Influence of Metal Diboride and Dy₂O₃ Additions on Microstructure and Properties of MgB₂ Fabricated at High Temperatures and under Pressure

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High temperatures and under pressure (HTP) processing has been used to study the effects of chemical doping in MgB₂. ZrB₂, TiB₂ and NbB₂ were selected as additives since, like MgB₂, they have an AlB₂-type structure and similar lattice parameters. Dy₂O₃ was selected as it has been reported to generate nanoscale, secondary intragrain phases in MgB₂. While C is known to enter the B-sublattice readily, attempts to dope Zr and other elements onto the Mg site have been less successful due to slow bulk diffusion, low solubility in MgB₂, or both. We have used high-temperature, solid-state sintering (1500 °C), as well as excursions through the peritectic temperature (up to 1700 °C), to investigate both of these limitations. Bulk MgB₂ samples doped with MB₂ (M = Zr, Ti and Nb) and Dy₂O₃ additions were synthesized and then characterized. Lattice distortion and high densities of crystal defects were observed in the MgB₂ grains around nano-sized MB₂ inclusions, this highly defected band contributed to a large increase in $B_{c2}$ but was not large enough to increase the irreversibility field. In contrast, distributed intragrain precipitates were formed by Dy₂O₃ additions which did not change the lattice parameters, $T_c$, $T_c$ distribution or $B_{c2}$ of MgB₂, but modified the flux pinning.

Extensive efforts have been expended in doping MgB₂ to enhance its superconductive properties, particularly its upper critical field, $B_{c2}$. The substitution of C for B has been shown to significantly increase MgB₂’s $B_{c2}$ beyond that of the unalloyed sample1–6. Unfortunately, C doping is successful only at low temperatures (<20 K) since it reduces $T_c$ and increases electron impurity scattering only in the $\sigma$ band, leaving the high temperature (>20 K) $B_{c2}$ unchanged or even reduced. In order to enhance the $B_{c2}$ of MgB₂ in the higher temperature regime, many attempts have been made to find effective dopants for Mg-site substitution to increase electron impurity scattering in both the $\sigma$ band and the $\pi$ band7,8, but without much success in terms of improved properties. Although the substitution of Al for Mg has been demonstrated, it was found to reduce $B_{c2}$9,10.

Further studies focusing on the AlB₂-like metal diborides ZrB₂, TiB₂ and NbB₂, (e.g. refs 11–16) yielded contradictory results. Feng et al.11,12 reported an enhancement in $B_{c2}$ in response to 10 mol% Zr doping; Bhatia et al.13 observed a significant increase in $B_{c2}$ (from 20.5 T to 28.6 T at 4.2 K) after adding 7.5 mol% ZrB₂ to MgB₂ bulks. On the other hand, Zhang et al.14 reported no $B_{c2}$ enhancement in ZrB₂-doped MgB₂ tapes. In any case, $B_{c2}$ enhancements have been noted by various researchers working with MgB₂ PIT or powder type processes, no one has reported enhanced transport current, suggesting that the effect may be in a surface layer. The one effort to date which has clearly injected Zr deeply into the grain, resulting in a pulsed laser deposition (PLD) synthesized ZrB₂-doped MgB₂ thin film15,16, showed a much stronger response to the presence of Zr, and in this case a decrease of $T_c$ and $B_{c2}$ with increasing Zr content. These various observations give rise to the question: what is the actual influence of Zr doping in MgB₂? The possible roles of Zr in MgB₂ can be summarized in terms of: 1) extrinsic effects, such as modified intergranular connectivity and reduced grain size11,12; 2) intrinsic effects, such as an influence on $B_{c2}$ of Zr substitution for Mg13–16, or increased flux pinning by a distribution of nano-sized ZrB₂/Zr

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precipitates. On the other hand, incomplete microscopic evidence of Zr substitution for Mg has been provided, at least for materials made by equilibrium processes (contrasting to the non-equilibrium processing of the films of \( \text{ZrB}_2 \)). Therefore further study on the limits of Zr doping was deemed necessary.

