CALPHAD-assisted development of in-situ nanocrystallised melt-spun Co-Fe-B alloy with high $B_s$ (1.57 T)

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**Abstract**

A thermodynamics-based approach, Calculation of Phase Diagram (CALPHAD), combined with topological instability parameters are proposed and experimentally evaluated, in order to optimise in-situ nanocrystallisation of rapidly quenched CoFeB alloys and exploit their remarkable $B_s = 1.57$ T. The high $M_s$ of the alloy is attributed to the precipitation of the metastable Co$_7$Fe$_3$ nanocrystalline phase dispersed heterogeneously in the amorphous matrix. High $M_s$ of Co$_7$Fe$_3$ phase can also be inferred from the high hyperfine magnetic field of the Fe nuclei deduced from Mössbauer spectra. It is worth noting that the in-situ nanocrystallisation is a volume phenomenon, instead of surface crystallisation at the air-side of ribbons owning to lower cooling rates. We judge, based on nucleation theory, that the formation of the metastable phase is kinetically favoured, when compared to the equilibrium phases, hence promoting the high $M_s$ when compared with conventional Co-rich amorphous alloys. The local atomic order of nanocrystallised phase was confirmed by X-ray and electron diffraction techniques. Using Mössbauer spectroscopy and the extracted distribution of the hyperfine magnetic field, it is asserted that cobalt atoms form clusters, as they attract each other to form ordered structures, and boron atoms undergo only short-range ordering, likely due to covalent bond formation, governed by the size and electronegativity differences with the atoms in the amorphous matrix. We suggest the proposed CALPHAD-assisted design of nanostructured alloys, along with an in-situ nanocrystallisation, provides a practical scheme to develop novel functional alloys with the best possible balance of coercivity and saturation, exclusively aimed for a high-tech application.

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1. Introduction

The design of multifunctional materials is always prompted by an ever-increasing demand of advanced systems functionality: examples include miniaturised electronic devices, ultra-fast computational and communication capabilities, and ultra-high density data storage media. Sensors, actuators, and nano-micro-electromechanical systems (NEMS-MEMS) already integrate multifunctional materials and smart structures [1,2]. In this context, state-of-the-art magnetic materials, ranging from ultra-soft (Fe- and Co-rich amorphous alloys) to semi-hard (FePt-based) to permanent magnets (NdFeB-type), play a vital role in designing smart and high-performance systems, including efficient power conversion [3–6], ultra-high density data storage media, and clean energy generation [7]. Amorphous magnetic alloys are well-known for their soft magnetic performance, high corrosion resistance, exceptional mechanical toughness and tensile strength, thanks to their unique disordered atomic structure to support this excellent combination of properties [8]. Particularly, CoFe-based alloys are of significant importance, due to their broad range of industrial applications, including data storage (e.g., MRAM) and integrated power conversion (e.g., PwrSoc) concepts [9]. However, the random atomic distribution in CoFe amorphous alloys contributes to the lower $M_s$ which eventually reduces their functionality for high magnetic flux applications. It is envisaged that the formation of nanocrystalline ordered phase in CoFe alloys is beneficial to enhance the $M_s$. Particularly, chemically ordered Co$_7$Fe$_3$ with CsCl structure has remained a focus of extensive research due to its high $M_s$ and good
chemical stability [10,11]. However, bare CoFe bimetallic nano-
particles are highly pyrophoric in nature; alloys exposed to air result
in the formation of the corresponding oxides. Thus, the ease of ox-
idation, their potential toxicity and intrinsically low relative density,
hinder their functionality and hence stimulate developing alternative
routes to grow the nominal phase and to materialise the advantages

