

Phase evolution study on the melting and recrystallization of ceramic core in the (Bi,Pb)-2223 tape

J.Y. Li^{a,b}; L. Soubeyroux^c; H.L. Zheng^b; C.S. Li^b; Y.F. Lu^b;
L. Porcar^c; R. Tournier^d; L. Zhou^{a,b}

^a Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China

^b Northwest Institute for Nonferrous Metal Research, 96 Wei yang Road, P.O. Box 51, Xian, Shaanxi 710016, PR China

^c Laboratoire de Cristallographie, CRESTA/CNRS, 25 avenue des Martyrs, 38042 Grenoble, France

^d Consortium de Recherches pour L'Emergence de Technologies Avances, CNRS, 25 avenue des Martyrs, 38042 Grenoble, France

ABSTRACT

The phase evolution during melting and recrystallization of ceramic core in Ag-sheathed (Bi,Pb)-2223 monofilamentary tape has been studied. The tape was fabricated by PIT process with powders containing nearly pure (Bi,Pb)-2223 phase. Short samples were melted at 805°C, 808°C, 812°C, 816°C and 831°C, slowly cooled down at 1.5°C/hr. and quenched in air at room temperature. X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) were applied for the phase identification. XRD patterns of samples show that (Bi,Pb)-2223 core is partially melted at 805°C, 808°C, 812°C, and well reformed directly from the melt during the slow cooling. More (Bi,Pb)-2223 phase is decomposed at temperatures higher than 816°C and can not recrystallize, indicating that a partial melting at some temperatures around a given temperature range is essential for (Bi,Pb)-2223 phase reformation. The results of EDS analysis show that the melt composition moves from that between "2223" and "2212" stoichiometries towards 2212-like stoichiometry with increasing temperature, and Bi-containing 2:1 phase is the main secondary phase. This seems to lead to the conclusion that (Bi,Pb)-2223 phase decomposes incongruently into a 2212-like liquid and (Ca,Sr)-cuprates. 2:1 phase plays the most important role in (Bi,Pb)-2223 melt-recrystallization process. Our results also reveal that plate-like shape (Bi,Pb)-2223 grains can be obtained via melting and recrystallization if the optimum processing conditions are used.

Keywords: (Bi,Pb)-2223 tape, melting and recrystallization, phase evolution

1. Introduction

For more than one decade, it was shown a slow increase in J_c of Bi-2223 conductors in spite of the remarkable progresses achieved. The J_c -limiting mechanism is attributed to the weak connectivity between the grains in polycrystalline (Bi, Pb)-2223 tapes^[1]. The platelet alignment far from perfect, the low density of ceramic core, the presence of non-conducting and low- T_c secondary phases, voids and cracks resulting from the deformation are responsible for the poor intergrain links^[2]. A melt-processing route, via partial melting of the superconducting core, may facilitate contacts and interactions between the crystals, reduce porosities, heal cracks and increase the core density^[3]. As a result, homogeneous microstructure, good grain connectivity and high critical current density in superconducting tapes can be attained. Besides, the alignment of the grains can be improved by melting processes, also combined with the applications of magnetic and/or temperature fields.

The Bi-2223 melt-processing has long been attempted. However, following the traditional formation mechanisms of (Bi,Pb)-2223 phase, this high- T_c phase occurs via nucleation from a local transient liquid, which is not stable and homogeneous, and usually far from equilibrium^[4,5]. consequently, the J_c -limiting factors of (Bi,Pb)-2223

conductors work still. It is believed that (Bi,Pb)-2223 phase formation from a liquid being either stable or close to equilibrium will be beneficial to tape processing. Many efforts and detailed investigations have been performed on the melting behavior or melt evolution of BPPSCO system. Some works have indicated the feasibility of the Bi-2223 recrystallization from the melt. *Giannini et al.* [4,5] have observed the Bi-2223 reformation directly from the melt. The (Bi,Pb)-2223 phase was found to decompose incongruently into $(\text{Ca,Sr})_2\text{CuO}_3$ (2:1), $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ (14:24) and a (Bi,Pb)-rich liquid phase, then recrystallized through the inverse reaction, showing that equilibrium formation of (Bi, Pb)-2223 can be implemented.