There are many roadblocks to clarifying the true role of chemical doping in MgB\(_2\). Chief among them is that homogeneous doping is very hard to achieve. Traditional powder synthesis is generally performed at 600–1000 °C – too low to form homogeneously doped samples. To overcome this problem a high temperature under pressure (HTP) route (see below) was developed to explore solubility limits of dopant species in MgB\(_2\) and maximize diffusion during reaction. MgB\(_2\) bulks synthesized by HTP should have a greater depth of dopant penetration into the MgB\(_2\) for any species introduced (if it is soluble) given the increase in diffusion rate at higher temperatures. HTP samples also have large grain size (over 5 \( \mu \text{m} \)) making chemical analysis easier. The purpose of the HTP method is to minimize any diffusion limitations so that we can explore the solubility limits of doping, rather than to fabricate MgB\(_2\) bulk samples with high \( J_c \). Also, the use of existing metal diborides (MB\(_2\)) with a structure isomorphous to MgB\(_2\) (P\( \text{6}_3/m\text{mmm} \)) as a vector for effective metal element doping is a promising way to investigate possible changes of superconducting properties like \( B_{c2} \) and \( T_c \). Thus, three sets of MgB\(_2\) bulks doped with ZrB\(_2\), TiB\(_2\) and NbB\(_2\) powders were prepared.

Most additions which have been attempted for MgB\(_2\) tend to accumulate at the grain boundaries, with the exception of the above-mentioned C-bearing additions. On the other hand, several studies have shown that a very small amount of Dy\(_2\)O\(_3\) can form nanosize precipitates within the MgB\(_2\) grains and thereby enhance flux pinning without changing \( T_c \). Thus a Dy\(_2\)O\(_3\) doped MgB\(_2\) bulk was also included in this study for comparison.

The changes in microstructure and lattice parameter, as well as the superconducting properties \( B_{c2} \), \( T_c \) and flux pinning were studied for all samples and are discussed below.

Results and Discussion

Influence of MB\(_2\) and Dy\(_2\)O\(_3\) doping on XRD and lattice constants. The X-ray diffraction data for all HTP bulks are presented in Fig. 1 where the Bragg reflections are indexed for only the MgB\(_2\) phase for simplicity. MgO and Mg were present at some level in all samples (MgO was less than about 2 wt% for samples reacted below the peritectic). MgB\(_4\) peaks are also present for samples HT at 1700 °C. Only a very small peak shift (less than 0.2 degree) at both (110) and (002) was observed in MB\(_2\) doped samples while no peak shift was observed for the Dy\(_2\)O\(_3\) doped sample. Peaks corresponding to MB\(_x\) impurity phases were observed in all MB\(_2\) doped samples. The lattice parameters extracted from pseudo-Voigt fitting the MgB\(_2\) peak reflections and the calculated lattice parameters by Vegard’s law are given in Table 1. For the Dy\(_2\)O\(_3\) added sample HTP-DY, similar to Chen’s report, the lattice parameters \( a \) and \( c \) did not change with Dy\(_2\)O\(_3\) addition. Similarly, for the MB\(_2\) added samples, even though both lattice parameters \( a \) and \( c \) were slightly changed, these changes were very small and none of the doped samples obeyed Vegard’s law, unlike C-doped MgB\(_2\) HTP bulks. Therefore it seems that even under HTP processing the metal borides (ZrB\(_2\), TiB\(_2\) and NbB\(_2\)) mainly acted as impurity phases and did not form homogeneous solid solutions with MgB\(_2\), at least not to an extent detectable by XRD. However, the small changes in lattice parameters suggest that a distortion of the MgB\(_2\) lattice was present. Such distortion, caused by strain generated around these dopant impurities (see below) rather than elemental substitution, appears to be the driver for the modified upper critical field \( B_{c2} \) of the doped samples.

Influence of MB\(_2\) and Dy\(_2\)O\(_3\) doping on microstructure - SEM and TEM. The results of back-scatter (BSE) SEM characterization performed on the ZrB\(_2\) doped samples are presented in Fig. 2. The microstructures of HTP-Zr-01 (1500 °C, below the peritectic temperature) and HTP-Zr-02 (1700 °C, above the peritectic temperature) are shown in Figs 2(a) and 3(b) (for comparison, the microstructures of the undoped bulk can be found...
Nano-size TiB₂ inclusions can also contribute to the high defect density observed in MgB₂ grains in Fig. 3(c,d). MgB₂ samples. Other MgB₂ grains have fewer intragranular defects. The EDS results in Fig. 4(e) confirm that these inclusions are DF image clearly confirms that the MgB₂ grain contains a high density of defects. Detailed in-grain analysis was performed using HAADF imaging. Figure 3(e) shows a HAADF image of MgB₂ grains with high defect density.