One of the alternative routes to developing the nanocrystalline
alloys is a post-annealing of rapidly quenched amorphous precursors
at elevated temperatures. However, nanocrystallisation of amor-
phous alloys is a multi-step process and requires a special scheme
(additives and cooling rate) to control the nucleation and grain
growth process of a particular phase. In a first step, high purity
transition metals along with different glass formers are melt-spin to
fabricate the amorphous precursors. As a second step, heat treat-
ment is performed, in order to precipitate the nanocrystalline
phases. However, the growth of a particular phase, with optimal
performance is challenging. In addition, the heat treatment process
(of nanocrystallisation) causes the embrittlement of the ribbons and,
therefore, deteriorates the manufacturability in subsequent proce-
dures [12]. An alternative approach to synthesise nanostructured
alloys without post heat treatment is “in-situ nanocrystallisation”
using rapid-quenching. However, this requires a careful design of
alloy composition, with low or moderate amorphisation capability
(AMC) to avoid both, vitrification into a glassy state, or precipitation
into a fully crystalline state, during the rapid-quenching [13]. Fur-
ther, the volumetric precipitation of the nanocrystalline phase is
essential to promote, instead of surface crystallisation of the melt-
spun ribbons, due to lower cooling rates at the air/gas-exposed side
of the ribbons. To synthesise an optimised alloy, using in-situ na-
ocrystallisation approach, the prediction of AMC by calculation of
the phase diagram (CALPHAD), combined with the topological in-
stability parameter (\(\lambda\)), based on configurational entropies, esti-
mated by mismatch factors, is established as an essential tool.
Similar method is also well-proven in the optimisation of the glass
forming ability of Fe- and Zr-based glassy alloys [14]. A number of
glass-forming criteria, based on the different phase transition tem-
peratures such as \(T_g\) (glass transition temperature), \(T_{onset}\) (onset crys-
tallisation temperature), \(T_l\) (onset liquidus temperature) and \(T_m\)
(melting temperature), can be calculated and combined together
with \(\lambda\) to predict the AMC of alloys. The room temperature amor-
phous phase is also thought to have the long-range disorder, which
is mainly contributed by mismatch and configurational entropies, as
estimated by mismatch factors [15]. Using a predictive modelling
approach, one can design the alloys with moderate AMC, in order to
fabricate nanocrystalline structures, when using rapid quenching,
without post heat treatment. Thus, one can benefit from the high
\(M_i\) of the bimetallic phase, in the form of CoFe\(_2\) nano-grains embedded in
an amorphous matrix, formed in-situ with no consecutive thermal
treatment.

In this work, thermodynamic parameters, predicted by the
CALPHAD approach, and the topological instability criteria, \(\lambda\), are
considered to design the Co-Fe-B alloy with a moderate AMC and
evaluate the formation of in-situ nanocrystalline structures of a
CoFe-based alloy with high \(M_i\) using rapid-quenching. The very-high
\(B_1\) (1.57 T) of the as-quenched alloy is clearly attributed to the for-
mation of the CoFe\(_2\) nanostructured phase, which is dispersed heterogeneously in the amorphous matrix, throughout the volume of the
melt-spun ribbons. The latter are subjected to detailed structural investigations, using XRD, TEM, and Mössbauer spectro-
scopy. Based on the compositional maps of the relevant parameters,
a model is proposed to enhance the probability of in-situ nano-
crystallisation, by adjusting the different thermodynamic and to-
pological parameters.

2. Experimental methods

The equilibrium phase diagram of Co-Fe-B is thermodynamically
modelled using Pandat™ software (version 2019). The cobalt-based
thermodynamic database of the software is utilised to predict the
enthalpy of mixing, the liquidus temperature and possible equili-
brium and non-equilibrium phases at room temperature for
Co\(_{70}\)Fe\(_{17.5}\)B\(_{12.5}\) (atomic %) composition. To melt-spin the nominal
alloy composition, first, the desired quantities of each element are
weighed out using a standard microbalance to a precision of \(-0.2\) mg
to make a 5 g ingot. The starting materials are Co pieces 99.5% trace
metals basis (TMB), Fe chips 99.98% (TMB), and boron crystalline
pieces 99.7%, all sourced from Sigma Aldrich. The alloy is prepared
by arc-melting in high purity argon. Heating up occurs from an
electric arc, which is created between a copper electrode and sharp
welding tip (2% thoriated red-tungsten). The elements to be melted
are contained within a water-cooled copper hearth. In general, the
lower melting point elements are placed under those of higher
melting point, except for boron, which is placed at the bottom of the
hearth in an adjusted excess amount, in order to retain stoichoio-
metry. The ingots are flipped and re-melted eight times to ensure
homogeneity and a uniform lustre. As a precaution, high purity ti-
nanium (in a separate hearth) is used as a getter for oxygen.