The aim of the present work is to understand the phase evolution in the melting process of (Bi, Pb)-2223 tape, as well as to investigate the feasibility of Bi-2223 recrystallization from the melt and the effect of melting temperature on the phase relationship in 2223 system. The (Bi, Pb)-2223 tape was fabricated following the standard PIT route, with near fully pre-reacted (Bi, Pb)-2223 powder in pure silver tube.

A series of maximum temperatures were applied in the melting processes. Short samples were melted, slowly cooled and quenched at different temperatures. Our results indicate that (Bi, Pb)-2223 phase in the silver sheath might well reform during the slow cooling. A partial melting at a defined temperature and under partial oxygen pressure is essential to (Bi,Pb)-2223 phase reformation. The 2:1 phase plays an important role in the melt-recrystallization process.

2. Experimental

Nearly pure (Bi,Pb)-2223 powder was synthesized from precursors prepared from mixtures of co-precipitated oxalates with a nominal stoichiometry $\text{Bi}_{1.76}\text{Pb}_{0.34}\text{Sr}_{1.83}\text{Ca}_{1.91}\text{Cu}_{3.16}\text{O}_{10+\delta}$ after about 150 hours annealing at 840-857°C in air with intermediate grindings. Silver-sheathed (Bi,Pb)-2223 tapes were prepared by standard PIT method. Pre-reacted powder, which contains >94% (Bi,Pb)-2223 phase and traces of Bi-2201 and (Ca,Sr)-cuprates, was packed into silver tube and the composite was drawn and rolled into mono-filamentary tapes with a width of 3-4 mm and thickness of 0.2-0.3 mm.

Short samples, with length of 60 mm cut from (Bi,Pb)-2223 tape and sealed at both ends, were subjected to the melting treatment in a tubular furnace under flowing 7.5% O_2 balanced with argon. The gas-flow rate was 15ml/min. Samples were initially ramped up at 5 °C /hr. to a temperature 5 °C lower than maximum heating temperature (T_p) then at 0.2 °C / hr. to T_p , dwelled there for 30 min, subsequently slow-cooled at 1.5 °C /hr. from T_p to the final temperature (T_E) of treatment, and quenched in air at room temperature as shown in Figure 1. 805°C, 808°C, 812°C, 816°C, 831°C as T_p s were used in order to obtain the appropriate temperatures at which (Bi,Pb)-2223 phase could reform from the melt. Phase identification was performed by means of X-ray diffraction analysis (XRD). Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) was applied to characterize the cross-section and the surfaces near to silver sheath of quenched ceramics cores.

3. Results and discussion

3.1 Melting behavior

It is believed that the maximum temperature plays a central role for melt-processing of the Bi-based superconducting phase [6]. Control of this parameter is essential for avoiding too much segregation from the melt forming large (Ca,Sr)-cuprates and CuO precipitates and also bismuth and oxygen volatilization. Figure 2 shows the X-ray diffraction patterns for the samples quenched after the melting of (Bi,Pb)-2223 tapes at different T_p s. The (Bi, Pb)-2223 diffraction peaks, which are predominant for the tape not suffered melting treatment, become subordinate gradually up to disappear along with the T_p increase from 805°C to 831°C. Bi-2201 peaks, accordingly, turn into the leading

ones. 2:1 AEC fractions clearly increased in comparison to the tape before melting. Some other (Ca,Sr)-cuprates with different Sr:Ca ratios were also found, indicating that these phases precipitated from the (Bi,Pb)-2223 decomposition. Besides, CaO peaks arise in the samples heated above 808°C and reach the strongest at T_p Figure 2: X-ray diffraction....=816°C, meanwhile, the traces of CuO become clear. CaO and CuO precipitates formed by melting (Bi,Pb)-2223 core are the decomposition products of (Ca,Sr)-cuprates^[7]. No (Bi,Pb)-rich crystalline phases grow when the (Bi,Pb)-2223 decomposed, meaning that (Bi,Pb)- 2223 phase may incongruently melt into a (Bi,Pb)-rich liquid and (Ca,Sr)-cuprates. This is in agreement with the studies in ref. [4,5].

From Figure 2, it is surprising to find that the (Bi,Pb)-2223 core begins to decompose into Bi-2201 phase and (Ca,Sr)-cuprates even at the temperatures lower than 805°C and melt fully at ones lower than 831°C under the present experimental conditions, very different from that reported by other researchers. This could be attributed to the combined effects of the low oxygen partial pressure, the presence of silver as sheath and the composition of the precursor. This result should have a beneficial influence on the Bi-2223 system, preventing more Ca and Cu segregation and bismuth and oxygen volatilization from the melt.

