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Highlights

- MgB_2 wires doped with Ir (iridium) were prepared and reacted in Ar.
- The solubility limit of Ir in the MgB_2 lattice is not larger than 1.5 at.% relative to Mg.
- The critical current density is degraded in the Ir-doped samples.
- The main flux pinning mechanism was identified as ΔT_c pinning.

Influence of iridium doping in MgB_2 superconducting wires

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Abstract

MgB_2 wires with iridium doping were manufactured using the *in-situ* technique in a composite Cu-Nb sheath. Reaction was performed at 700°C, 800°C or 900°C for 1h in argon atmosphere. A maximum of about 1.5 at.% Ir replaces Mg in MgB_2 . The superconducting transition temperature is slightly lowered by Ir doping. The formation of IrMg_3 and IrMg_4 secondary phase particles is evidenced, especially for a nominal stoichiometry with 2.0 at.% Ir doping. The critical current density and accommodation field of the wires are strongly dependent on the Ir content and are generally weakened in the presence of Ir, although the effect is less pronounced at lower temperatures.

Keywords: MgB_2 ; doping; iridium; wires

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Introduction

Owing to its critical temperature (T_c) of 39 K. which is intermediate between those of classical low temperature superconductors and high- T_c cuprates, associated to advantages such as low materials costs, absence of weak links at grain boundaries [1] and straightforward processing as metal-sheathed wires [2], MgB_2 is an outstanding material in view of small and large scale power applications. During recent years, various prototypes have been developed, including cryogen-free MRI systems [3,4] and induction heating units [5], while other applications including generators, transformers, fault current limiters as well as magnetic shields for deep-space missions are foreseen for a near future [6,7]. Furthermore, based on the low activation of MgB_2 upon neutron irradiation [8], MgB_2 wires are serious contenders for use in future commercial fusion reactors. Nevertheless, for this latter usage as well as some specific applications involving high magnetic fields, improvements are still needed to enhance the critical current density (j_c) performance of MgB_2 wires. In this endeavour, different strategies can be adopted like grain size refinement [9,10], nanoparticle inclusions [11-13] or doping with other elements. Introducing carbon on the boron sites was shown to be very efficient under high magnetic fields [14-17], but tends to decrease the self-field j_c so that further improvements are still needed if performance has to be improved in a wide magnetic field range. Beside boron site doping, numerous attempts have been made at doping various elements on the Mg sites. Unfortunately, while Al can replace up to 40 at.% Mg [18-21], for other elements solubility is limited to a few percent in most cases [22-40] and is often below detection limit [41-46].

Platinum group metals present various behaviours. Pd and Pt are virtually not soluble in MgB_2 [41], whereas about 1 at.% Ru and Os can be substituted for Mg [34,35]. Rh has a slightly higher solubility limit of 2.2 – 2.5 at.% [40]. Iridium appears to be an exception with a maximum

solubility limit of 6 at.% relative to Mg according to a study performed on bulk samples [36]. In that work, the effect of Ir substitution on the critical current density (j_c) was not reported. Furthermore, the determination of 6 at.% as a solubility limit was not straightforward, because T_c as well as the lattice parameters given in [36] were continuously varying up to 12 at.%, whereas impurity peaks were already visible in the XRD patterns for 2 at.% Ir doping. It was thus of interest to reassess the solubility limit of Ir in MgB_2 and to study its possible effect on j_c . In principle, substitutions on the Mg sites are not expected to result in j_c improvements due to enhanced interband scattering [47,48]. However, other effects such as the appearance of nanometer sized non-superconducting particles beyond the solubility limit of dopants or inhomogeneities in the dopant concentration might positively affect the behavior of MgB_2 under applied magnetic fields so that potential substitutions on Mg sites are still worth studying.