Ribbons are subsequently produced by induction melting and
melt-spinning the arc-melted ingots (in 1 g batch) into argon atmo-
sphere. An argon jet (at an overpressure of 0.7 bar) is used to
in-situ weld the molten liquid contained in a fused silica vial. Typical
experimental parameters and conditions applied are quartz vial of
60 mm length, 8 mm inner diameter and 0.5 mm diameter orifice, a
nozzle to wheel angle of 10° from the perpendicular, a nozzle to
wheel separation of ~0.1 mm, wheel diameter of 90 mm and a wheel
speed of 80 m/s. Using the as-mentioned conditions, ribbons of
\(-14\) µm thickness and \(-1\) mm width are obtained.

The X-ray powder diffraction (XRD) data of the melt-spun rib-
bons are collected using a Phillips PANalytical X’pert Pro dif-
fractometer, with an operational wavelength of 1.5405 Å (Cu-K\(\alpha\)
anode and a Ni filter). For transmission electron microscopy (TEM)
analysis, each selected ribbon is first processed using a focused ion
beam microscope (FEI Quanta 3D FEG). A protective metallic (Pt-
based) layer is deposited on the surface before milling to create an
ultrathin lamella, and two stair-step FIB trenches are cut at both
sides of the area of interest. Next, the specimen is further thinned to
less than 1 µm in thickness. Final milling down to less than 100 nm
is carried out by employing successively lower voltages up to 2 kV.
The obtained lamellae are removed using a micromanipulator and
welded to a Cu grid suitable for transmission electron microscopy
(TEM) analysis. TEM imaging of the ultrathin lamellae is performed
using a JEOL JEM-2100F (S) TEM microscope operating at 200 kV
with a LaB\(_6\) filament. In addition, the coercivity and anisotropy field
of the ribbons, along their length, is measured using a B-H loop
tracer (at \(f = 10\) Hz) with a maximum magnetic field of 0.1 Tesla.
Additionally, the \(M_i\) of the sample is studied by superconducting
quantum interference device (SQUID-based) magnetometry (MPMS
5XL, Quantum Design, USA) at RT in fields of up to \(\mu_0H \leq 2\) T. Room
temperature transmission Mössbauer spectra are collected using a
conventional constant acceleration spectrometer with \(^{57}\)Co sealed in
the Rh matrix source. In this geometry, the \(\gamma\)-ray direction is per-
dicular to the ribbon plane. The electrical resistivity measurements
were carried out at room temperature using a DC four-probe method
with fixed distances (\(i.e., 1\) mm) between the four probes. The
potential drop is picked up on the 22 mm long specimen, with an
equivalent resistance error of \(\pm 0.001\) Ω. All samples are measured
at six different voltage levels, and the data is regressed upon, in
order to diminish the role of contact non-linearities and heating.
3. Results and discussions

3.1. CALPHAD-assisted alloy design

Several criteria have been established to evaluate the amorphisation capability of rapidly quenched metallic alloy systems [14], suggesting how the disordered atomic structure in metallic alloys can be preserved on vitrification with the lowest possible cooling rates (defined as critical cooling rate, a well-known measure of the AMC of the amorphous alloys) [14]. However, all parameters are empirical and based on trial-and-error. More recently, there has been some interest in an alternative evaluation of the AMC criterion for the amorphous alloys, using the CALPHAD approach, augmented by the topological instability factor $\lambda$. This predictive model of amorphisation has worked well, in a couple of examples, hence suggesting a working alternative for the prediction of the glass forming ability of alloys [16,17]. Interestingly, this criterion can be useful, when there is an interest in the growth of metastable nanocrystalline structures using the rapid quenching process. The alloy composition can be tuned, in a particular region of the phase diagram, where $\lambda$ is not favourable for high AMC, and hence, the chance of precipitation of the desired metastable phases increased, during vitrification. Keeping this in mind, the following thermodynamic parameters, along with $\lambda$, are scrutinised in a specific region of the phase diagram to regulate the moderate AMC and design an alloy, in which the metastable nanocrystalline phase precipitates during melt spinning process.