Some SEM images are shown in Figure 3. The influence of the maximum heating temperature can be clearly observed. Larger dimensions and quantities of blacker secondary-phases appear in the matrix of samples melted at high maximum temperatures, indicating more 2223 decomposed as T_p rises up. The main secondary phases found by SEM/EDS are Bi-containing 2:1 with the composition $\text{Bi}_{2.05-2.52} \text{Sr}_{3.91-5.93} \text{Ca}_{18.30-19.81} \text{Cu}_{10.36-13.33} \text{O}_x$. Some small precipitates were identified as Cu-rich phases with the composition $\text{Bi}_{8.38-14.19} \text{Pb}_{0.62-1.24} \text{Sr}_{7.96-13.06} \text{Ca}_{7.11-16.78} \text{Cu}_{21.31-51.45} \text{O}_x$. According to the XRD patterns above, the matrix of ceramic core after melting and subsequent quenching could consist of a mixture of an amorphous phase with 2223 phase not completely melted and crystallized 2201 plates or just the latters. Interestingly, the SEM/EDS analysis carried out in the present work shows that the 2:1 islands are not embedded in a Bi-2201 matrix after any treatments. The matrix compositions for the quenched melted samples at different temperatures are shown in the Table 1. It shows that the matrix compositions are located between the 2223 and 2212 stoichiometries, and Ca content in the matrix decreases gradually as more 2223 decomposes into (Ca,Sr)-cuprates at higher temperature, indicating that the melt composition moves from 2223 towards 2212 as temperature increases. These results, together with the discussion above, seem to allow the conclusion that 2223 may decompose into 2212-like liquid and (Ca,Sr)-cuprates, mainly 2:1 phase. That the XRD patterns of quenched samples exhibited high Bi-2201 content could not be clarified in our present work. It was considered as the cause of its high crystallization rate from melt, even during quenching^[8]. Perhaps the dimensions of this precipitate emerging via quenching in our specimens are too fine to be detected by EDS.

Table 1
The matrix compositions after melting at different T_p

T_p	805 °C	808 °C	812 °C	816 °C
Bi	9.09–12.44	9.60–10.95	10.77–12.94	9.87–10.27
Pb	0.65–1.18	0.97–1.16	0.96–1.53	0.0–0.68
Sr	8.96–11.24	9.90–10.37	10.89–11.13	9.96–10.18
Ca	7.33–8.08	6.21–7.15	5.33–5.58	5.16–5.19
Cu	10.64–14.29	10.69–13.16	9.29–10.48	10.02–10.88

3.2 Resolidification of (Bi,Pb)-2223 phase

Figure 4 shows the XRD patterns of (Bi,Pb)-2223 tape after melting at 812°C, cooled down to 788°C at 1.5°C/hr and quenched in air. The (Bi,Pb)-2223 peaks have reverted to their predominant status, and that Bi-2201 peaks have almost disappeared, and the amount of 2:1 phase has been reduced obviously, indicating that the (Bi,Pb)-2223 phase is well-reformed directly from the melt. Similarly, clear indications of 2223 reformation were found in another set of experiment, in which silver-sheathed tapes were heated to 808 °C and slowly cooled down to 784 °C at the same rate. However, no 2223 was reformed from the melt above 816°C. It indicates that this temperature is too high for melt-processing. Actually, an excessively too high temperature produces many large 2:1 precipitates in the melting specimens (see Figure 3 (d)). The development of large 2:1 islands will prevent the 2223 formation in those samples, due to degradation of stoichiometry of the remaining ceramic phase, as well as increasing the difficulty in dissolving such large precipitates to provide sufficient Sr and Ca to a (Bi,Pb)-rich melt, in the amount necessary to form 2223.

It is obvious that a partial melting at some temperatures in an appropriate temperature range is important for (Bi,Pb)-2223 phase reformation.