Table 1. Doping levels, heat-treatment parameters, lattice parameters and MB₄ impurity amounts for the MgB₂ samples. These ratios were based on the mole ratios between the dopants and B in the mixtures. The a_{calc} and c_{calc} were the calculated values based on Vegard’s law by assuming that all dopants form a homogeneous solid solution with MgB₂. The x in MB₄ is 2 in the MB₂ doped samples and 4 in the Dy₂O₃ doped sample, respectively.

| Sample   | Dopant:B ratios¹ | HTTs at 10 MPa | a, Å   | a_{calc}, Å² | c, Å   | c_{calc}, Å³ | MB₄ Impurities³ |
|----------|------------------|----------------|--------|--------------|--------|--------------|-----------------|
| HTP-01   | —                | 1500°C, 30 min | 3.082(5) | —            | 3.521(7) | —            | —               |
| HTP-Zr-01| ZrB₂:B = 1:40    | 1500°C, 30 min | 3.086(4) | 3.085(1)     | 3.522(2) | 1 wt% ZrB₂   | —               |
| HTP-Zr-02| ZrB₂:B = 1:19    | 1700°C, 20 min | 3.090(2) | 3.091(4)     | 3.527(4) | 3.522(5)     | 8.6 wt% ZrB₂    |
| HTP-Ti-01| TiB₂:B = 1:40    | 1500°C, 30 min | 3.089(3) | 3.082(4)     | 3.522(7) | 3.516(8)     | 1.7 wt% TiB₂    |
| HTP-Ti-02| TiB₂:B = 1:19    | 1700°C, 20 min | 3.085(4) | 3.077(2)     | 3.520(7) | 3.492(8)     | 11.3 wt% TiB₂   |
| HTP-Nb-01| NbB₂:B = 1:40    | 1500°C, 30 min | 3.086(3) | 3.084(2)     | 3.517(4) | 3.517(5)     | 2.7 wt% NbB₂    |
| HTP-Dy   | Dy₂O₃:B = 1:800  | 1500°C, 30 min | 3.082(9) | —            | —      | —            | 1.4 wt% DyB₂    |

in⁶,¹⁸,¹⁹. Two phases are visible: MgB₂ (majority phase, dark grey) and ZrB₂ (minority phase, white) in HTP-Zr-01, while in HTP-Zr-02, Mg and MgB₂ phases were present since it experienced (upon cooling) the reaction MgB₂ + Mg ⇒ 2MgB₂.

Figure 2(c) represents the bright-field (BF) TEM image obtained from a thin foil extracted from HTP-Zr-02 (1700°C). This foil contains a cross section of several grains. The results from the energy dispersive spectroscopy analysis (EDS) and selected area diffraction (SAD) confirm that these large grains are MgB₂. An intragranular crack and dislocation loops are present in one of the grains. Since HTP-Zr-02 was processed above the peritectic, the crack presumably resulted from volume expansion taking place during cooling as the MgB₂ converted into MgB₂. TEM examination revealed a number of impurity phases in the form of 30–80 nm inclusions around the MgB₂ grains. The results of EDS analysis performed on these inclusions are presented in Fig. 2(e). It is clear that these inclusions contain Zr, or possibly ZrB₂, which is likely dispersed around the MgB₂ grains in the bulk. Compared to other areas inside the MgB₂ grains, the regions around these ZrB₂ inclusions have much higher contrast under BF condition, which suggests that strain fields were generated around these inclusions and that the MgB₂ lattice was distorted locally. This local lattice distortion may be the origin of the slight lattice parameter changes observed by XRD analysis in Section 3.1. Figure 2(f) shows HAADF imaging for one of these nano-size inclusions. Since HAADF imaging is sensitive to variations in the atomic number (Z-contrast), these white inclusions should have a higher average atomic number than MgB₂. A STEM-EDS line scan applied using 21 distinct points over ~100 nm across this inclusion confirmed it was ZrB₂. The Zr signal dropped to zero quickly outside of the inclusion, beyond the ZrB₂/MgB₂ interface. The spatial resolution of the STEM-EDS line scans is about 5 nm, thus these observation indicate that Zr did not notably penetrate into the MgB₂ lattice.