3.1.1. Liquidus temperature

When a liquid melt is cooled down from the liquid state to a temperature below the $T_L$, the viscosity of the melt increases to a high value, and consequently, glass is vitrified. The effective viscosity at $T_L$ is known to be fixed at 10$^{12}$ Pa.s, as initially suggested by Turnbull [18], which is originally based on the kinetics of crystal nucleation and the viscosity of the melts. It suggests that the ratio of $T_L$ to the liquidus temperature, $T_g$, also well-known as reduced glass transition temperature, $T_{rg}$ (Eq. 1), can be a good indicator of the susceptibility to amorphisation of the alloys. The higher the value of $T_{rg}$, the higher is the viscosity, and therefore the alloy melt could easily be solidified into the amorphous state, at a lower critical cooling rate. In other words, an alloy composition with a high value of $T_g$ and a low value of $T_L$ is preferable to promote high amorphisation capability.

$$T_{rg} = \frac{T_g}{T_L}$$

Further, it has been experimentally proven that the value of $T_g$ changes slowly with solute contents. On the other hand, $T_L$ of an alloy usually decreases with increasing solute content in most of the alloy systems. Particularly, phase diagrams of some alloy systems show that liquidus curves drop very steeply with solute content [19]. Furthermore, an alloy with a eutectic temperature significantly lower than the melting points of the individual elements is referred to as a “deep” eutectic. In such cases, the $T_{rg}$ value around the “deep” eutectic composition is a strong function of the alloy composition and exhibits its highest value at the eutectic composition. Therefore, it should be possible to quench this alloy composition easily into a glassy state.

On the other hand, if the liquidus temperature of an alloy also decreases slowly with the solute content, then the $T_{rg}$ value at the eutectic composition may not be high. In such a situation, it will be challenging to produce such an alloy in the glassy state. Thus, the Turnbull criterion of high $T_{rg}$ and deep eutectics converge at the deep eutectic compositions [14]. Fig. 1 illustrates the liquidus projection in the Co-Fe-B phase diagram, in which the liquidus isotherms are shown every 25°C decreasing towards the eutectic point. The composition is chosen to be in the region where this parameter is neither highly negative, towards the boron-rich alloys, nor extremely positive towards the Fe-rich alloy compositions. The moderate $\Delta H_{mix}$ could result in a moderate AMC, which can lead to the in-situ fabrication of nanocrystallised alloy.

3.1.2. Enthalpy of mixing

According to Inoue’s empirical rule [20], the enthalpy of mixing, $\Delta H_{mix}$, significantly favours the formation of amorphous structure and is a good measure of the AMC. It has been suggested that a significant negative heat of mixing would lead to an increase in the energy barrier at the liquid-solid interface, and a decrease in the atomic diffusivity through the growth interface. The large mixing enthalpy would be expected to lower the effective mobilities of even the lightest species (i.e. boron) in the melt, which following Einstein’s relation, would in turn increase the effective melt viscosity [21]. Thus, the more negative the $\Delta H_{mix}$, the higher the AMC of an alloy [2,4].

The chemical mixing enthalpy is calculated according to Eq. (2) based on the extended regular solution model [22]:

$$\Delta H_{mix} = \Omega_{cdef} c_D c_E + \Omega_{cdef} c_D c_F + \Omega_{cdef} c_E c_F$$

where $\Omega_{c}$ is the regular solution interaction parameter between $i$ and $j$ elements, which can be expressed by the mixing enthalpy of binary alloys ($\Omega_{c} = 4\Delta H_{mix}^{ij}$), and $c_i$ is the molar fraction of the $i$ element [23]. Ternary diagram of enthalpy of mixing in the Co-Fe-B system is presented in Fig. 2. The labelled alloy composition is chosen to display an enthalpy of mixing, ~9.56 kJ/mol, which is the region where this parameter is neither highly negative, towards the boron-rich alloys, nor extremely positive towards the Fe-rich alloy compositions.
3.1.3. Atomic mismatch factor