Experimental details

The starting reagents were elemental powders: Mg (Alfa Aesar, 99.8 % purity), amorphous boron (Aldrich, 95-97 %) and Ir (Alfa Aesar, 99.8 %). They were mixed according to the following nominal ratios: $\text{Mg}_{1-x}\text{Ir}_x\text{B}_{2.04}$ ($0.00 \leq x \leq 0.02$ with $\Delta x = 0.01$). The slightly B-enriched starting stoichiometry is based on a earlier work taking into consideration the impurities (including some Mg) present in the B commercial powder used for the present work [49]. Mixing was performed in a mechanical blender (Bachofen, type T2C). The mixed powders were then loaded into 4 cm long Nb tube sections with 5 mm external diameter and 0.3 mm wall thickness (Goodfellow Ltd). These tubes were mechanically deformed by groove rolling into wires with 4.0 mm external diameter and inserted into Cu tubes (Goodfellow Ltd., 5 mm external diameter, 0.5 mm wall thickness). The composite tubes and the powder core were further deformed into wires with square cross section of about $1.6 \times 1.6 \text{ mm}^2$. 6 cm long pieces of the wires were heat

treated at different temperatures (700°C, 800°C or 900°C) for 1 h under Ar atmosphere with a heating rate of 100°C/h and furnace cooling.

XRD patterns were recorded in a Bruker X-ray diffractometer with CuK α radiation ($\lambda = 1.5406$ Å) on powders that had been mechanically extracted from the wires after heat treatment. Silicon powder (Alfa Aesar, 99.999%) was mixed to the ground powders as an internal standard for lattice parameters determination. The calculations were performed with the UnitCell least square refinement programme [50]. The microstructure of the ceramic core of the wires and the composition of the impurity phases present after reaction at 700°C, 800°C or 900°C were studied by means of scanning electron microscopy (SEM) in a table-top TM3000 microscope from HITACHI equipped with a QUANTAX 70 EDS analyser. For magnetic measurements, 8.0 ± 0.5 mm long segments were cut in the middle of the reacted wires. The superconducting critical temperature (T_c) was determined as the onset of the diamagnetic transition measured by means of a vibrating sample magnetometer (VSM) in a CRYOGENIC Ltd Mini-CFMS under a magnetic field of 1 mT applied parallel to the MgB₂ filament after cooling under zero field conditions. For the estimation of the critical current density, magnetisation hysteresis loops were recorded with the magnetic field parallel to the long axis of the wires and j_c was calculated using the Bean model. The accommodation field (B^*) was determined as the magnetic field at which j_c is reduced to 90% of its value under self-field conditions.

Results and discussion

Figure 1 shows the XRD patterns of the powders mechanically extracted from the wires reacted during 1 h at different temperatures. While MgB₂ is the dominant phase in all cases, there are some important differences to note. Unreacted Mg is still present in the undoped sample reacted at 700°C, showing that these conditions are not good enough for ensuring the completion of the

MgB₂ phase formation. In contrast, no Mg was detected in the other samples. The pattern of the ceramic core of the undoped wire also reveals other low intensity peaks at $2\theta = 35.3^\circ$, 37.3° , 39.6° and 44.4° , which could be due to some Mg₂Cu that might form if liquid Mg infiltrates through the Nb protective layer and reacts with the outer Cu sheath. It should however be noted that Mg₂Cu is not stable above 568°C [51] so that it can be excluded that this impurity is formed during the reaction at 700°C. Furthermore, no Cu was detected in the core of this wire by EDS analysis. These peaks can in fact also be due to unreacted boron. Indeed, the commercial boron powder used for this study, although labelled as “amorphous”, presents broad XRD reflections at 2θ angles corresponding to the values listed above. This conclusion is more compatible with the observation of unreacted Mg. A reflection at $2\theta \approx 40.8^\circ$ in the sample with 2 at.% Ir substitution for Mg, reacted at 700°C, could be due to elemental Ir.

The lattice parameters are listed in Table 1. There is no obvious trend for a systematic influence of the Ir content on the a-axis or c-axis length. This is very different from the result in [36], according to which at 2 at.% Ir substitution for Mg, the a-axis length was reported to increase by 0.0008 Å and the c-axis length to decrease by as much as 0.08 Å. Nevertheless, the XRD patterns of the present samples contain much less impurity peaks than in [36] for the same Ir doping level.