Figure 3 shows the BSE images of the TiB₂ doped samples, HTP-Ti-01 (1500°C, below the peritectic) and HTP-Ti-02 (1700°C, above the peritectic). Similar to the behavior of ZrB₂, TiB₂ mainly acts as an impurity phase (light grey in Fig. 4(a,b)) and is widely distributed. A TEM thin foil containing a cross section of both TiB₂ and MgB₂ grains was carefully extracted from HTP-Ti-01. A BF image including MgB₂, TiB₂, and their interface is represented in Fig. 3(c). A large number of defects can be observed inside the MgB₂ grains close to the TiB₂/TiB₂ interface. Inclusions 100–200 nm in size are found at the interface as well as at MgB₂ grain boundaries. EDS analysis confirms that these inclusions are MgO. Dark-field (DF) imaging was also used to examine the dislocations and the interface since crystal defects have stronger contrast under DF conditions. In Fig. 3(d), the DF image clearly confirms that the MgB₂ grain contains a high density of defects. Detailed in-grain analysis was performed using HAADF imaging. Figure 3(e) shows a HAADF image of MgB₂ grains with high defect density. Nano-size inclusions (~10–30 nm, white) dispersed both in and around MgB₂ grains were observed. EDS analysis performed on randomly selected white inclusions confirmed that they were TiB₂ (EDS spectrum of spot E in Fig. 3(f)). No Ti was detected by EDS in the other regions of MgB₂ grains (EDS spectrum of spot D in Fig. 3(f)). STEM-EDS analysis was applied across inclusion E, and beyond the TiB₂/TiB₂ interface the intensity of the Ti signal quickly dropped to zero, indicating that Ti did not dissolve into the MgB₂ lattice. These nano-size TiB₂ inclusions can also contribute to the high defect density observed in MgB₂ grains in Fig. 3(c,d).

In the NbB₂-added sample HTP-Nb-01 (HT below the peritectic), three phases are visible in the BSE images of Figs 4(a) and 5(b): MgB₂ (majority phase, dark grey), MgO (minority phase, light grey) and NbB₂ (minority phase, white). In Fig. 4(b), based on fractured secondary electron (SE) imaging by ‘through the lens’ (TTL) detection, NbB₂ particles are observed outside the MgB₂ grains. These particles are small (~300–500 nm), well connected with the MgB₂ grains, and dispersed throughout the bulk.

Further analysis was performed on a TEM thin foil sectioned from HTP-Nb-01. Both BF (Fig. 4(c)) and DF images (Inset of Fig. 4(c)) show nano-size inclusions (~300 nm) embedded in the MgB₂ grain boundaries. Moreover, a large number of defects can be observed inside the MgB₂ grains around these inclusions, while the other MgB₂ grains have fewer intragranular defects. The EDS results in Fig. 4(e) confirm that these inclusions are NbB₂. HAADF imaging performed on MgB₂ grains with high density of defects is presented in Figs 4(d) and 5(e). Nano-size inclusions (~10–50 nm, white) were found inside these grains and high strain fields were observed around them. EDS analysis was applied on these distinct inclusions and several randomly selected spots in the matrix; those for spot C (matrix) and spot D (inclusion) are presented in Fig. 4(f). These EDS results confirm that these white inclusions were NbB₂. A STEM-EDS line scan was applied across inclusion D. The intensity of...
Nb signals abruptly decreased from ~10^4 to 0 across the NbB_2/MgB_2 interface and no Nb was detected in other regions of the MgB_2 grains.

The microstructure of HTP-DY (HT above the peritectic) was investigated by BSE in Fig. 5(a). Five phases are visible: MgB_2 (majority phase, dark grey), Mg (main phase, grey), MgB_4 (minority phase, black), MgO (minority phase, light grey) and Dy-containing inclusions (minority phase, white). These Dy-containing inclusions (DyB_4 according to XRD results) with a size of ~100 nm were dispersed throughout the bulk. Bright-field TEM examination revealed a number of impurity phases in the form of ~10–50 nm inclusions inside the MgB_2 grains in Fig. 5(b). A low density of large inclusions (over 100 nm) was also observed (Fig. 5(c)). HAADF imaging (Fig. 5(c)) showed that these nano-size inclusions had a higher average atomic weight. EDS indicates that these inclusions contained Dy and B suggesting they are the previously XRD-identified DyB_4. STEM-EDS analysis was applied across inclusion B (the red dashed line in Fig. 5(c)) and the result is shown in Fig. 5(e). No Dy was detected outside the inclusion.