In addition to thermodynamic parameters, a topological parameter has also been used to predict the amorphisation capability of a metallic system. This effect has long been accounted for the empirical requirement for constituent atoms with at least a 12% size difference [14]. A more continuous approach to the question of topology has been linked to a critical lattice strain, caused by the volumetric mismatch of the species, required to suppress crystallisation. This concept was developed by Sá Lisboa et al. [24] through the atomic mismatch factor, \( \lambda \) in multicomponent systems [16],

\[
\lambda = \sum_{i=B}^{Z} c_i \left( \frac{r_i}{r_A} \right)^3 - 1
\]

(3)

where \( i \) denotes the different solutes \( B \) to \( Z \) in matrix \( A \), \( c_i \) is the concentration of solute \( i \) in matrix \( A \) (mol%), \( r_i \) is the solute atomic radius (nm), and \( r_A \) is the solvent atomic radius (nm).

Yan et al. [25] noted that optimal glass-forming happens at \( \lambda = 0.18 \) for several investigated multicomponent systems. When assuming that an amorphous material is made up of numerous clusters of icosahedra, the packing efficiency peaks at \( \lambda = 0.18 \). It can also be inferred from [26] that \( \lambda = 0.18 \pm 0.04 \) can be considered as a region with a reasonably high AMC in several distinct alloy systems. Thus, the alloy composition is chosen on the boundary of the region with optimum \( \lambda \) to show moderate AMC, as shown in Fig. 3 where the \( \lambda \)-lines are superimposed in the Co-Fe-B phase diagram, to in-situ nanocrystallise the alloy during quenching. In other words, based on the \( \lambda \) parameter, the AMC of the alloy is lower as compared to the alloys inside the green region, but considerably higher when compared to the alloys outside the green region. This moderate (tuned) AMC can lead to in-situ nanocrystallisation of the alloy during melt spinning.

Thus, the proposed predictive model of in-situ nanocrystallisation encompasses both, the thermodynamic and topological, aspects of the alloy system and amalgamates the information on the compositional regions with middle-range \( T_i \) enthalpy of mixing and atomic mismatch factor for the amorphous microstructure. It predicts moderate values of AMC, by identifying the region of interest using \( T_i \), \( \Delta H_{mix} \), and the \( \lambda \)-factor on the phase diagram. It will be shown that the rapid quenching of alloys with tuned AMC can result in an in-situ nanocrystalline alloy.

3.2. Structural characterisation

Fig. 4 shows the XRD pattern of the wheel-side of the as-quenched Co\textsubscript{70}Fe\textsubscript{17.5}B\textsubscript{12.5} ribbons. A sharp Bragg peak at 45.27° <110> and a broader diffused peak at 83.82° <211> can be seen in the XRD pattern, which both represent the Co\textsubscript{70}Fe\textsubscript{17.5} phase formed on the side which experienced higher cooling rate (copper wheel side). Additionally, a sample from the middle region of the cross-section of the ribbon has been examined by TEM to corroborate the local nanocrystal microstructure. Fig. 5a shows a typical TEM image of the nanocrystals in the glassy matrix. The Selected Area Electron Diffraction (SAED) pattern (Fig. 5c), shows the presence of a typical amorphous halo ring pattern, from the matrix, with discrete diffraction spots corresponding to [110], [211], and [220] reflections confirming the presence of the Im\textsubscript{3}m structured Co\textsubscript{70}Fe\textsubscript{17.5} phase. Most of the equiaxed, rather than dendritic, nanocrystalline grains are smaller than 100 nm in size. These results confirm the in-situ formation of Co\textsubscript{70}Fe\textsubscript{17.5} nanocrystals in Co\textsubscript{70}Fe\textsubscript{17.5}B\textsubscript{12.5} ribbons. It is worth...
noting that as XRD was performed on the wheel-side and the TEM sample was from the middle of the cross-section of the ribbon, the *in-situ* nanocrystallisation is a volumetric phenomenon, instead of surface crystallisation which possibly can start due to the lower cooling rates at the air-side of the ribbons. The surface crystallisation takes place when the alloy is not well designed with large AMC [27]. The volumetric formation of *in-situ* nanocrystallisation is essential to get the advantage of the high-flux density of the alloys.

