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Effect of additions of Ca compounds to the filling powder on the reduction of MgO and the critical current density properties of *ex situ* processed MgB₂ tapes



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ABSTRACT

We have studied the effect of additions of Ca compounds, CaC₂ and CaH₂, to the filling powder on the transport critical current density (J_c) properties of *ex situ* processed MgB₂ tapes. These additives are expected to reduce MgO present in as-received commercial MgB₂ powder and improve the grain coupling of MgB₂ in the tapes. Heat treatment of the hand mixed powders, MgB₂ and the Ca compounds, brings about both disappearance of MgB₄ and formation of CaB₆ and Mg, compared with heat treated MgB₂ powder. They are observed much more clearly for the mixtures with CaH₂ addition. The MgO content decreases by the additions, suggesting no reactions of substitutions of Ca for Mg and C for B in MgB₂. The J_c properties of the tape samples using the hand mixed filling powder with CaC₂ addition degrade, whereas those with CaH₂ addition are slightly improved. When using the ball milled mixtures, slight contraction of the *a*-axis parameter occurs only by CaC₂ addition. Although the additions cause the reactions similar to those observed for the hand mixed powders, the MgO content reduces more clearly, compared with the MgB₂ content. The J_c properties of the tape samples using the tapes are enhanced in the high-field and low-field regions by the additions of CaC₂ and CaH₂, respectively. These enhancements are attributed to the carbon substitution, the improved grain coupling and the increased content of MgB₂.

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1. Introduction

Since the discovery of superconductivity in MgB₂ [1], this material has been developed as a substitute for Nb–Ti in such applications as cryocooled systems [2,3]. As a fabrication process for the conductor, the powder-in-tube (PIT) technique has been widely adopted [4,5]. Alternatively, the internal Mg diffusion (IMD) process has been developed [6–8], which uses a Mg rod and B powder.

In the PIT technique two processes, *in situ* and *ex situ*, are used. For both processes, the quality of the filling powder is important to obtain superior critical current density (J_c). The surfaces of the filling powders for both processes are gradually contaminated in air, by oxygen and moisture. These damaged surface layers act as obstacles during sintering or reaction to the superconducting phase

and result in weak coupling of grains and hence poor J_{c} [9–11].

Compared with the *in situ* process, the *ex situ* processed wires and tapes show relatively poor J_c properties because the abovementioned weak coupling is more serious [12]. Furthermore, high-temperature heat-treatment required for the improvement of grain coupling results in the decomposition of MgB₂ and the formation of impurity phases such as MgB₄ acting as obstacles to the supercurrent path in the *ex situ* process.

Nevertheless the *ex situ* process still has the advantage of a high density of the MgB₂ layer over the *in situ* process [12]. The low density of the core layer in the *in situ* process is due to the large volume reduction at the formation of MgB₂ from Mg and B powder mixtures. This low density is a disadvantage for the fabrication of wires and tapes with a fine multi-filament structure, which is essential for stabilization of the conductors.

We previously reported that the J_c properties of *ex situ* processed tapes in the high-field region are improved when using commercially available MgB₂ powder treated with organic acid solutions



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[13]. This treatment brings about the dissolution of MgO on the surface layers and helps promote subsequent carbon substitution for boron in heat-treated tapes. The treatment with just organic solvent such as pure benzene does not cause the carbon substitution, suggesting that the dissolution of the MgO layers is required for the substitution reaction. Carbon substitution is one of the most effective techniques to improve the J_c properties in the high-field region due to the enhancement of the upper critical field (B_{c2}) [14,15]. Alternatively, the MgO surface layers are mechanically removed by a ball-milling process, which is also effective in promoting the carbon substitution reaction [16–19].

