

Critical Current Limiting Factors in Post Annealed $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ Tapes

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Abstract—Processing $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Bi-2223) tape by the oxide-powder-in-tube technique normally includes two heat treatments and one intermediate rolling. A three-step heat treatment was applied for the second heat treatment (HT2). Experimental procedures were designed for understanding the roles of each processing step in HT2 and the post anneal. It was found that post annealing improved the critical temperature T_c , critical current density J_c and flux pinning characteristic field H_p . The midpoint T_c was raised from 103 to 109 K by post anneal, while H_p was increased from 126 to 183 mT. Post anneal at about 790°C precipitated Pb from Bi-2223 phase to form a Pb-rich phase, thus the microstructure looked worse but T_c , J_c and H_p were raised. J_c was raised as the Bi-2212 phase signature in the T_c trace decreased. The most important observation is that raising T_c and minimizing residual Bi-2212 are decisive factors for increasing J_c at 77 K in Bi-2223 tapes.

Index Terms—Bi-2223, critical current density, critical temperature, $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ tape, post anneal.

I. INTRODUCTION

THE processing of long length Ag-clad $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Bi-2223) tapes is a complex, multi-parameter oxide-powder-in-tube process [1]–[3], which includes processing precursor powder, packing the powder into silver tube, mechanically deforming the loaded tube into a wire, and heat treating the wire twice with an intermediate rolling. The critical current limiting mechanisms are many and complex in Bi-2223 tape [3], [4]. The key to high performance is to improve the electrical connectivity, which is compromised by weak flux pinning regions, by lower T_c intergrowths [5], cracks or porosity [3], [4]. Slow cooling [6], two-step sintering [7], [8], and post anneal [9] have been found to improve the critical current density (J_c). This later two-step sintering involved a sintering step at 840°C, followed by a second step at 820°C in the second heat treatment [7], [8]. Both slow cooling and the second step of the two-step sintering were believed to convert the residual liquid or amorphous phase, which forms Bi-2201 at a normal cooling rate, into Bi-2212, thus improving connectivity [6]–[8].

In this work, we applied a three-step heat treatment to the second heat treatment (HT2), which included 36 hours at 828°C, 48 hours at 822°C and 24 hours at 805°C. The first step at 828°C is a bit higher than the normal Bi-2223 sintering

temperature 820–825°C in 0.075 atm. oxygen partial pressure. It was used for healing cracks created by intermediate rolling, and forming Bi-2223 phase under the belief that the higher temperature promotes more liquid to enhance the reaction. The second step at 822°C was applied for further Bi-2223 formation but with less liquid. The third step at 805°C was for reducing the residual liquid, similar to the second step of the two-step sintering [7], [8]. After HT2, samples were annealed for 24 hours at temperature between 750°C and 800°C. It was found that post annealing boosts the critical current density significantly. Thus, further experimental procedures were designed for understanding the roles of each processing step in HT2 and the post anneal. Two of the three steps of HT2 (822°C/48 h and 805°C/24 h), and 787°C/24 h were chosen for the further post anneal procedures. Cai *et al.* developed a technique for probing internal Bi-2212 intergrowths and grains by SQUID magnetometer that was applied to analyze the effect of post anneal on Bi-2212 intergrowth [10]. We found that raising T_c and minimizing Bi-2212 are decisive factors for increasing J_c in Bi-2223 tapes.

II. EXPERIMENTAL DETAILS

Monocore Bi-2223 tapes with powder composition of $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_{1.9}\text{Ca}_{2.0}\text{Cu}_{3.0}\text{O}_x$ were prepared by the oxide-powder-in-tube (OPIT) process, using a thermomechanical treatment based on two heat treatments (HT1 and HT2) and one intermediate rolling, as described previously [11]. The dimensions of the tape are 0.13 mm by 3.5 mm. HT1 was done at 828°C for 36 hours in a flowing 7.5% O_2 /balance N_2 atmosphere. After HT1, the tape thickness was reduced by 15–20% in one pass. As shown in Fig. 1, a three-step heat treatment was used for HT2, which includes 36 hours at 828°C, 48 hours at 822°C and 24 hours at 805°C. As shown in Fig. 2, samples after HT2 were annealed for 24 hours at temperature between 750°C and 800°C. It was suggested from Fig. 2 that the optimal temperature for the lowest temperature post anneal was between 770 and 790°C. Thus, 787°C was chosen for the post anneal. Further post anneal procedures are described in Fig. 1. Samples taken at the end of each stage were labeled TA-1 to TA-6.