The SEM images of the samples resulting from the treatment at $T_p=812^\circ\text{C}$ and slowly cooled down to 788°C are shown in Figure 5. The EDS results are consistent with the previous XRD observations. (Bi,Pb)-2223 phase with the composition of $\text{Bi}_{9.49}\text{Pb}_{0.93-1.04}\text{Sr}_{9.79-9.86}\text{Ca}_{7.88-8.18}\text{Cu}_{14.19-14.98}\text{O}_x$ reformed directly from the melt becomes the dominant phase. The main residual secondary-phase islands have been identified as the 2:1 phase with the composition of $\text{Bi}_{0-0.80}\text{Sr}_{3.42-4.29}\text{Ca}_{22.04-23.35}\text{Cu}_{13.65-13.57}$

Most of these particles had been consumed in the samples slowly cooled to 788°C from 812°C, but some large grains remained in the samples slow-cooled down to the same temperature (see Figure 3 (a), (b)).

The cross-section image of the sample slowly cooled to 788°C reveals that those regions have a plate-like shape, in comparison to the ones of the specimen melted at 812°C (see Figure 3 (c) and (d)). The EDS analysis of such plates gives $\text{Bi}_{6.77-7.86}\text{Pb}_{0-0.83}\text{Sr}_{7.96-8.42}\text{Ca}_{6.45-8.26}\text{Cu}_{10.50-14.34}\text{O}_x$ compositions, falling in the vicinity of the 2223 primary phase field, indicating the presence of (Bi,Pb)-2223 phase. Their morphological evolution suggests that partial melting and recrystallization has taken place.

The fact that 14:24 AEC, which was found as an equilibrium product of the 2223 decomposition and reformation^[4,5], has not been detected in our samples, and is probably associated to its limited stability range, as well as to the present experimental conditions and precursor composition. The exact nature of the liquid in equilibrium with the 2223 phase remains to be clarified. Our results suggest that 2:1 phase is the most important secondary phase involved in the melting recrystallization, in relations to 2223 tapes, and plate-like 2223 grains may be obtained if the optimal treatment conditions can be found.

Summary

The phase evolution during melting and recrystallization of ceramic core in Ag-sheathed (Bi,Pb)-2223 monofilamentary tape was studied. The tape was fabricated by PIT process with powders containing nearly pure (Bi,Pb)-2223 phase. Short samples were melted at different temperatures, slowly cooled at 1.5°C/hr. and quenched in air at room temperature. XRD and SEM/EDS were applied to the phase identification. XRD patterns of the samples being melted and quenched reveal that the ceramic core was partially melted at temperatures lower than 805°C and fully melted at ones above 831°C, Bi-2201 becomes gradually the predominant phase along with temperature increasing, 2:1 is the main secondary phase. The results of EDS analysis show that the melt composition moves from that between "2223" and "2212" stoichiometries towards 2212-like with temperature increasing, indicating that (Bi,Pb)-2223 core decomposes incongruently into a 2212-like liquid and (Ca,Sr)-cuprates, mainly Bi-containing 2:1 phase. During the slow cooling, (Bi,Pb)-2223 phase well reforms directly from the melt.

Too high temperature is not helpful to (Bi,Pb)-2223 reformation. It is indicated that a partial melting at some temperatures in an appropriate temperature range is essential to (Bi,Pb)-2223 phase reformation. 2:1 phase plays most important role in (Bi,Pb)-2223 melt-recrystallization process. Plate-like shape (Bi,Pb)-2223 grains can be attained via melting and recrystallization if the optimum processing conditions are used.

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FIGURE Caption

Figure 1. Temperature profile of melting experiments

Fig. 2. X-ray diffraction patterns of (Bi,Pb)-2223 tapes after quenched from different maximum temperatures

Fig. 3. SEM images of (Bi,Pb)-2223 tapes after quenched from different maximum temperatures (backscattered) (a) 805 C; (b) 808 C; (c) 812 C and (d) 816 C.

Fig. 4. X-ray diffraction patterns of (Bi,Pb)-2223 tape after melted at $T_p = 812$ C and cooled down at 0.025 C/min.