MgO is reduced with CaC₂, in accordance with the following reaction [20]:

$$MgO + CaC_2 \rightarrow Mg + CaO + 2C \tag{1}$$

This reaction starts to occur around 900 °C. In the reaction of degraded MgB₂ and CaC₂, MgO surface layers are expected to be removed. Such reaction can also occur for other Ca compounds. In case of CaC₂, resultant product C can act as a source for the carbon substitution, in accordance with the following reaction:

$$MgB_2 + pC \rightarrow MgB_{2-p}C_p + pB \tag{2}$$

The released B from MgB₂ in (2) may react with Mg in (1) to form MgB₂ or the excess CaC₂ to form CaB₆. Here the reduction of MgO on the surface layers is expected to improve the coupling of MgB₂ grains and the possible formation of MgB₂ and CaB₆ means the collection of the B released from MgB₂ in (2). The local formation of MgB₂ and CaB₆ may suppress the deterioration of the grain coupling compared with the released B scattered all over the samples, although CaB₆ is non-superconducting phase.

In this paper first we study the reactions of MgB_2 with Ca compounds, CaC_2 and CaH_2 , and then the superconducting properties of *ex situ* processed tapes using MgB_2 powder with the additions of those compounds.

2. Experimental

MgB₂ (Alfa Aesar; 325 mesh) was mixed with CaC₂ (Aldrich; 80% in purity; pieces) or CaH₂ (Strem Chemicals; 95%, granules) with molar ratios of MgB₂: R = 100: x ($R = CaC_2$ and CaH₂; x = 0, 1, 3, 6 and 10). The CaC₂ pieces and the CaH₂ granules were preliminary crushed in an agate mortar in an Ar gas-filled glove box. The above-mentioned mixtures were obtained by hand and through a ball milling process. In the milling process, 2 g of those mixtures were put in a WC jar and ball milled at a speed of 500 rpm with 5-mm diameter WC balls for 1 h. The mixtures obtained by those two techniques were pelletized and then sealed in a stainless steel tube in an Ar atmosphere. Subsequently they were heat treated at 800–920 °C for 1 h.

Some of those mixtures were packed into a Fe tube with an outer diameter of 6.35 mm and an inner diameter of 3.5 mm and subsequently sealed in the glove box. Then, they were deformed into a rectangular-shaped tape, with a width of 4 mm and a thickness of 0.6 mm, by means of groove rolling and flat rolling machines. These tapes were heat treated at 800-950 °C for 1 h in a flow of Ar gas. Multiple powder and tape samples were prepared to check reproducibility.

Chemical analyses on the ball milled powders were carried out by inductively coupled plasma (ICP) - optical emission spectroscopy (OES) with an Agilent 720-ES. The analyses were performed twice for the same powder to check reproducibility. Thermogravimetric Analysis (TGA) was performed with a MAC Science TG-DTA2000 differential thermogravimetric analyser at a heating rate of 5 °C/ min in a flow of Ar gas. The packing factor of the core layer in the tape samples using MgB_2 powder was calculated by dividing the density of the core by that of MgB_2 , 2.63 g/cm³. The density of the core was estimated by dividing the mass of a piece of the core by the volume of the piece. The volume was roughly calculated by measuring the size of the piece with a vernier calliper.

Phase identification was carried out by an X-ray diffraction (XRD) method with a Rigaku RINT-TTR III X-ray diffractometer with Cu K α radiation. XRD patterns of the tape samples were recorded after peeling off the Fe sheath. Therefore, the interface region between the core layer and the sheath was investigated. The microstructural observation was performed with a Hitachi SU-70 scanning electron microscope (SEM) with an energy dispersive X-ray (EDX) spectrometer.

The temperature dependence of the direct-current (dc) magnetization was measured for the heat-treated tape samples by means of a Quantum Design MPMS XL superconducting quantum interference device (SQUID) magnetometer. The dc magnetization measurements were carried out at temperatures above 5 K in a field of 10 Oe in a zero-field cool (ZFC) mode. The fields were applied perpendicularly to the tape surface after peeling off the Fe sheath. The critical temperature (T_c) was defined as the onset temperature at which a diamagnetic signal was observed. The dc critical current (I_c) measurement of the tape samples was carried out at 4.2 K and in fields up to 12 T applied parallel to the tape surface by a conventional four-probe resistive method. The I_c criterion was 1 μ V/cm.