Measurements of critical current (I_c) were made in liquid nitrogen in a 1 Tesla electromagnet with the magnetic field H applied perpendicular to the broad tape surface, making H nominally parallel to the c axis [12]. The criterion for I_c is 1 $\mu\text{V}/\text{cm}$ and J_c was defined as I_c/A , where A is the average of two or three Bi-2223 cross-section measurements. Magnetic moment was measured by zero field cooling (ZFC) samples to 5 K, then applying a field of 0.5 mT parallel to the broad tape surface

Manuscript received August 6, 2002. This work was supported by the Department of Energy – Energy Efficiency and Renewable Energy and also benefited from partial facilities support from the National Science Foundation – MRSEC on Nanostructured Materials and Interfaces.

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Digital Object Identifier 10.1109/TASC.2003.812057

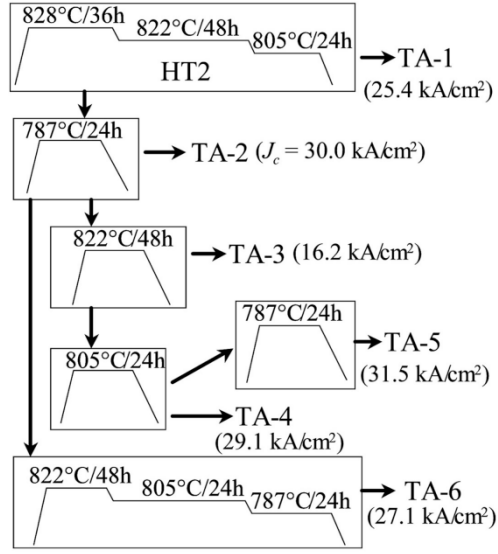


Fig. 1. Schematic diagram of heat treatment procedures and $J_c(0\text{ T}, 77\text{ K})$ for samples TA-1 to TA-6.

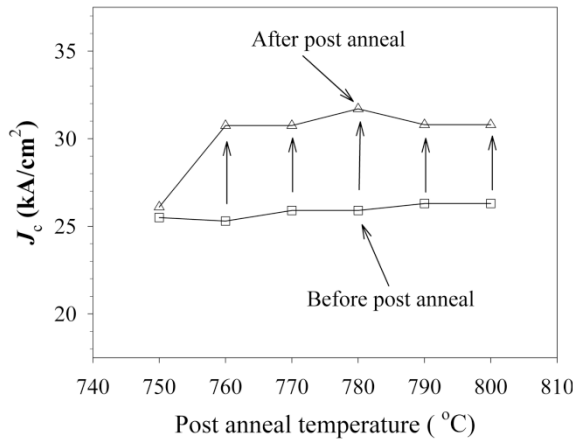


Fig. 2. Critical current density $J_c(0\text{ T}, 77\text{ K})$ versus the post anneal temperature for samples before and after post anneal at temperature between 750–800 °C. All samples before post anneal had been heat treated at 828 °C for 36 hours, 822 °C for 48 hours, and 805 °C for 24 hours.

in a Quantum Design magnetometer. Microstructural examinations were made in a JSM-6100 Scanning Electron Microscope (SEM).

III. RESULTS AND DISCUSSION

As shown in Fig. 2, J_c was improved from $\sim 26\text{ kA/cm}^2$ to $\sim 31\text{ kA/cm}^2$ (0 T, 77 K) for samples annealed at temperature between 760 °C and 800 °C. The J_c value for the sample annealed at 750 °C was almost the same as that before post anneal, even though a significant amount of Pb-rich phase (Pb-3221) was observed in this annealed sample by SEM and X-ray diffraction (XRD).

