Is there any 123 remaining after sintering which could affect the recrystallization from the 211-barium cuprate system ? Does the texture resulting from compaction of the powder influence the development of orientation during sintering ?

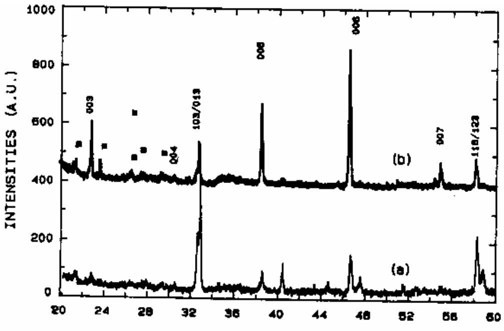

Figure 4. XRD pattern of coarse sample (a) green samples with surface oriented layer removed and (b) after annealed at 980 °C for 0 hour (no annealing)

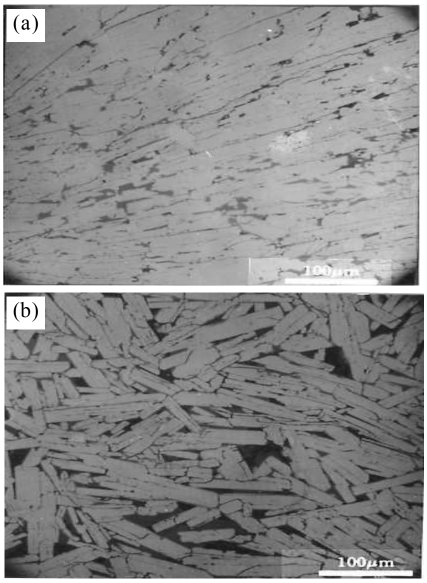

Figure 5. SEM image of (a) fine sample and (b) coarse sample annealed for 100 hours at 980 °C

In the fired sample, green (unfired) orientation has no effect since X-ray data indicates that all 123 is gone after 2.5 hours sintering at 1030 °C. This observation is based on X-ray diffraction analysis on the bulk samples showing no 123 (Figure 1). The 211 present shows no indication of aligned grains, based on X-ray analysis. The quenched sample shows 211 and $BaCuO_2$. At 1030 °C, 211 is solid while $BaCuO_2$ is liquid according to reaction of incongruently melting of 123 in air as follows:

$$2YBa_2Cu_3O_{7-x\,(s)} \xrightarrow{1030} Y_2BaCuO_{5(s)} + 3BaCuO_{2(l)} + 2CuO_{(l)} + \tfrac{1}{2}\,O_{2-4x} \quad \ldots \quad (1)$$

In order to answer second question, the oriented surface of a bar made from coarse powder was removed and the remaining bar, which showed no surface texture, was then melt processed at 1030 °C, cooled to 980 °C with no hold and cooled to room temperature. The XRD pattern of the new, fired surface shows the development of texture which can not be related to green (unfired) orientation (Figure 4).

The XRD pattern of the top surface of a coarse and fine samples quenched from 980 °C is shown in Figure 2. The enhancement of (001) peak is clearly seen in the coarse sample while the pattern of the fine samples shows little alignment. The quantization of the grain alignment shows that the coarse sample has a Lotgering factor of 0.91, while the fine samples has a Lotgering factor of 0.16. Higher Lotgering factor indicates higher oriented layer on the surface of the samples. The definition of Lotgering factor has been explained elsewhere [16]. When heated, the samples undergoes peritectic decomposition in which Y_2BaCuO_5 (211) solid and a liquid are formed as shown in Equation 1. After holding at 1030 °C for 2.5 hours, the samples, now composed of 211 and liquid phase, are cooled to 980 °C. Nucleation starts from the surface of the sample since cooling begins on the surface. In order to minimize the free surface energy, the growth of 123 will be parallel to the surface. This event will be followed by nucleation of 123 underneath the surface and the grain will orient themselves parallel to the grain on the surface due to torque produce as a result of capillary action, as long as nothing to prevent them from doing so. This proposed sequence of steps would explain the development of an oriented layer seen in isothermally melt processed 123 both on top and side surface. No orientation on the bottom was observed since this surface interacted with 123 powder, separating the specimen from the setter.