3. Results and discussion

3.1. Powder sample

The as-received CaC_2 powder exhibited light red brown colour and XRD data recorded under Ar atmosphere indicated that it contains CaO as main impurity. By a reference intensity ratio (RIR) method, the CaO content was estimated about 7wt%. On the other hand, the as-received CaH₂ powder showed white colour and some negligible small peaks unassignable to MgB₂ in the XRD pattern.



Fig. 1. A TGA curve of as-received CaH_2 powder. The sample weight starts to decrease around 700 °C, as indicated by an arrow.

Fig. 1 shows a TGA curve of as-received CaH₂ powder. The profile shows a decrease of the sample weight starting around 700 °C. This suggests that CaH₂ starts to release H₂ gas around this temperature.

Fig. 2(a) and (b) shows XRD patterns of sintered hand mixed powders with the additions of CaC_2 and CaH_2 with x = 10. Here the XRD pattern of sintered pure MgB₂ powder is also shown in Fig. 2(c). The sintering temperature for those samples was 920 °C. which is optimized for the I_c properties of the tape samples using those hand mixed powders. The sintered MgB₂ contains a trace of MgO and MgB₄. The MgB₄ was not observed in the as-received MgB₂ powder. MgB₄ is formed by the decomposition of MgB₂ in the sample without addition. Some XRD peaks which cannot be assigned to MgB₂ are observed for Fig. 2(a) and (b). These impurities were identified as MgO, CaB₆ and Mg. Although they are observed for both samples, those other than MgO are less clearly observed for the sample with CaC₂ addition. XRD peaks assigned to CaB_6 were more appreciable with increasing x, and those assigned to other Ca compounds and MgB₄ are not detected for both samples.

XRD patterns of the sintered ball milled powders with the additions of CaC₂ and CaH₂ with x = 6, and without addition are shown in Fig. 3(a) – (c), respectively. The sintering temperature for those samples was 850 °C, which is optimized for the J_c properties of the tape samples using those ball milled powders. Compared with the sintered pure MgB₂ powder shown in Fig. 2(c), the corresponding sintered ball milled sample shows additional XRD peaks, which are assigned to WC. The content of WC in the ball milled MgB₂ powder was around 1mass% by ICP analysis. Furthermore, XRD peaks assigned to MgB₄ are much more appreciable. The additions of the Ca compounds result in the formation of CaB₆ and the reduction of MgB₄, which was also observed for the sintered hand mixed samples, as shown in Fig. 2(a)–(c). In the samples with the additions, the Ca compounds react with MgB₄ or decomposed MgB₂ to form CaB₆ and reduce the formation of MgB₄.

XRD peaks assigned to Ca compounds other than CaB_6 were not detected for both sintered hand mixed and ball milled samples with the additions of the Ca compounds. However, some of the observed XRD peaks assigned to CaB_6 were broad for those samples with CaC_2 addition. This suggests that the XRD peaks assigned to



Fig. 2. XRD patterns of sintered hand mixed powders with the starting compositions of MgB₂: R = 100: 10 (R = (a) CaC₂ and (b) CaH₂), together with the pattern of (c) sintered pure MgB₂ powder. The sintering temperature was 920 °C. XRD peaks assigned to MgB₂ are indexed, whereas the peaks assigned to MgO, CaB₆, MgB₄ and Mg are indicated by triangles, rectangles, rhombuses and circles, respectively.



Fig. 3. XRD patterns of sintered ball milled powders with the starting compositions of MgB₂: R = 100: 6 (R = (a) CaC₂ and (b) CaH₂), and (c) sintered ball milled pure MgB₂ powder. The sintering temperature was 850 °C. XRD peaks assigned to MgB₂ are indexed, whereas the peaks assigned to MgO, CaB₆, MgB₄ and WC are indicated by triangles, rectangles, rhombuses and circles, respectively.

unknown phases which are possibly formed by the reaction between MgB_2 and the impurities in the as-received CaC_2 are superimposed on those of CaB_6 .