Fig. 5. SEM images of (Bi,Pb)-2223 tapes after quenched from 812 C (a,c) and slow-cooled down to 788 C (b,d), (a) and (b) surfaces of ceramic core near the Ag-sheath (backscattered), (c) and (d) cross-sections

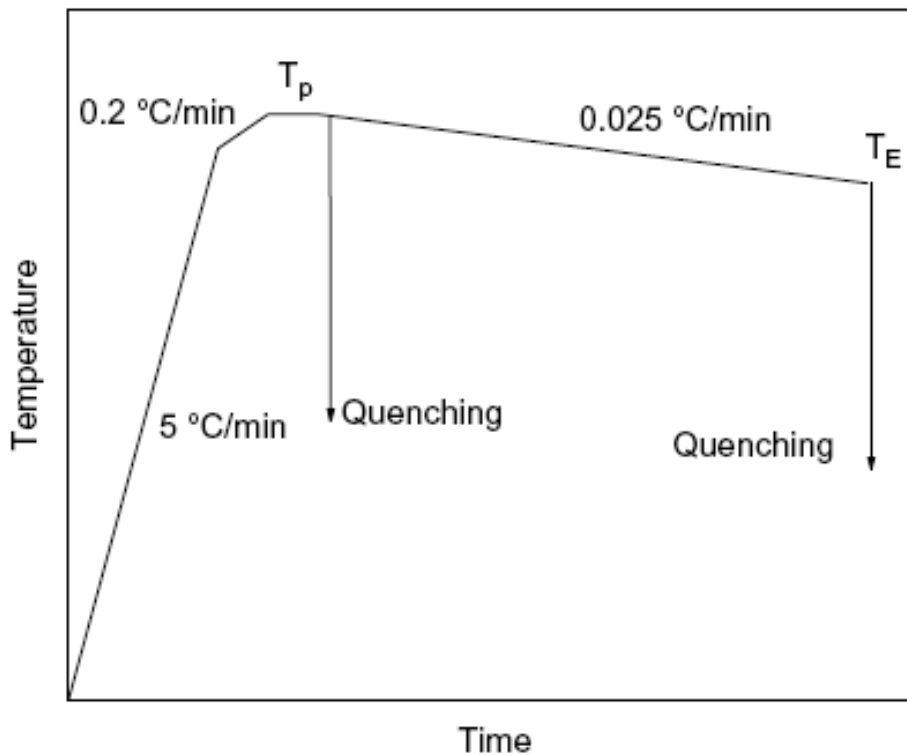


Fig.1

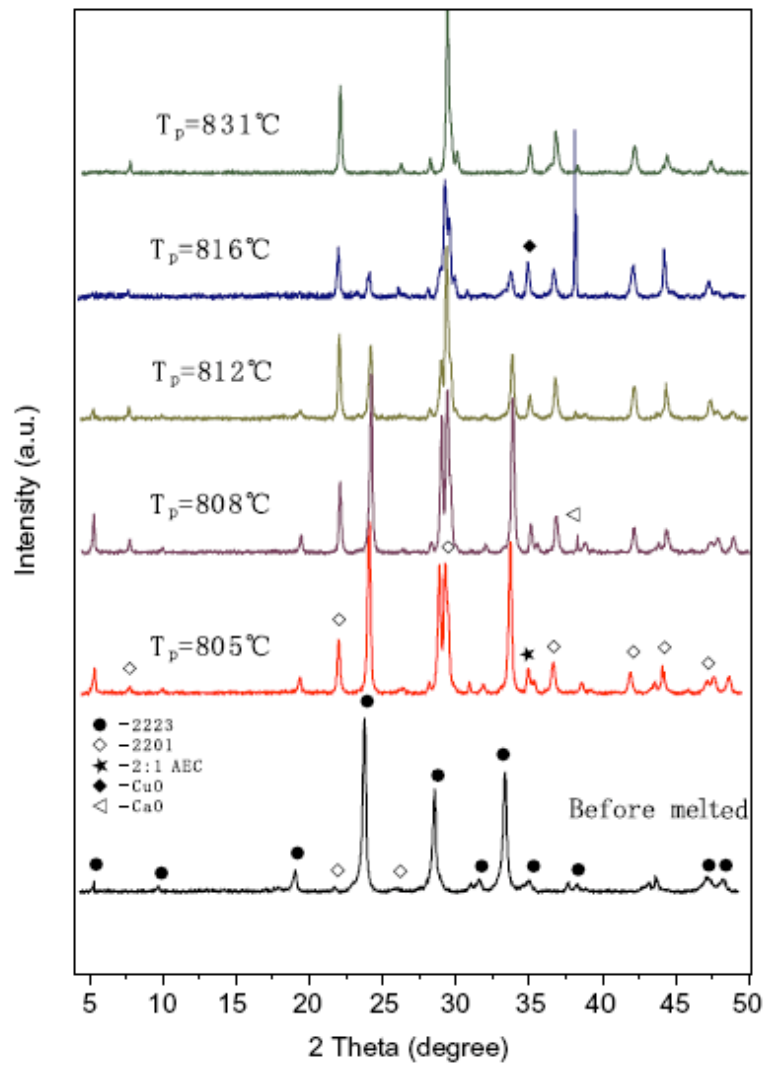