Fig.2 presents overview SEM micrographs in backscattering mode of all samples after reaction. For all 3 reaction temperatures, the undoped samples exhibit a typical microstructure for MgB₂ ceramic samples with significant porosity (black areas) and boron-rich Mg-B phases (dark grey) embedded in the MgB₂ matrix (light grey). The only, albeit significant difference in the Ir- doped samples is the appearance of white particles that increase in number for higher doping level. Compositional analysis of these particles was performed by means of EDS. A

typical result is shown in Fig.3 for the sample with 2 at.% Ir doping reacted at 800°C. As expected from their bright contrast, the white particles are rich in Ir. They also contain Mg but no quantifiable amount of B. Their composition corresponds to IrMg_3 and IrMg_4 , two phases which happen to be stable up to 1020°C and 920°C respectively according to Nayeb-Hashemi and Clark [52]. The dark grey particles were confirmed to consist of B-rich magnesium borides with preponderance of MgB_7 , whereas MgB_4 and MgB_{12} are less frequent. Another type of defect is emphasized in Fig.3a by a circle. In this area, only Mg was detected in association with oxygen. This is therefore a cluster of MgO , a phase which is also evidenced in the XRD patterns by a peak at $2\theta \approx 62.2^\circ$ (Fig.1), especially for reaction temperatures above 700°C. EDS elemental analysis performed on large areas ($\approx 10.000 \mu\text{m}^2$) yield Mg:Ir atomic ratios very close to the nominal stoichiometry for all samples with 1 at.% and 2 at.% Ir substitution, notwithstanding of the heat treatment temperature. On the other hand, local EDS analysis on areas that do not include white particles in Fig. 3a reveal an Ir at.% ratio of 1.58 ± 0.24 relative to Mg. This value is lower than the overall Ir 2.0 at.% nominal substitution level. Since it cannot be excluded that these analyzed areas include some smaller IrMg_3 or IrMg_4 particles that cannot be distinguished from the MgB_2 matrix or that are lying just below the cross-section surface, it must be considered that $x = 0.0158 \pm 0.0024$ is an upper limit for the solubility of Ir in $\text{Mg}_{1-x}\text{Ir}_x\text{B}_2$. From these observations, it can be concluded that the actual substitution level of Ir in MgB_2 is rather low under the present experimental conditions and comparable to that of Ru or Os [34,35]. This is further supported by the superconducting critical temperature (T_c) that is only slightly affected by the presence of Ir (Fig.4 and Table 1). Except for the samples reacted at 700°C, there is a tendency for a lowering of T_c with increase of the Ir content, but it is much smaller than reported in [36] based on electrical resistivity measurements that were showing a T_c of 33.2 K for 2 at.%

Ir doping. The inset in Fig.4 shows typical data for the three doping levels (reaction at 800°C). The transition width is not dependent on the amount of Ir. Slight irregular features close to the onset of the diamagnetic transition in the samples with $X = 0.00$ and 0.02 could suggest that there are two distinct transitions that may originate from a phase separation. However, they are more likely attributable to the accuracy of the temperature control (measurement accuracy of about 0.05 K for these data collected with a heating rate of 2 K/min) as well as dynamic effects in the magnetic flux penetration into the samples. Since $\text{IrMg}_3/\text{IrMg}_4$ particles are already seen in the SEM images for 1 at.% Ir doping, the slight T_c decrease observed in the present samples could in fact be due to stoichiometry effects resulting from Mg depletion [53-57] rather than from actual Ir doping, although the near saturation of the T_c decrease when going from $x = 0.01$ to $x = 0.02$ in the samples reacted at 700°C and 800°C fits well with a solubility limit situated in between these two values. Furthermore, the fact that stoichiometry variations affect the T_c of the MgB_2 phase is not supported by studies on single crystals [58], so that the presently observed effect is most probably due to Ir substitution in the MgB_2 lattice.

The critical current density of the wires was calculated from $M(H)$ hysteresis loops using the Bean model with the following formula corresponding to elongated samples with the longest dimension parallel to the applied magnetic field:

$$j_c = \frac{2\Delta M}{a\left(1 - \frac{a}{3b}\right)V} \quad (1)$$

where ΔM is the opening of the volume magnetisation hysteresis loop, a and b are the linear dimensions of the cross-section of the superconducting core of the wire perpendicular to the applied magnetic field ($a < b$), and V the volume of the superconducting core.

Fig.5 shows two sets of examples of $M(H)$ loops at 10 K, 20 K and 30 K for the samples without Ir and the highest studied Ir content after reaction at 800°C for 1h. Besides lower magnetization values at equivalent temperatures, it can be observed that the asymmetry for the undoped sample is more pronounced, indicating weaker flux pinning in the Ir doped wire. This last feature is reflected in the stronger field dependence of the normalized j_c versus field curves for the Ir doped wire, also shown in Fig.5. This behavior has been systematically observed for all Ir-doped samples and is reflected in the B^* values (= the applied field resulting in a reduction of j_c to 90% of its value in self field), which are listed in Table 1. At 30 K, B^* is systematically highest in the undoped wires for all reaction temperatures. Nevertheless, with decreasing temperature, the B^* values increase faster in the doped wires so that at 10 K, the B^* of the 1 at.% doped wires is comparable to that of the undoped wire notwithstanding of reaction temperature.