Fig. 4(a) and (b) shows the region of 102 peak of MgB₂ and 220 peak of MgO in the XRD patterns of the sintered hand mixed and ball milled powders shown in Fig. 2(a)–(c) and Fig. 3(a)–(c), respectively. Tables 1 and 2 list the content of each phase observed in those sintered samples. Regarding the relative intensity between the 102 peak and the 220 peak, the relative intensity of the 220 peak does not change remarkably by the additions of the Ca compounds for the sintered hand mixed samples. The MgO content was estimated to be 12.0(19)wt% for sintered pure MgB₂, whereas those were 10.4(9) and 8.5(3)wt% for the additions of MgB₂ to MgO were 6.8, 7.7 and 8.1 for those samples.

For the sintered ball milled samples, in contrast, the relative intensity clearly decreases by the additions. The MgO content was estimated to be 8.4(5)wt% for sintered pure MgB₂, whereas those were 4.9(6) and 8.1(3)wt% for the additions of CaC₂ and CaH₂, respectively. The corresponding MgB₂ contents were 65.0(17), 81(3) and 78.6(13)wt%, and the content ratios of MgB₂ to MgO were 7.7, 16.5 and 9.8 for those samples. The decrease of MgB₄ and MgO is linked with the increase of MgB₂ and CaB₆ for the samples with the additions of the Ca compounds.

Although 220 peak of CaB_6 and 303 peak of MgB_4 are superimposed on 102 peak of MgB_2 [21,22], the contents of CaB_6 and MgB_4 are low in those samples, compared to that of MgB_2 . Furthermore, the relative intensities of the 220 and the 303 peaks to the strongest peaks of CaB_6 and MgB_4 are 47.3/1000 and 1.3/ 1000, respectively. Therefore, the contribution to the intensity of the 102 peak of MgB_2 by those impurities is negligible. Thus, the reduction of MgO and the increase of MgB_2 occur by the additions of the Ca compounds. This is more effective through the ball milling process, probably because the as-received materials are damaged by moisture and oxygen and the ball milling process successfully improves the reactivity of those materials.

Fig. 5(a) and (b) shows 002 and 110 XRD peak profiles of MgB₂ in various sintered ball milled powders, respectively. The profiles are shown for the samples with the additions of the Ca compounds and



Fig. 4. The profiles of 102 XRD peak of MgB₂ and 220 XRD peak of MgO for (a) sintered hand mixed powders with the additions of (i) CaC_2 and (ii) CaH_2 with x = 10 and (iii) without addition. (b) The corresponding profiles for sintered ball milled powders with x = 6 and without addition.

Table 1 The content of each phase observed in the sintered hand mixed powders with the additions of the Ca compounds with x = 10 and without addition. The content was estimated with the XRD patterns of Fig. 2 by a RIR method in wt %.

| Sample | MgB ₂ | MgO | MgB ₄ | CaB ₆ | Mg |
|------------------|------------------|----------|------------------|------------------|---------|
| $CaC_2 (x = 10)$ | 80(3) | 10.4(9) | - | 5.2(3) | 4.53(9) |
| $CaH_2 (x = 10)$ | 69(3) | 8.5(3) | - | 18(5) | 3.2(1) |
| $MgB_2 (x = 0)$ | 82(5) | 12.0(19) | 5.8(4) | — | - |

Table 2

The content of each phase observed in the sintered ball milled powders with the additions of the Ca compounds with x = 6 and without addition. The content was estimated with the XRD patterns of Fig. 3 by a RIR method in wt %.