Fig. 2

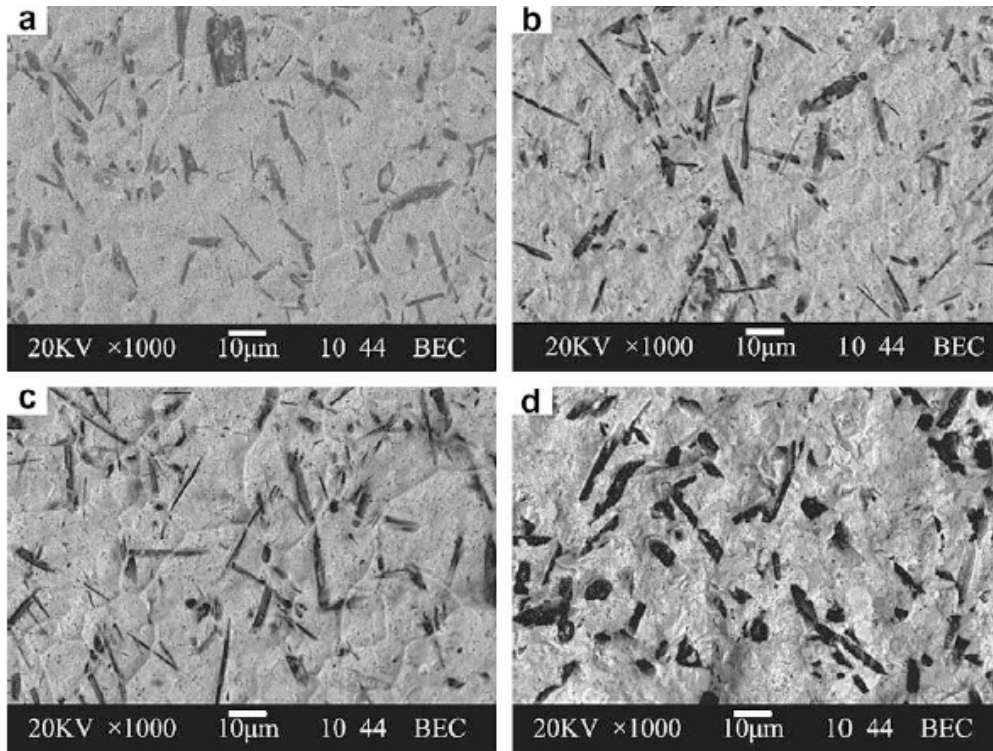


Fig. 3

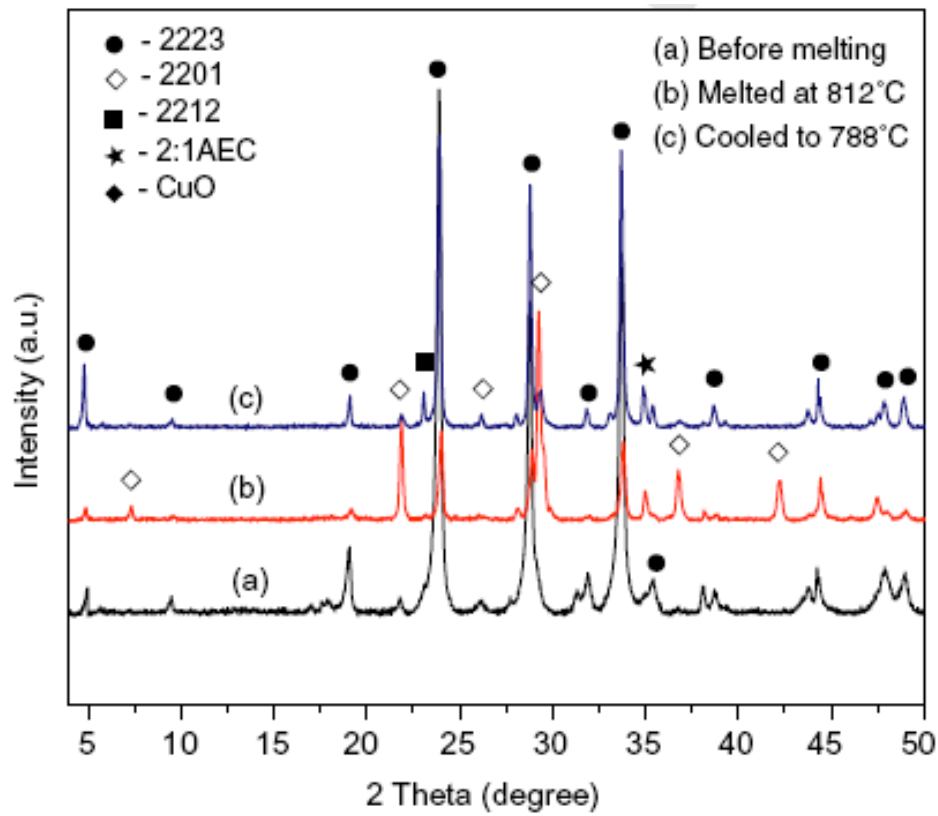


Fig.4

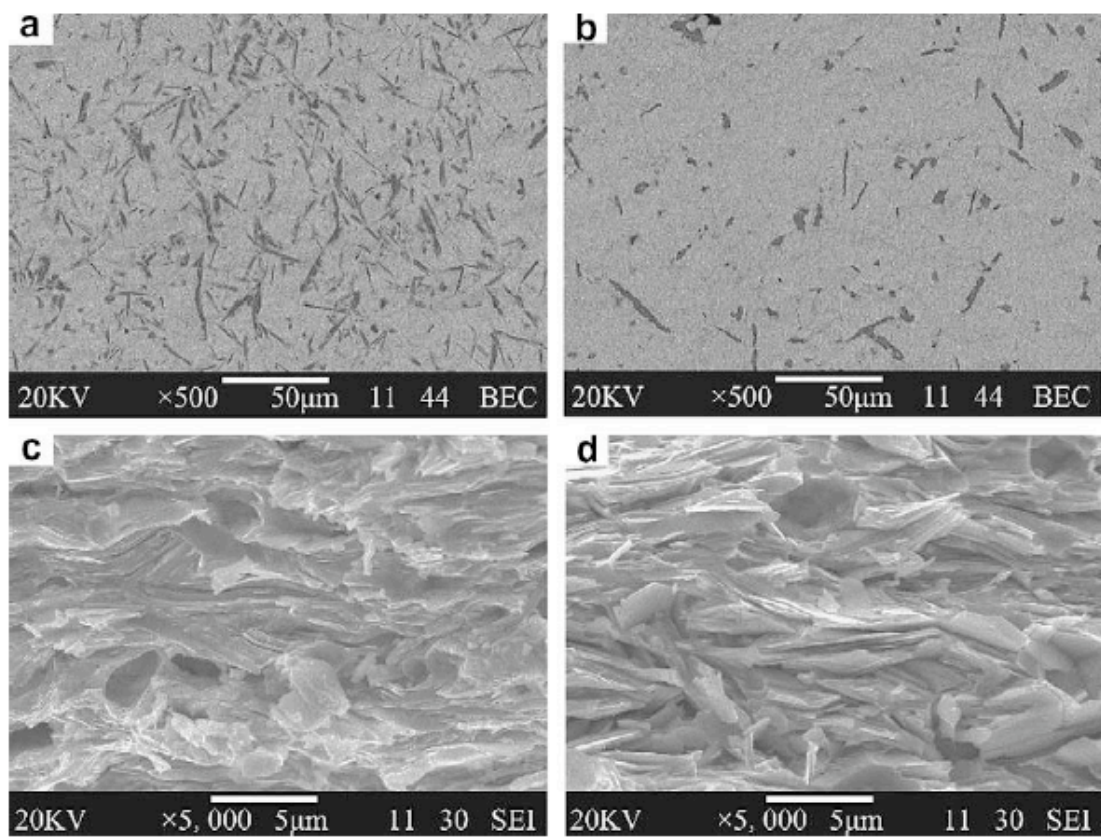


Fig. 5