The difference in orientation between coarse and fine samples is probably due to the difference in the size of 211 crystals. In the coarse specimens, the 211 crystallites are larger and their distribution are less homogeneous than those in the fine specimens. Therefore, 123 nuclei can easily reach critical size because there is enough 211 matrix to supply the yttrium for 123 formation. For fine specimens, the 211 is finely dispersed and it is more difficult for nuclei to obtain necessary yttrium to grow beyond the critical size. This difference should result in more crystal nuclei larger than critical size in the coarse sample. At the peritectic temperature, nucleation is unfavorable but when the samples are cooled from 1030 °C to 980 °C, nucleation commences.

The closer the recrystallization temperature to the melting temperature, the larger is the critical radius. The relationship between critical size requirements and the temperature of undercooling has been suggested as [17]:

$$r^o = \frac{2\sigma}{\Delta T_f \Delta S_f} \qquad \text{..} \quad (2)$$

where :

r^o = Critical size of a crystal

σ = Spesific interface energy

ΔT_f = Undercooling temperature

ΔS_f = Volume freezing entropy

The larger the ΔT_f is, the smaller r^o can be. In agreement with this hypothetical model, X-ray analysis on the surface of the samples shows a clear difference between bars prepared from coarse and fine powders (Figure 2). At 0 hour anneal of the coarse sample, the reversible reaction to form 123 is almost complete, as shown in the bottom pattern in Figure 2. The predominant phase is 123.

The difference of grain alignment of the two samples is proposed as due to the difference in microstructure of both samples after peritectic decomposition at 1030 °C. The difference in the microstructure can also be quantified in term of the distance between 211 grains in the two samples. For the coarse samples, the size of the area between grains, where liquid is located at higher temperature, is about 57.5 ± 32.8 μm, while in the fine samples is about 33.1 ± 17.7 μm. If 123 is nucleating in the liquid as suggested by other researchers [6,9,12], the 123 nuclei in the coarse powder can grow rapidly as compared to fine sample because it has larger reservoir of Y to draw on. More embryonic nuclei would grow to exceed the critical size in the coarse microstucture as discussed earlier.

The SEM microstructure of both samples annealed at 980 °C for 100 hours are shown in Figure 5. In the fine sample, domain-like areas have formed. The domain structure most likely begins with a few large crystallites, which grow at the expense of small crystallites surrounding the larger one. The larger crystallites act as seeds for rapid growth especially at a higher temperature [18], where the driving force for nucleation is smaller. The description for the development of grain alignment is conventional liquid phase sintering with specific details determined by reaction kinetics, the viscosity of the liquid phase and particle size distribution. 123 demonstrates anisotropic crystal growth, with the a-b plane undergoing rapid, non-faceted growth [19,20]. Along the c-axis, the growth is limited by the surface reaction rate which produces facets and atomically smooth interfaces [15]. The tendency of a crystal to enlarge preferentially in one direction results from anisotropy of interface energy and atomic attachment kinetics [11]. The faceted growth in the c-direction seems to be consistent with the [001] platelike habit of 123 crystallites that are generally reported [5,10,18]. This type of crystallites is critical to the mechanism of grain alignment in 123 superconductor produced by isothermal melt processing proposed here. Veneva [21], based on electron backscattered (EBSD) mapping which resulted in high quality Kikuchi patterns and enabling automated mapping of the individual crystal orientation, suggested that the formation of small 211 in the melt does not disturb the 123 matrix, whereas presence of large 211 particles leads to formation of subgrains.