| Sample | MgB ₂ | MgO | MgB ₄ | CaB ₆ | WC |
|-----------------|------------------|--------|------------------|------------------|---------|
| $CaC_2 (x = 6)$ | 81(3) | 4.9(6) | 8.3(12) | 3.9(1) | 1.7(1) |
| $CaH_2 (x = 6)$ | 78.6(13) | 8.1(3) | 3.45(3) | 8.9(3) | 0.98(3) |
| $MgB_2 (x = 0)$ | 65.0(17) | 8.4(5) | 26.3(11) | - | 0.36(7) |

without addition. The positions of those XRD peaks do not shift appreciably by CaH₂ addition. The corresponding sintered hand mixed sample did not show an appreciable peak shift, either. These indicate no variation of the lattice parameters of MgB₂ by CaH₂ addition for both sintered hand mixed and ball milled samples.

Regarding the CaC_2 addition, the positions of those XRD peaks did not shift appreciably for the sintered hand mixed sample, either. In contrast, for the sintered ball milled sample, a slight shift of the 110 peak is observed, whereas a shift of the 002 peak is not appreciable. This indicates the contraction of the *a*-axis parameter of MgB₂.

Although attempts of preparation of Ca-substituted MgB₂, Mg_{1-z}Ca_zB₂, have been carried out so far, the substitution reaction does not take place even under high-pressure (HP) heat-treatment under 3.5 GPa and 900 °C when using CaH₂ as a starting material, judging from that the CaH₂ or Ca doping does not change the lattice parameters of MgB₂ [23]. On the other hand, when using Ca₃B₂N₄ as a Ca source, the HP heat-treatment under 5 GPa and 1100 °C brings about the formation of Mg_{1-q}Ca_qB₂ and both the *a*-axis and the *c*- axis parameters of $Mg_{1-q}Ca_qB_2$ increase with increasing q [24]. Therefore, taking into account the results that no appreciable variation of the lattice parameters of MgB_2 is observed by the additions of the Ca compounds and that the CaB_6 content increases with increasing x for those samples, Ca is probably not incorporated into the MgB_2 lattice. This is presumably due to the insufficient pressure for the reaction.

Therefore, slight contraction of the *a*-axis parameter suggests that carbon substitution occurs in the sintered ball milled samples with CaC₂ addition. CaC₂ acts as carbon source for the substitution reaction. The carbon substitution decreases the *a*-axis parameter of MgB₂, while the *c*-axis parameter is not influenced by the substitution [15,25,26]. The substitution amount was estimated to be p = 0-0.01 in MgB_{2-p}C_p from the *a*-axis parameter.

3.2. Tape sample

No binary compounds are reported in the Ca–Fe system [27] and XRD analyses on the tape samples indicated that only Fe_rB (r = 1 and 2) are present at the interface region.

Fig. 6(a) and (b) shows dc magnetization curves as a function of temperature for various tapes using filling powders with the additions of CaC₂ and CaH₂, respectively, together with the curves of the tapes using MgB₂ powders without addition. The magnetization *M* is normalized to that measured at 5 K, *M*(5K), for each tape. The transition widths (ΔT_{c} s), defined as 10–90% transition, of the magnetization curves increased with increasing *x* for the tape samples using the hand mixed filling powders with the additions of the Ca compounds. The increase of the ΔT_{c} was much larger for the samples with CaC₂ addition. The ΔT_{c} values were 7.6 and 4.3 K for the samples with the additions of CaC₂ and CaH₂ with *x* = 10, respectively, whereas the corresponding value was 0.9 K for the sample without addition.

The ball milling process decreased the T_c and increased the ΔT_c for the tapes using pure MgB₂ powder. They are probably caused by the stress in MgB₂ crystal and the increased content of MgB₄ and WC particles, which were brought about by the milling process. Tapes using ball milled powders with CaH₂ addition does not show the increase of the ΔT_c appreciably as those using the



Fig. 5. (a) 002 and (b) 110 XRD peak profiles of MgB₂ in sintered ball milled powders with the starting compositions of MgB₂: R = 100: 6 (R = (i) CaC₂ and (ii) CaH₂), together with (iii) the profiles in sintered ball milled pure MgB₂ powder. The dashed lines are drawn at $2\theta = 52.0^{\circ}$ and 60.0° for (a) and (b), respectively.