$J_c(0\text{ T}, 77\text{ K})$ and $J_c(0.1\text{ T}, 77\text{ K})$ are listed in Table I. The higher $J_c(0\text{ T})$, the higher $J_c(0.1\text{ T})$. After HT2, $J_c(0\text{ T}, 77\text{ K})$ was 25.4 kA/cm^2 for sample TA-1. As described in Fig. 1, TA-2 was obtained by annealing TA-1 at 787 °C for 24 hours, and $J_c(0\text{ T}, 77\text{ K})$ was raised to 30.0 kA/cm^2 . TA-3 was made by

TABLE I
TEMPERATURE OF LAST HT STEP, $J_c(0\text{ T})$ AND $J_c(0.1\text{ T})$ AT 77 K, CHARACTERISTIC FIELD H_p AND $T_c(50\%)$.

Sample	Last HT	$J_c(0\text{ T})$ kA/cm ²	$J_c(0.1\text{ T})$ kA/cm ²	H_p , mT	$T_c(50\%)$, K
TA-5	787 °C	31.5	9.9	183	108.6
TA-2	787 °C	30.0	8.8	180	107.6
TA-4	805 °C	29.1	8.5	179	107.0
TA-6	787 °C	27.1	7.6	171	106.4
TA-1	805 °C	25.4	6.8	163	105.7
TA-3	822 °C	16.2	3.7	126	103.4

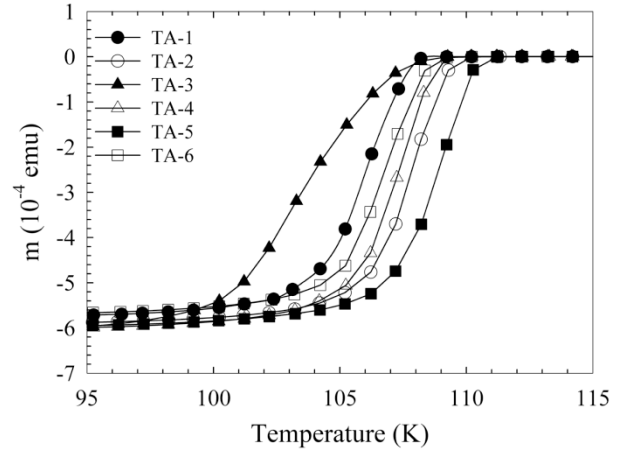


Fig. 3. Zero field cooled DC magnetization as a function of temperature for samples TA-1 to TA-6 measured by SQUID in a field of 0.5 mT parallel to the broad tape surface.

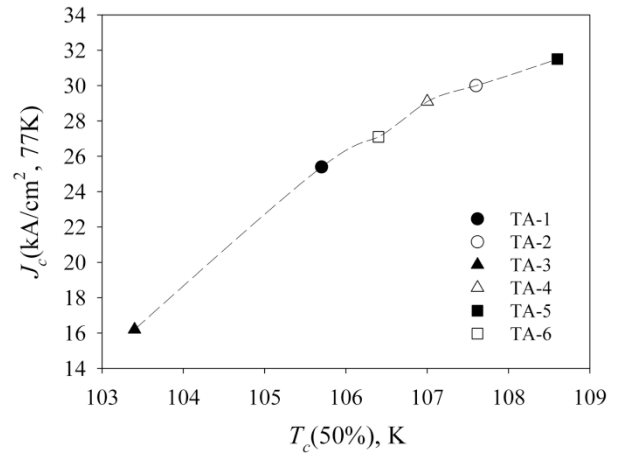


Fig. 4. $J_c(77\text{ K}, 0\text{ T})$ as a function of $T_c(50\%)$ for samples TA-1 to TA-6.

annealing TA-2 at 822 °C for 48 hours. This step was supposed to grow more Bi-2223 phase. But, in fact $J_c(0\text{ T}, 77\text{ K})$ for TA-3 dropped significantly, to 16.2 kA/cm^2 , only half that of TA-2. Sample TA-4 was prepared by annealing TA-3 at 805 °C for 24 hours, and $J_c(0\text{ T}, 77\text{ K})$ remarkably increased from 16.2 to 29.1 kA/cm^2 . Sample TA-5 was obtained by further annealing TA-4 at 787 °C for 24 hours. $J_c(0\text{ T}, 77\text{ K})$ of TA-5 further improved to 31.5 kA/cm^2 , even better than that of TA-2 (30.0 kA/cm^2). Another approach, TA-6, was to combine the three heat treatments, 822 °C/48 hours, 805 °C/24 hours and