Fig.6a and b compares the j_c versus applied magnetic field (B) of all samples at 10 K and 30 K. In these graphs, only the j_c values at a few fields are plotted for the sake of clarity. Except for the $x = 0.01$ sample reacted at 900°C, there is a clear tendency for lower j_c values for increasing Ir contents in the wires. However, at 10 K, the performance of the $x = 0.01$ wires reacted at 700°C and 800°C become closer to that of the undoped wires, especially at $B \geq 2$ T. The lower j_c of the wire with $x = 0.01$, reacted at 900°C might be due to macroscopic defects such as local failure of the Nb protective layer separating the MgB_2 core from the outer Cu sheath. The general trend for lower j_c values in the doped wires may not be exclusively due to the substitution of Ir in the MgB_2 phase. In fact, the amount of impurities in the form of $IrMg_3$ and $IrMg_4$ is relatively large, especially in the samples with $x = 0.02$. Their volume has not been taken into account in the calculation of j_c .

The normalized pinning force ($F_p/F_{p \text{ max}}$) is plotted versus ($B/B_{Fp \text{ max}}$) in Fig.7 for all samples and compared to the three different models corresponding to surface pinning (2), normal point pinning (3) and $\Delta\kappa$ pinning (4) [59]:

$$f(b) = \frac{25}{16} \sqrt{b} \left(1 - \frac{b}{5}\right)^2 \quad (2)$$

$$f(b) = \frac{9}{4} b \left(1 - \frac{b}{3}\right)^2 \quad (3)$$

$$f(b) = 3b^2 \left(1 - \frac{2b}{3}\right) \quad (4)$$

where $f(b)$ is the pinning force F_p divided by the maximum value of F_p ($=F_{p \text{ max}}$) and $b = B/B_{Fp \text{ max}}$ is the applied magnetic field B divided by the field corresponding to $F_{p \text{ max}}$.

At 10 K, the data for all samples show a similar dependence below the pinning force maximum, with a shape close to that predicted for ΔT_c pinning. At higher fields, the samples with 1 at.% Ir doping or without Ir continue following the same model, whereas the 2 at.% samples all depart from this trend and their behavior becomes closer to the surface pinning model. As the temperature is increased, the behavior of the undoped and 1 at.% Ir doped wires is unchanged, but that of the 2 at.% Ir doped wire is moving more towards surface pinning, also at low applied magnetic fields.

Of course, the fact that the normalized pinning force follows a particular pinning model does not necessarily mean that this kind of pinning is the only one at play, but generally reflects the dominant pinning mechanism. Surface pinning is playing an important role in MgB_2 polycrystalline samples [60] and is most probably also acting in the samples produced within the present study. However, here ΔT_c pinning is obviously rather important in most samples, which may be due to inhomogeneities, themselves resulting from the fact that the reacted powder inside

the wires cannot be extracted, homogenized by mechanical means and reacted again. Interestingly, Ir doping tends to shift the $F_p/F_{p\max}$ curves towards the surface pinning behavior. This could be due to either weakening of the ΔT_c pinning or a relative increase of surface pinning. The latter effect could result from a decrease of the MgB_2 grain size but no evidence was found for XRD peak broadening. On the other hand, the Mg-rich side of the Ir-Mg binary phase diagram [52] shows that interaction with Ir induces a lowering of the melting point of Mg, with formation of a molten phase at 615°C (eutectic). This means that adding Ir can increase the amount of liquid during reaction, which can potentially help homogenizing the MgB_2 phase and thus decrease the ΔT_c pinning contribution. The admixture of various elements such as Ag, Cu, Bi, Sb, Ge, Sn and In that also result in a decrease of the Mg melting temperature, has been the topic of a few previous publications [8,61-66]. Unfortunately, the effect of these additives on the flux pinning mechanism behavior does not appear to have been documented except in the case of In, where a similar tendency was observed, although in that case the samples consisted in bulk pellets [46]. Systematic studies would be useful to find out whether elements inducing a lowering of liquid phase formation should be avoided, or the use of such elements requires developing specific heat treatments for minimizing the weakening of ΔT_c pinning.