Fig. 6. Temperature dependence of the dc magnetization curves for various tapes using the hand mixed and ball milled powders with the starting compositions of x = 0, 1, 6 and 10 in MgB₂: R = 100: x (R = (a) CaC₂ and (b) CaH₂). The measurements were carried out in a magnetic field of 10 Oe in a zero-field cool (ZFC) mode. The magnetization *M* is normalized to that measured at 5 K, *M*(5K), for each tape.

corresponding hand mixed powders. In contrast, CaC_2 addition causes tremendous broadening. The sample with CaC_2 addition with x = 6 shows very broad transition with a kink at about 22 K. The increase of the ΔT_c suggests weak coupling of grains. Therefore, CaH_2 addition does not cause remarkable weak coupling, whereas severely weak coupling occurs by CaC_2 addition when $x \ge 6$. This severely weak coupling is probably brought about by the impurities in the as-received CaC_2 , since the addition of CaC_2 reduces MgO, which is considered the obstacles to the supercurrent path, more effectively than that of CaH_2 , as shown in Fig. 4(b) and CaB_6 formed in the sintered samples is main impurity phase for both additives. Furthermore, the content of another main impurity phase MgB₄ in the samples with CaC_2 addition is much lower than that in the sample without addition. The sample without addition shows smaller ΔT_{c} , compared with those with CaC₂ addition.

Fig. 7(a) and (b) shows the transport J_c as a function of magnetic field for the tapes using the filling powders with the additions of CaC₂ and CaH₂, respectively. For the hand mixed filling powders, the optimized heat treatment temperature at which the best performance in J_c was obtained did not change remarkably by the additions of the Ca compounds. The J_c properties of the tapes using powders with CaC₂ addition slightly degrade with increasing x. In contrast, they are improved by the addition of a slight amount of CaH₂, $x \le 3$. However, further addition degrades the J_c properties and tapes using the powders with $x \ge 6$ in the J_c property are inferior to those with x = 0.



Fig. 7. Transport J_c at 4.2 K as a function of magnetic field for various tapes using the hand mixed and ball milled powders with the starting compositions of x = 0, 1, 3, 6 and 10 in MgB₂: R = 100: x (R = (a) CaC₂ and (b) CaH₂). The magnetic field was applied parallel to the tape surface.

The ball milling process decreased the optimized heat treatment temperature by 50–80 °C, which was independent of the additives. The J_c property of the tape with x = 0 is enhanced by the process in spite of the increase of the volume fraction of MgB₄ and the J_c value at 9 T is improved by two orders of magnitude. Such J_c improvement by using ball milled filling powder was reported for the *ex situ* processed wires and tapes [16–19,28]. The difference between the packing factors of the core of the tapes with x = 0 using the asreceived and the ball milled MgB₂ powders was not appreciable and the factors were 0.55–0.60 for both powders. This J_c enhancement is probably due to the increased pinning force and enhanced B_{c2} by grain refinement [28].

The additives further improve the I_c properties. The I_c properties are enhanced in the high-field and low-field regions for the tapes with the additions of CaC_2 and CaH_2 , respectively. These J_c enhancements are observed just for $x \leq 3$ for both additives. The samples with $x \ge 6$ show significant J_c degradation, that is independent of the additives. Especially, the samples with CaC₂ addition with $x \ge 6$ did not carry supercurrent at all. This is probably because CaB₆ formed by the additions of the Ca compounds is not negligible to the grain coupling for $x \ge 6$ and the as-received CaC₂ contains a substantial amount of impurities such as CaO. Those already existing impurities and/or impurities produced after heat treatment of the samples other than CaB₆ can act as obstacles to the supercurrent path. The formation of such newly produced impurities is suggested by the broadenings of XRD peaks in the sintered ball milled powder samples with CaC₂ addition, as mentioned above. For the tapes with CaC₂ addition, those impurities cause large ΔT_c and the kinks in the transition curves shown in Fig. 6(a), and hence weak coupling of MgB₂, although substantial *I*_c enhancement was expected from the large reduction of MgO observed for the sintered ball milled samples with CaC₂ addition.