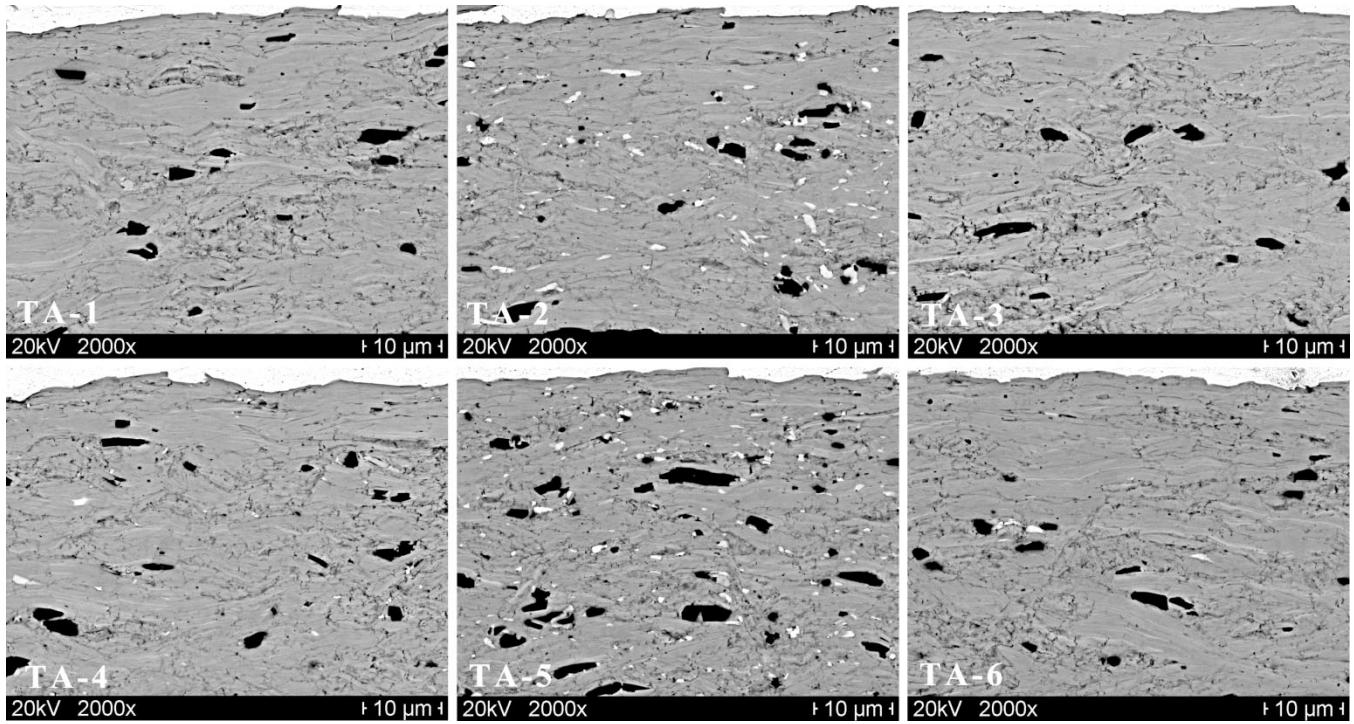


Fig. 5. Backscattered scanning electron microscopy images of cross sections for samples TA-1 to TA-6. The dark gray matrix, the white particles and the large black particles are Bi-2223, Pb-3221 and alkaline earth cuprate (AEC) phases $[(\text{Ca}, \text{Sr})_2\text{CuO}_3]$ and $[(\text{Ca}, \text{Sr})_{14}\text{Cu}_{24}\text{O}_x]$, respectively.

787 °C/24 hours into one heat treatment with three steps shown in Fig. 1. Sample TA-6 was obtained by annealing TA-2 in this way. So sample TA-6 had similar heat treatments to TA-5, except that TA-5 experienced cooling to and warming from room temperature between each HT step. $J_c(0 \text{ T}, 77 \text{ K})$ of TA-6 was 27.1 kA/cm², 20% lower than that of TA-5. Apparently the heating and cooling steps present in TA-5 and absent in TA-6 are beneficial for J_c .