**Influence of MB_2 and Dy_2O_3 doping on superconducting properties - Magnetic Results.** The superconducting transition temperature T_c and the distribution of T_c of all samples were extracted by magnetization measurements, Fig. 6. The onset T_s and the full-width half maximum (FWHM) of all samples are listed in Table 2. The undoped sample HTP-01 shows a very sharp superconducting transition with T_c of 39.5 K and a FWHM of ~0.4 K. Below we describe the results for the doped samples.

**ZrB_2 Doping.** In the ZrB_2 doped samples, the onset T_s is ~39.2 K in HTP-Zr-01 and ~39.4 K in HTP-Zr-02, respectively. The unchanged T_s suggest that a portion of these ZrB_2 doped samples was unaffected with a T_c equal to that of the undoped sample. Figures 6(a,b), show very broad transitions and bi-modal peak in the T_c distribution. This effect became more severe in HTP-Zr-02 indicating the presence of regions with various T_s.

**TiB_2 Doping.** Similarly, in the TiB_2 doped samples, the onset T_s were unchanged, while their FWHMs were increased to ~0.5 K in HTP-Ti-01 and ~2.8 K in HTP-Ti-02, respectively.

**NbB_2 Doping.** The NbB_2 doped sample HTP-Nb-01 has an onset T_c of 39.8 K and a FWHM of ~1.0 K.

**Dy_2O_3 Doping.** The Dy_2O_3 doped sample HTP-DY has an onset T_c of 39.2 K and a FWHM of ~0.5 K.

The results for each of the MB_2 samples was similar after MB_2 doping, the onset T_s were relatively unaffected, however their transition widths were significantly enhanced. We interpret this effect in terms of the presence of nanoscale MB_2 (where M = Zr, Nb, or Ti) second phases which produce locally distorted regions separated by
large regions of unaffected MgB\(_2\), leading to broadened \(T_c\) distributions with a wide \(T_c\) variation ranging from 39 K to low values. Since these MB\(_2\) additives are isomorphous to MgB\(_2\) and their lattice parameters are close to those of MgB\(_2\), the localized distortion is probably due to the coherent strain generated around the MB\(_2\) inclusions. However, in HTP-DY both the onset \(T_c\) and FWHM did not change by adding Dy\(_2\)O\(_3\), which is consistent with Chen's observation\(^{17}\). The lattice parameters and crystal structures of Dy\(_2\)O\(_3\) (cubic with space group Ia-3)\(^{20}\) and DyB\(_4\) (tetragonal with space group P4/mbm)\(^{21}\) are very different from MgB\(_2\) (hexagonal with space group P6/mmm)\(^{22}\), therefore it is unlikely that the Dy-contained inclusions in HTP-DY can generate coherent strain in the MgB\(_2\) grains.

As indicated above the MB\(_2\) dopants were mostly found as distinct impurity inclusions that only influenced the surrounding MgB\(_2\) grains through the MgB\(_2\)/MB\(_2\) interfaces. Increasing the concentration of MB\(_2\) inclusions produced more "affected zones" leading to a wider \(T_c\) distribution, Fig. 6(b). The behaviors of MB\(_2\) doped samples are quite different from those of C-doped MgB\(_2\) bulks\(^8\). After doping with 6.2 at.\% C Susner \textit{et al.}\(^6\) observed a significant decrease in the onset \(T_c\), from 39.5 K to \(~24\) K, while the FWHM changed from 0.65 K to 1.4 K\(^6\). Since C is known to be a substitutional defect, if homogeneous C doping is achieved, the onset \(T_c\) and the lattice parameter \(a\) will decrease simultaneously with increasing C doping levels\(^5\). Under MB\(_2\) doping, it seems that Zr, Ti and Nb did not substitute for Mg or form homogeneous solid solutions with MgB\(_2\), even under 1700°C and 10 MPa. However, the properties of the host lattices in the vicinities of these dopants were indeed affected and their \(T_c\)s were clearly altered, possibly due to local compositional changes caused either by Mg diffusion into MB\(_2\) particles or by local strain. Both of these possibilities could cause \(T_c\) reduction, comparable to the effect of Al doping in MgB\(_2\);\(^{23-25}\) Based on the results in the previous section, the affected vicinities probably had thicknesses similar to or smaller than 5 nm—the resolution of STEM-EDS line scans used in this study.