The field dependence of the J_c properties for the tapes using ball milled powders with CaC₂ addition with $x \le 3$ was lower than that for the corresponding tape with x = 0. This is due to enhanced B_{c2} brought about by carbon substitution [14,15]. The sintered ball milled sample with CaC₂ addition shows a slight shift of the 110 XRD peak of MgB₂, as shown in Fig. 5(b), suggesting a slight amount of carbon substitution.

The J_c enhancement by CaC₂ addition was observed only when using the ball milled filling powders. This is probably because the as-received CaC₂ and MgB₂ powders were contaminated by moisture and oxygen. The ball milling process can remove those damaged surface layers and activate those powders. Thus, the reactions of the reduction of MgO and the substitution of carbon which is supplied from the CaC₂ are promoted, although the substation amount is currently close to 0.

For the samples with CaH₂ addition, when the using hand mixed filling powders, J_c enhancement in the high-field region is observed for small x. In contrast, when using the ball milled filling powders, the J_c enhancement shows an opposite trend. The J_c enhancement in the low-field region is clearly observed, while that in the highfield region is not appreciable. The field dependence of the J_c properties of the tapes using the hand mixed powders is almost the same as that using the ball milled powders. This enhancement is probably due to the improved grain coupling and the increased content of MgB₂, since the ΔT_c of the tape with x = 1 is smaller than that of the tape with x = 0, as shown in Fig. 6(b).

Fig. 8(a) – (c) shows SEM images of the fractured surface of the core layer of the tapes using the ball milled powders without addition and with the additions of CaC₂ and CaH₂ with x = 6, respectively. The average grain size of MgB₂ decreases by the ball milling process from several hundred to a few hundred microns for the tape using the powder without addition. The CaC₂ addition does not change the grain size remarkably, whereas the CaH₂ addition improves the grain connectivity and promotes the grain growth up to 1 µm. CaH₂ starts to decompose and release H₂ at around 700 °C and the melting point of Ca is 842 °C. The Ca acts as reducing agent for MgO and probably promotes the grain growth of MgB₂.

Elemental mapping for the fractured surface of the core layer of the tapes using the ball milled powders with the additions of the Ca compounds revealed that Ca-rich region is present in the core layer in those tapes. However, CaB_6 grains were not detected clearly by SEM. In contrast, WC particles with the size of a few hundred nanometres were observed clearly.



Fig. 8. SEM images of the fractured surface of the core layer of the tapes using the ball milled (a) MgB₂ powder and mixtures with the starting compositions of x = 6 in MgB₂: R = 100: x (R = (b) CaC₂ and (c) CaH₂).

4. Conclusion

Heat treatment of MgB₂ powder with the additions of Ca compounds, CaC₂ and CaH₂, results in the formation of CaB₆ and Mg. The MgO content in those samples decreases compared with that in the sintered pure MgB₂ powder. This is due to the reduction of MgO by the Ca compounds. The lattice parameters of MgB₂ do not change appreciably by CaH₂ addition, whereas the *a*-axis parameter contracts slightly by CaC₂ addition when using ball milled mixtures. Ca is probably not incorporated into the MgB₂ lattice and the variation of the lattice parameters in the samples with CaC₂ addition is attributed to carbon substitution. The *J*_c properties of the tapes are enhanced in the high-field and low-field regions by the additions of CaC₂ and CaH₂, respectively when using the ball milled mixtures as filling powders. These enhancements are attributed to the carbon substitution, the improved grain coupling and the increased content of MgB₂.

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