The scheme of grain growth in both samples can be described as follows. On cooling, nucleation will start from the surface since the surface will cool first. Some nuclei form on the surface and grow. Due to anistropic growth, platelike crystallites would be produce. On the surface, the largest dimension of the platelet crystallites would be parallel to the surface due to capillary forces. Then ideally, the c-axis of all crystallites con would be parallel to the surface. This prediction is supported by the fact that the top and the side surface of the coarse sample show the same degree of orientation. In the fine samples, the crystallite size produced during 123 recrystallization would be smaller. Therefore, on the surface the driving force for the alignment would be smaller because the surface are smaller. That is why the grain alignment on the surface of the coarse sample is larger than in the fine sample.

In the early stage of annealing of the coarse samples, the crystallites would be larger than in the fine samples as previously described. It is anticipated that some of the larger crystallites in the fine samples will be as large as those occuring in the coarse samples. This based on the micrographs of quenched coarse and fine specimens, which show some crystallites in the fine samples to be as large as those seen in the coarse samples. This progression is illustrated in Figure 6. Some small grains remain on surface in the fine sample. As cooling continues, the formation of nuclei and growth of crystals continues to occur in the bulk sample. The orientation of platelet crystals in the bulk is random as shown in Figure 6. When two platelet crystallites touch one another at one edge in the presence of a liquid force, a torque will be produced to capillary action according to Cahn's model [22]. The torque will rotate the particles to bring the flatter surface together.

Cahn's model applied to coarse and fine samples explains the difference in microstructure development. In the case of particles in contact, the torque will bring the flat surface together and the shear force causes the flat surface to slide on each other, moving crystallites to increase the area of solid-solid contact to form layered structure. The arrangement of particle is time dependent. Therefore, the longer the time at the appropriate temperature, the more layered structure is formed as shown in our previous work [16] and other work [13].