The \(T\) dependencies of the upper critical fields \(B_{c2}\), of all the samples are presented in Fig. 6(c). The \(B_{c2}\)s at 20 K linearly extrapolated from Fig. 6(c) are listed in Table 2. It is clear that \(B_{c2}\) was increased by MB\(_2\) doping, but not by Dy\(_2\)O\(_3\) doping. It is important to note, however, that since these MB\(_2\) doped samples were not homogeneous (as evidenced by the microstructure and the \(T_c\) distribution), the \(B_{c2}\) values represent the properties of only a small fraction of the bulk samples. In other words, some “affected zones” inside these doped bulks have higher \(B_{c2}\)s than those in the unaffected MgB\(_2\), therefore their measured \(B_{c2}\) was enhanced. The observed high defect densities in the MgB\(_2\) grains, which increase electron scattering and reduce the electron mean free path, are likely responsible for the \(B_{c2}\) enhancement. These regions are at the edge of the grains, and can therefore act as connected percolative paths. In the Dy\(_2\)O\(_3\) doped sample, although nano-size inclusions were observed inside the MgB\(_2\) grains, \(B_{c2}\) did not change. This observation together with the absence of changes in the lattice parameters, and lack of change...
in the $T_c$ and FWHM suggested that Dy2O3, unlike the metal diboride additions, did not cause a band of defect structure at the boundary of the MgB2 grain.

The magnetic critical current density $J_{cm}$ and flux pinning behaviors of selected samples were calculated based on Bean’s critical state model:

$$J_{cm} = \frac{2\Delta M}{b(1 - b/a)}$$  

where $\Delta M$ is the width of the hysteresis loop at a given field $B$, $a$ and $b$ are the edge lengths of the sample orthogonal to $B$ ($a > b$). The results at 15 K are shown in Fig. 7. The $J_{cm}$s for most of the field range were either not changed, or even reduced after MB2 doping; for HTP-DY, its $J_{cm}$ was slightly increased at all measured fields. A “tail” in $J_{cm}(B)$ can be observed in all MB2 doped samples, Fig. 7(a). Based on the microstructural evidence and results of $B_{c2}$ and $T_c$, this “tail” in $J_{cm}$ of the MB2 doped samples is probably caused by regions in the samples with different $B_{c2}$. However these regions were too small to have significant influence on the overall $J_c (>100 \text{ A/cm}^2$). The irreversibility field, $B_{irr}$, defined as the point where flux pinning vanishes, is often taken as the field at which $J_c(B) = 100 \text{ A/cm}^2$. The results for these samples are given in Table 2; no increase in $B_{irr}$ is seen, and in some cases there is a decrease. This definition of $B_{irr}$ does not capture the high field and super-low-$J_c$ “tail” observed in Fig. 7(a).

MgB2 is primarily a grain boundary pinner, and thus the starting place to describe its pinning is the Kramer function (although deviations are seen). In order to perform such analysis, a Kramer field is needed. A Kramer plot, $J_{cm}^{0.5}B^{0.25}$ versus $B$, is shown in Fig. 7(b). The $B_{c2}$s taken at the cross-intercepts of linear fittings (Black dash lines in Fig. 7(b)) are listed in Table 2. The values of $B_{c2}$, similarly to those of $B_{irr}$, were stable or slightly reduced after MB2 doping, unlike the values of $B_{c2}$, which increased with doping. This effect is due to several factors: (1) the higher $B_{c2}$ region was apparently small, presumably restricted to the defected zones near the grain boundaries, these regions will not substantially influence the measured $B_{c2}$; (2) the $B_{c2}$ is also affected by the sample connectivity, possibly reduced with second phases present. For samples with Dy2O3 additions, $B_{c2}$, $B_{irr}$, and $B_{c2}$ were not affected.