Conclusion

Under the present experimental conditions, i.e. *in-situ* reaction at 700°C, 800°C or 900°C for 1 h inside Cu/Nb-sheathed wires the amount of Ir that can be substituted for Mg in MgB_2 is limited to 1.6 at.% at most. Impurity phases consisting of IrMg_3 and IrMg_4 with diameters reaching up to 4 μm form in the MgB_2 matrix. T_c is slightly lowered by Ir substitution. On the other hand, the critical current density is decreased and the flux pinning strength is weaker in the doped samples. A progressive shift from ΔT_c pinning to surface pinning mechanism was observed in Ir-doped

samples, especially at 30 K. The solubility limit of Ir is lower than previously reported and is similar to that of other platinum group metals (Ru, Rh and Os), with comparable effects on T_c .

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Figure captions

Figure 1: XRD patterns of the powders mechanically extracted from the wires after annealing at 700°C, 800°C or 900°C. The reflections with Miller indices originate from MgB_2 , ● Mg, ○ Boron. The x value refers to the amount of Ir in the nominal composition $\text{Mg}_{1-x}\text{Ir}_x\text{B}_{2.04}$.

Figure 2: SEM images (backscattering mode) of polished cross-sections of samples after reaction at 700°C (a), (b) and (c), 800°C (d), (e) and (f) or 900°C (g), (h) and (i) with $\text{Mg}_{1-x}\text{Ir}_x\text{B}_{2.04}$ nominal compositions (x = 0.00 (a), (d) and (g) 0.01 (b), (e) and (h), 0.02 (c), (f) and (i).

Figure 3: SEM image (backscattering mode) of the sample with $\text{Mg}_{0.98}\text{Ir}_{0.02}\text{B}_{2.04}$ nominal stoichiometry after reaction at 800°C (a) and EDS elemental maps showing the relative concentrations of Mg (b), B (c) and Ir (d). The numbers in Fig.3a refer to B-rich magnesium borides: “7” = MgB_7 and “12” = MgB_{12} .

Figure 4: Critical temperature (T_c) versus nominal composition for the samples reacted at various temperatures. The inset shows three typical transition curves.

Figure 5: Double logarithmic plots of the normalized critical current density (j_c) versus applied field (B) at various temperatures for the samples without Ir and with 2 at.% Ir substitution for Mg, both reacted at 800°C. The insets show the magnetization hysteresis loops used for calculating the j_c values.

Figure 6: Critical current density (j_c) values versus applied field (B) for all samples at 30 K (a) and 10 K (b).

Figure 7: Normalised pinning force plots for 10 K and 30 K for all samples as well as theoretical curves calculated on the basis of different flux pinning mechanisms.

Table caption

Table 1: a and c lattice parameters, critical temperature (T_c) and accommodation field (B^*) for all samples. The T_c and B^* values have uncertainties of 0.15 K and 1% respectively.

ACCEPTED MANUSCRIPT

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

x^1	$T_{\text{react}} [^{\circ}\text{C}]$	$a [\text{\AA}]$	$c [\text{\AA}]$	$T_c [\text{K}]$	$B_{30\text{K}}^* [\text{mT}]$	$B_{20\text{K}}^* [\text{mT}]$	$B_{10\text{K}}^* [\text{mT}]$
0.00	700	3.0829(4)	3.5223(5)	38.14	342	746	995
0.01	700	3.0823(11)	3.5232(14)	37.67	308	723	1005
0.02	700	3.0823(11)	3.5220(13)	38.05	265	580	810
0.00	800	3.0824(2)	3.5203(3)	38.67	420	811	1045
0.01	800	3.0816(6)	3.5233(8)	38.10	327	711	973
0.02	800	3.0814(3)	3.5251(3)	37.76	228	491	691
0.00	900	3.0822(4)	3.5218(5)	38.63	390	742	950
0.01	900	3.0814(8)	3.5217(9)	37.94	324	705	968
0.02	900	3.0823(4)	3.5222(5)	37.84	258	530	719

¹in $\text{Mg}_{1-x}\text{Ir}_x\text{B}_{2.04}$