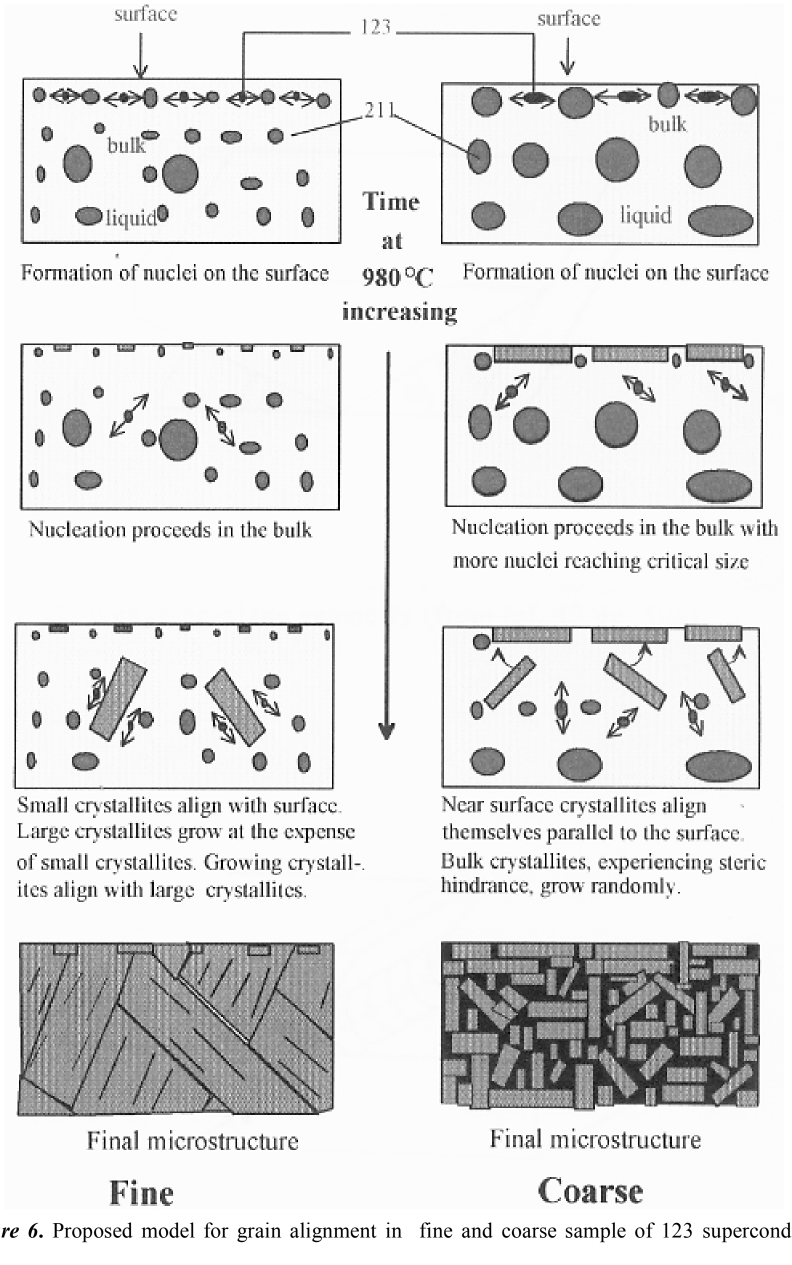

Figure 6. Proposed model for grain alignment in fine and coarse sample of 123 superconductor.

The mechanism described above is quite adequate to explain the appearance of the coarse microstructure shown in Figure 6. In the case of the fine sample, it seems that only a few large crystallites are formed, surrounded by many small crystallites. If the small crystallites arrange themselves, rotate and slide toward the bigger particles, the formation of domain structure would develop. The orientation of the domain depends on the orientation of the original large crystallites.

This process can be considered capillary mechanism, since capillary forces are driving crystallite motion during annealing.

Jin [7] and Bateman[6] proposed that the layered microstructure in the 123 superconductors is most likely created by symphatetic nucleation as in metal alloys. In this model, nucleation first occurs homogenously in the melt. The crystallites which attain critical size will then act as a nucleation site for the next crystals. Symphatetic nucleation model can explain the formation of "domain" structure as found in the fine sample but not in the microstructure of the coarse sample. The microstructure of the bulk of coarse contain randomly oriented platelike grains indicating that many nucleation sites for 123 develop independently. The platelike grains are not grown on the surface of the other crystals as sympathetic nucleation would predict.

Based on the microstructure of both samples quenched from 1030 °C, the proposed model suggests that in the coarse samples, inhomogeneity produces more nuclei that attain the critical size for further growth. In the fine sample there are many nucleation sites as well, but only those that have reached the critical size can survive, while the other nuclei will dissolve, becoming source material for the coarsening the larger crystals. The small 123 nuclei that reach critical size will survive, producing small grains. These grains rotate and align themselves with the large crystallites which lead to the development of domain structure. Another possibility is that some small 123 nuclei appear on the surface of the larger crystallites and grow, as the sympathetic nucleation model predicts. So, in the case of the fine samples both sympathetic nucleation and the capillary mechanis may take place and produce the domain structure when processed isothermally and long-range grain alignment when processed in gradient [7,23]. The possibility of undocumented, alternative reaction pathways have been addressed. Small changes in composition can have large effects on nucleation behavior.

CONCLUSIONS

A mechanism for grain alignment in the coarse samples has been proposed as due to capillary forces, while in fine sample capillary action or sympathetic nucleation may occur.

The difference in alignment mechanism has been proposed as due to difference in the size of the recrystallized 123 which resulted from the difference in the 211 crystallite size and distribution after peritectic melting

In the coarse samples, the proposed mechanism leads to a randomly oriented structure in the bulk despite a highly oriented layer on the surface, while in the fine samples a domain-type structure is formed in the bulk and less alignment on the surface of the sample

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