Figure 7 (c) is a plot of bulk pinning force density ($F_p = J_{cm} \times B$) vs $B$; the maximum values, $F_{p,\text{max}}$, are listed in Table 2. Compared to the literature values, the $F_{p,\text{max}}$ of these HTP processed bulks is quite small. Spark-plasma sintering gives a $J_c$ at 2 T and 15 K of about $10^4 \text{ A/cm}^2$, while our values here are closer to $2 \times 10^3 \text{ A/cm}^2$. The $F_{p,\text{max}}$ of the undoped sample HTP-01 is only $\sim 0.095 \text{ GNm/m}^3$ while according to Susner at 15 K the $F_{p,\text{max}}$ of an undoped MgB2 wire was about 2 GNm/m$^3$. The main reason for the difference is that the MgB2 grains in these HTP
bulks (>5 μm) are much larger than those in the traditional synthesized samples (typically 30–500 nm). Other factors could also contribute to this difference in $F_{p,\text{max}}$, including some reduction of connectivity by small amounts of MgO. However, as $J_c \propto 1/\text{grain size}$, and the grain size in our samples is roughly 50 times larger than the highest performing MgB$_2$, the grain size effect is expected to be dominant. Among all samples, the highest value of $F_{p,\text{max}}$ (~0.135 GN/m$^3$) was observed in HTP-DY. The normalized bulk pinning force density $f_p = F_p/F_{p,\text{max}}$ is plotted against normalized magnetic field $b = B/B_k$ in Fig. 7(d). The functions of grain boundary (GB) pinning from the Dew-Hughes model $27, f_p \propto b^{1/2}(1 - b)^2$, are also plotted for comparison. Although the undoped sample HTP-01 followed GB pinning function quite well, all doped samples show a deviation from the standard function. The peaks of $f_p$ in the doped samples were shifted from the value of $b = 0.2$ (the peak position of the GB pinning) to lower values. For example, the peaks in HTP-Zr-01, HTP-Ti-01, HTP-Nb-01 and HTP-DY were 0.12, 0.13, 0.11 and 0.10, respectively. This observation which was also reported by Matsushita et al. $28$ in C doped MgB$_2$ bulk samples can be explained by two possibilities: (1) These doped samples might contain a set of local $B_k$ instead of one distinct value (just like the $B_{c2}$ in the MB$_2$ doped samples), which can lead to an artificial error in the estimation of the peak positions; while the variation in $B_k$ of the undoped sample was small, thus the undoped sample followed the GB pinning function. (2) The deviation from $b_{\text{peak}} = 0.2$ might be caused by the operation of other pinning mechanisms (e.g., normal volume pinning in which $f_p$ maximizes at $b \rightarrow 0.0^{22}$) in association with the GB pinning. As noted above, we clearly see a distribution of Dy-based second phases, consistent with $27$. Also present were modest levels of MgO, known both to act as a pinner and in some cases reduce connectivity $29$. However, any small MgO effects should be present in all samples. The parameter $a$ of the flux line lattice (FLL) is given by $a = 1.07(\Phi_0/B)^{1/2}$, where $\Phi_0$ is the quantum of magnetic flux ($\Phi_0 = 2.07 \times 10^{-15}$ Wb). Based

Figure 5. (a) BSE image of HTP-DY, four different phases (MgB$_2$, MgB$_4$, Mg and MgO) are labeled; (b) BF TEM image of nano-size inclusions (10–50 nm) are found inside MgB$_2$ grains; (c) HAADF image of one MgB$_2$ grain, white precipitates are Dy-contained; (d) EDS spectra of spot A-C in (c); (e) the intensity of Dy$_{La}$ from STEM-EDS scanning (red dash line in (c)).
on this expression, the values of $a$ vary from ~50 nm at 1 T to ~20 nm at 6 T. By definition, the size of the volume pins needs to be larger than $a$. Considering the fact that these doped samples contained intragrain inclusions some of which were bigger than the FLL parameter $a$ at every measured field, it appears that volume pinning contributed to these shifts in $F_{\text{p,max}}$.

In summary, after adding MB$_2$, the $B_{c2}$ of MgB$_2$ HTP bulks increased, the $T_c$ distributions were broadened, but $T_c$, $B_{k}$ and $J_c$ remained unchanged (or slightly reduced). Considering the microstructural evidence, this observation can be explained as follows: only very small regions (possible $\leq 5$ nm in thickness) around dopant particles of the MgB$_2$ grains are influenced by doping, leaving the majority of MgB$_2$ unaffected. To the contrary, the Dy$_2$O$_3$ doping did not change the $T_c$, $T_c$ distribution and $B_{c2}$, instead it increased the $J_c$ and flux pinning apparently associated with the nano-size precipitates in MgB$_2$ grains.