Fig. 3 shows the T_c traces for samples TA-1 to TA-6. The onset T_c and transition width differed significantly, because the post anneal changes the T_c of Bi-2223. The midpoint values $T_c(50\%)$ are listed in Table I. It was found that $T_c(50\%)$ changes from 103.4 K for sample TA-3 to 108.6 K for sample TA-5. The values of $T_c(50\%)$ are plotted against J_c in Fig. 4. A strong correlation between J_c and T_c is found.

As reported previously [12], the $J_c(H)$ curves of Bi-2223 tape exhibit an exponential form above the self-field and weak-link dominated region, $J_c \sim \exp(-H/H_p)$, where the characteristic field H_p characterizes the in-field performance. As listed in Table I, H_p increased from 126 mT for TA-3 to 183 mT for TA-5. The important observation is that H_p exhibited the same trend as T_c , $J_c(0 \text{ T})$ and $J_c(0.1 \text{ T})$. The higher T_c , the higher J_c and H_p .

Fig. 5 shows backscattered SEM images for samples TA-1 to TA-6. It was found that annealing at 787 °C (TA-2, and 5) resulted in formation of Pb-3221, seen as white particles in the SEM images of samples TA-2 and TA-5, while annealing at 822 °C (TA-3) dissolved the Pb-3221 phase. The formation and decomposition of Pb-3221 in these samples were also confirmed by X-ray diffraction. As mentioned above and described in Fig. 1, samples TA-5 and TA-6 experienced similar post anneals, except that TA-5 was cooled and heated between HT

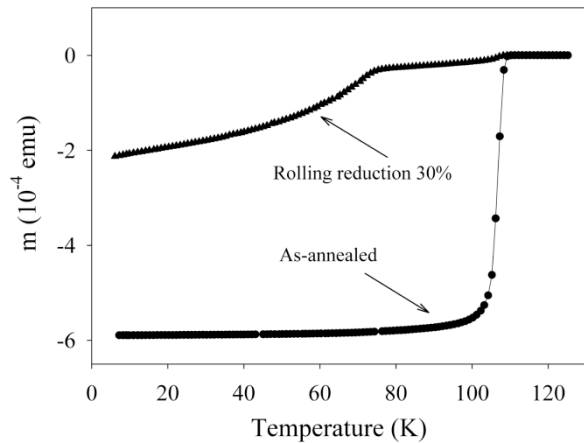


Fig. 6. Comparison of magnetic moment as a function of temperature for sample TA-6 as-annealed and after 30% rolling reduction. As indicated by the transition at 80 K in the rolled sample curve, the rolling deformation fragmented the tape and exposed the Bi-2212 intergrowth and grains.

steps. Eliminating the 2 heating and cooling steps markedly reduced the Pb-rich phase content in TA-6. This indicates that the heating and cooling helped the nucleation of the Pb-3221 phase. The reason is that the optimal formation temperature of Pb-3221 is about 750 °C and both the cooling and heating passed through this temperature. TA-5 contained the highest amount of Pb-3221, corresponding to the highest J_c . The precipitation of the Pb-3221 phase means that the Pb content in the Bi-2223 matrix is reduced. Thus, Pb may play a role in determining T_c . T_c variation with heat treatment was also observed by Däumling *et al.* [13]. The mechanism of the effect of post anneal may be complicated because forming Pb-3221 not only