In addition, a higher magnified TEM image of nanocrystals and corresponding SAED can be seen in Fig. 5d and e. The latter corresponds to [311]-bcc zone-axis pattern. Diffractions related to different atomic planes are indicated in Fig. 5e. The lattice parameter based on this lattice spacing between different atomic planes is in good agreement with the lattice parameter calculated from the Rietveld refinement analysis of the XRD pattern (Fig. 4). Thus, the observation of this pattern is also a strong evidence of the existence

![Fig. 5.](image-url)
of crystalline bcc-CoFe clusters in the as-quenched melt-spun CoFeB ribbon. It can also be noted that the background noise seen in the SAED patterns comes from weak scattering by atomic clusters (several atoms in size) in the amorphous matrix surrounding crystalline clusters. Interestingly, the nanocrystalline structure yields in high electrical resistivity ($168 \mu\Omega \cdot cm$) of the alloy. The electrical resistivity of the nanocrystalline materials is higher than both coarse-grained polycrystalline metals and amorphous alloys due to the increased volume fraction of atoms lying at the grain boundaries [28].

Additionally, some thermodynamic and kinetic aspects of these phase transitions are studied below. First, the phase transitions are studied by evaluating the equilibrium and non-equilibrium solidification simulation of the alloy composition using the Pandat™ software. As can be seen in Table 1, five different phases are predicted to crystallise as a result of equilibrium and non-equilibrium solidification of CoFeB alloy. Among these phases, CoFeB has minimum Gibbs energy of formation, $\sim 30 \text{kJ/mol}$. However, the nanocrystals of metastable CoFe phase form during melt-spinning, and they are stable at room temperature. Thus, this discrepancy between experiment and thermodynamic modelling should be addressed accordingly.

The nucleation of a metastable phase could likely to be more kinetically-favoured compared to that of the stable phase [29]. According to classical nucleation theory [30], the activation threshold for the formation of a critical nucleus is $\Delta G^*$, which is the free energy required to form the critical nucleus;

$$\Delta G^* = \frac{16\pi^2f^2(\varepsilon)}{3\Delta G_f}$$  \hspace{1cm} (4)

where $f(\varepsilon)$ is the catalytic potency factor for heterogeneous nucleation, which depends on the wetting angle $\theta$. $\Delta G_f$ is the Gibbs free energy difference between the liquid and the solid:

$$\Delta G_f = \Delta H_f T_m - T_m$$  \hspace{1cm} (5)

where $\Delta H_f$, $T_m$, and $T$ denote the enthalpy of fusion, melting temperature, and undercooling temperature, respectively. The interface energy $\sigma$ can be estimated by the model developed by Spaepen and Meyer [31]:

$$\sigma = \frac{\Delta S_f T}{(N_a V_m)^{1/3}}$$  \hspace{1cm} (6)

where $\alpha$ is a factor dependent on the structure of the solid nucleus and $\Delta S_f$, $N_a$; and $V_m$ are the entropy of fusion, Avogadro’s number, and the molar volume of the phase, respectively. Without the knowledge of the contact angle $\theta$ of the crystal nucleus to the substrate, the nucleation is assumed to be homogenous. Based on this theory, the activation threshold of the dominant stable and possibly metastable phases in this system is estimated and shown in Table 2.

As can be seen, the necessary activation energy for the formation of CoFe is about three orders of magnitude less than the one for (CoFe)$_3$B. Therefore, from the kinetics point of view, the nucleation of this phase is more favourable.