**Conclusion**
In this work we have used our HTP method for synthesizing doped MgB$_2$ bulks at high temperatures (up to 1700 °C) and at pressure (10 MPa) to explore solubility limits of dopant species in MgB$_2$, maximize diffusion, and (alternatively) attempt to form dense, nanoscale secondary phases during the sample synthesis. We explored both metal diborides (MB$_2$, where M = Zr, Ti and Nb) for attempted Mg site substitution and Dy$_2$O$_3$ for nanoscale intragrain precipitate formation. Using the HTP process we conclusively show that the large increases in $B_{c2}$ with metal diboride additions are due to a highly defected band within the grain, rather than substitution or inclusion within the grain, or grain boundary effects. High defect densities observed in MgB$_2$ grains around/with these MB$_2$ inclusions, cause electron scattering and therefore contribute to the $B_{c2}$ enhancement and $T_c$ distribution broadening. On the other hand, these regions ($\leq 5$ nm in thickness) were not large enough to significantly influence the high field $J_c$, $B_{irr}$ or $B_k$. This observation explains the frequently observed increases seen for $B_{c2}$ in materials with no accompanying increase in transport current. We also confirm the previously observed but sparsely distributed intragrain precipitates formed with Dy$_2$O$_3$ additions. Dy$_2$O$_3$ additions not change the lattice parameters, $T_c$, $T_c$ distribution and $B_{c2}$ of MgB$_2$, but increased the $J_c$ and flux pinning by forming an array of nano-size precipitates in MgB$_2$ grains.

**Methods**

**Sample Synthesis.** Three sets of MgB$_2$ bulks with various MB$_2$ (M = Zr, Ti and Nb) dopants were fabricated at high temperatures and under pressure. This HTP process$^{18,19}$ based on the reactive liquid Mg infiltration (Mg-RLI) method$^{20}$. Three metal borides with a structure isomorphous to MgB$_2$ (P6/mmm) were selected as vectors for Mg-site substitution: ZrB$_2$ (99.5%, Alfa Aesar), TiB$_2$ (99.5%, Alfa Aesar) and NbB$_2$ (99.5%, Alfa Aesar). As the Dy$_2$O$_3$ additive, Dy$_2$O$_3$ (>99.9%, <100 nm particle size, ALDRICH) was used. Amorphous B powder (50–100 nm in size) manufactured by Specialty Metals Inc.$^{31,32}$ was hand mixed with the dopant powder and high energy ball milled for 15 min in an Ar atmosphere. These dopants and B powder mixtures were then pressed into...
~8 mm tall by ~13 mm diameter pellets and placed in an MgO crucible. Mg turnings (~4 mesh, 99.98%, Alfa Aesar) were packed on top. The Mg:B ratio in the crucible was about 1:1 to avoid possible Mg deficiencies during heat treatment. This crucible was capped and placed inside the HTP autoclave (see also 18,19). All samples were heat treated at 10 MPa in an Ar atmosphere. Two heat treatment routes were used: (1) heating up to 1500 °C and soaking for 30 min; (2) heating up to 1700 °C and soaking for 20 min. A slow cooling rate of 5 °C/min was used in both HT routes to maintain thermal equilibrium. The first route was designed to limit the temperature to just below the peritectic decomposition point of the reaction, thus preventing decomposition while maximizing the diffusion of the dopant species. The second route was designed to allow the reaction to occur on the temperature upswing, and hence to form MgB2 directly from MgB4 and Mg+ dopant species on cooling:

$$\text{MgB}_4 + \text{Mg} \rightarrow \text{MgB}_2$$

where $T_p$ is the peritectic temperature (~1500 °C in our experiments).

**Measurements.** A Rigaku SmartLab X-ray diffractometer (using Cu Kα of 1.5406 Å) was used for structural characterization and the scanning angle 2θ ranged from 20° to 80°. A FEI/Philips Sirion scanning electron microscope (SEM) with a field-emission source and a through-the-lens (TTL) detector was used for microstructural imaging. An FEI Helios 600 dual beam focused ion beam instrument (FIB) with an Omniprobe micromanipulation tool was used to prepare TEM thin foils. The TEM imaging was performed on a FEI/Philips CM-200T transmission electron microscope (TEM) with a silicon drift detector (SDD) and energy-dispersive X-ray spectroscopy function (EDS). The high-angle annular dark-field imaging (HAADF) and EDS line scans with a resolution of

![Figure 7](https://www.nature.com/scientificreports/images/figure7.png)
Curves were taken at 1 T intervals from 0–14 T. The upper critical field, $M-T$ $J_{c}$, taken as the field at which $F_{p}$, the pinning force, deviates from $F_{c}$, was calculated from $F_{p} = J_{c}B$, where $J_{c}$ was extracted from the magnetization results at various temperatures.

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Author Contributions

M.D.S., E.W.C. and Y.Y. developed the topical area and thrust of this study. Y.Y. initiated this study, completed the experiments, and wrote the manuscript. M.D.S. and E.W.C. reviewed the results and the manuscript.
Additional Information

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