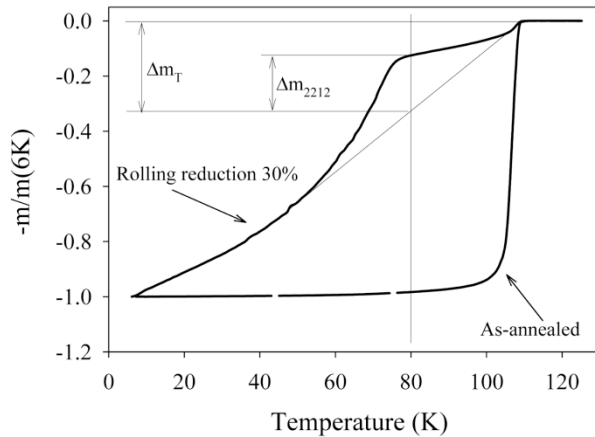


Fig. 7. Normalized magnetic moment as a function of temperature for samples TA-6 as annealed and after 30% rolling reduction. For quantitatively calculating the Bi-2223 content, a straight line is drawn between the high-temperature purely Bi-2223 component and the low-temperature magnetization in which all 2212 and 2223 shield flux. The contribution to magnetization at 80 K by 2212, and by both 2212 and 2223 are labeled as Δm_{2212} and Δm_T , respectively. The ratio $\Delta m_{2212}/\Delta m_T$ is defined as the relative amount of 2212.

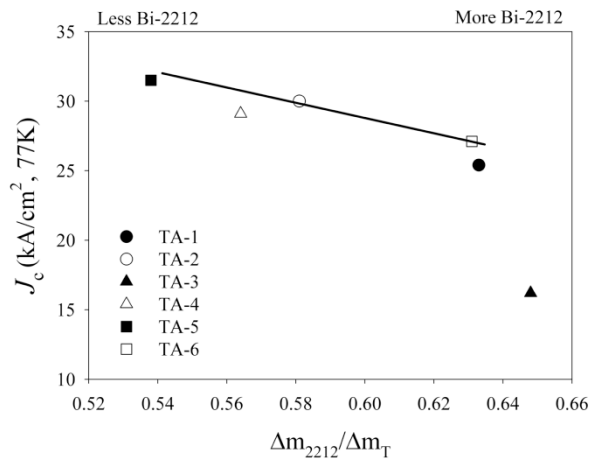


Fig. 8. Relative Bi-2212 content as a function of $J_c(0 \text{ T}, 77 \text{ K})$ for samples TA-1 to TA-6. The straight line is a guide to the eye.

pulls out Pb but also other elements such as Bi, Sr, and Cu from the Bi-2223 phase to form Pb-3221.

Fig. 6 shows the magnetic moment as a function of temperature for sample TA-6 as-annealed and after 30% rolling reduction. The rolling reduction fragmented the tape and exposed internal 2212 intergrowths and grains. The method for estimating the relative amount of Bi-2212 in the tape is described in Fig. 7 [10]. The relative amount of Bi-2212 against $J_c(0 \text{ T}, 77 \text{ K})$ for samples TA-1 to TA-6 is plotted in Fig. 8. A linear relation between J_c and the Bi-2212 content was found in these samples excluding sample TA-3. A similar relation was also found by Huang *et al.* in fully processed multifilamentary tapes [10]. But the data point of TA-3 is far away from the linear line in Fig. 8. This indicates that something in addition to Bi-2212 may play a

role in determining the properties of the lowest J_c sample TA-3. The Bi-2212 content of TA-3 was the highest, corresponding to the lowest J_c value. These results indicate that internal Bi-2212 intergrowths and grains play an important role in limiting J_c , as pointed out by Umezawa *et al.* [5].

IV. SUMMARY

We have investigated the effect of post anneal on J_c , T_c , Bi-2212 intergrowth and microstructure in monocoil Bi-2223 tapes. We conclude that raising T_c and minimizing residual Bi-2212 are decisive factors for increasing J_c at 77 K. The main findings are as follows:

- 1) HT finishing at 822 °C (TA-3) is really detrimental for J_c , T_c and H_p . T_c is lower in TA-3 and there is more Bi-2212 in TA-3 too.
- 2) There is a strong correlation between T_c and J_c . It had been thought that post anneal determined the doping level of Bi-2223 through precipitation of Pb-3221 and up take of O₂. Comparing TA-5 and TA-6, it seems as if precipitation of Pb-3221 may be more important. But there is also much more Bi-2212 in TA-6 than TA-5. So the Pb content in Bi-2223 and the amount of Bi-2212 present are linked.
- 3) The clean microstructures in TA-1 and 3 do not favor J_c . Higher J_c is seen for worse-looking microstructures (TA-2 and TA-5).

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