### Table 1

<table>
<thead>
<tr>
<th>Phase</th>
<th>Percentage</th>
<th>Phase</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CoFe)$_3$B</td>
<td>44</td>
<td>CoFeB</td>
<td>49.97</td>
</tr>
<tr>
<td>BCC (CoFe) S.S.</td>
<td>34</td>
<td>FCC (CoFe) S.S.</td>
<td>50</td>
</tr>
<tr>
<td>HCP (CoFe) S.S.</td>
<td>22</td>
<td>(CoFe)$_3$B</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*S.S. stands for solid solution.*

### Table 2

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\Delta G_f$ (kJ/mol)</th>
<th>$\sigma$ (J/m$^2$)</th>
<th>$\Delta G^*$ (J) $\times 10^{23}$</th>
<th>$\Delta G^*$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CoFe)$_3$B</td>
<td>52.34</td>
<td>1.99</td>
<td>4.85</td>
<td>0.3</td>
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<tr>
<td>CoFe</td>
<td>12.55</td>
<td>1.39</td>
<td>0.003</td>
<td>0.00019</td>
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</tbody>
</table>

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**3.2.1. Mössbauer spectra of nanostructured alloy**

Fig. 6 presents the Mössbauer transmission spectra of CoFeB nanocomposite ribbons, along with respective distribution $P(B_{hf})$ of Hyperfine Magnetic Field (HMF). The shape of the spectra is characteristic of a nanocomposite structure with a ferromagnetic arrangement. Thus, both building blocks of the microstructure, nanocrystals and amorphous matrix, can be scrutinised based on the correlated distribution of HMF.

**3.2.1.1. Local atomic order in nanocrystals.** The hyperfine interaction distribution can be analysed based on the local environment model [32], which has been reported for different ternary systems [33–36].

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**Fig. 6.** (a) Room-temperature Mössbauer spectra, and (b) hyperfine magnetic field distributions of as-quenched CoFeB ribbon.
In Fe–X, where X is treated as an impurity, and it can include different types of elements, every atom X which substitutes iron atom in the $i^{th}$ coordination sphere (or neighbour shell) of the $^{57}\text{Fe}$ isotope causes the change of the HMF at $^{57}\text{Fe}$ sites by the value of $\Delta B_i$. The changes in the HMF of iron, as $\Delta B_i$, are additive. In practice, the contributions from the first and the second coordination spheres are considered, and the value $B(m,n)$ of the hyperfine magnetic field at $^{57}\text{Fe}$ site can be described as [37]:

$$B(m, n) = B(0, 0) + m\Delta B_1 + n\Delta B_2$$

(7)

where $B(0,0)$ denotes the value of the HMF at $^{57}\text{Fe}$ nucleus, which is surrounded only by Fe atoms in the first and the second coordination spheres; $m$ and $n$ represent the number of impurity atoms in the first and second sphere, respectively; the changes of the HMF caused by impurity atoms in the first and the second neighbour shells, respectively. The values of $\Delta B_1$ and $\Delta B_2$ could be positive or negative. Relation (7) has been used for both disordered and ordered alloys in the broad range of impurity concentration [37].

In the FeCo, B2 structural type, there are eight cobalt atoms in the first sphere around an iron atom which is the same as the atomic orientation in Co$_2$Fe$_3$. However, there are just two iron atoms in the second sphere in Co$_2$Fe$_3$ compared to 6 iron atoms in the FeCo B2 structure. Thus, based on the fact that there are four fewer iron atoms in the second sphere in the Co$_2$Fe$_3$ phase and the as-mentioned local environment model, the HMF of Co$_2$Fe$_3$, based on its counterpart in FeCo, can be calculated as:

$$B_{\text{CoFe}} = B_{\text{FeCo}} - 4\Delta B_{2,\text{Fe}}$$

(8)

$B_{\text{CoFe}}$ is mentioned to be 34.3 T [38] and $\Delta B$ for an iron atom in the second sphere is measured to be 0.77 T [39], so based on Eq. (8), the HMF for an iron atom in Co$_2$Fe$_3$ is 31.22 T. This number is close to two peaks of the hyperfine field distributions, at 31 ($P(B) = 13.4\%$) and 32 ($P(B) = 19.2\%$) (Fig. 6b). The sum of probabilities for these two fields is 32.7, which agrees with the portion of nanocrystals formed in the amorphous matrix calculated based on the TEM image in Fig. 5a.

3.2.1.2. Local atomic order in the amorphous matrix. A relatively large portion of the structurally disordered matrix, about 70% (Fig. 5a), leads to the broadening of the experimental HMF peak and a significant contribution of low-field background in the total HMF distribution (Fig. 6b). For every HMF field ($B_i$), excluding the ones correlated to Co$_2$Fe$_3$ nanocrystals, the number of cobalt and boron atoms in the first sphere around the iron atom can be estimated based on the following Equation [33,37]:

$$B_i = B(0, 0) + m\Delta B_{i,\text{Co}} + n\Delta B_{i,B}$$

(9)

where $m$ and $n$ denote the numbers of Co and B atoms in the first coordination sphere, while $\Delta B_{i,\text{Co}}$ and $\Delta B_{i,B}$ denote changes of the HMF caused by a single Co and B atoms respectively. Statistically, the probability of finding $n$ of Co atoms and $m$ of B atoms in the first coordination shell of $^{57}\text{Fe}$ in the amorphous matrix can be calculated using multinomial distribution [33,37]:

$$P(m, n) = \frac{N!}{m!n!(N-m-n)!} x^m y^n (1 - x - y)^{N-m-n}$$

(10)

where $N$ is the number of all atoms in the first coordination sphere, $x$ and $y$ denote the chemical concentration of the cobalt and boron in the amorphous matrix. Among different pairs of $m$ and $n$, the ones with the highest $P(m, n)$ are chosen. Then ($m$) and ($n$) are calculated based on:

$$\langle m \rangle = \sum m P_{\text{exp}}(m, n)$$

(11)

$$\langle n \rangle = \sum n P_{\text{exp}}(m, n)$$

(12)

where $P_{\text{exp}}$ denotes the probability of the configuration ($m, n$) of impurity atoms obtained from the analysis of the experimental Mössbauer spectra. Therefore, the Warren–Cowley parameters for cobalt ($\alpha_C$) and boron ($\alpha_B$) atoms have the following form [33,37]:

$$\alpha_C = \frac{(m) - 8x}{8(1 - x)}$$

(13)

$$\alpha_B = \frac{(n) - 8y}{8(1 - y)}$$

(14)

The interpretation of the values of the Warren–Cowley parameters is as follows: when $\alpha_1 = 0$ then the distribution of impurity atoms is random; if $\alpha_1 < 0$ the impurity atoms form clusters, i.e. they attract each other, and finally when $\alpha_1 > 0$; the impurity atoms undergo the short-range order (SRO) effect, i.e. they are attracted by the matrix atoms [33,37]. Based on this theory, cobalt atoms cluster as $\alpha_C = -1.17$. As the most stable local configuration of cobalt is highly dense hcp, this element shows the high tendency for clustering in a large variety of systems with either metallic or covalent bonding. The strong drive for clusterisation of the cobalt atoms, which leads to a local increase in their concentration, in addition to the tendency of boron atoms to undergo SRO leads to the nucleation of ordered cobalt-rich Co$_2$Fe$_3$ phase (Figs. 4 and 5). Warren–Cowley parameter for boron atoms is 0.12, implying that they, indeed, undergo SRO. A repulsive potential between the small boron atoms and attraction between the boron atoms and large cobalt/iron atoms could lead to the formation of a tetrahedron of four cobalt/iron atoms surrounded by boron, minimising the voids in the Bernal dense random packing structure [40], and thereby stabilising the structure against easy crystallisation.

3.3. Magnetic properties

The evolution of magnetisation, measured along the length of the ribbons, as a function of the applied magnetic field, is presented in Fig. 7. It can be seen that the coercivity, $H_c = 381.5$ A/m, and the anisotropy field, $H_k = 728.5$ A/m, are high which could be attributed to the effect of magnetocrystalline anisotropy of the ordered nanocrystals of the Co$_2$Fe$_3$ phase. The as-mentioned effect can be measured quantitatively, by the anisotropy energy ($K_u$), which is calculated based on the following Equation [41]:

$$K_u = \frac{H_u \mu_0 M_i}{2}$$

(15)

where $\mu_0 M_i = 1.57$ T.

Fig. 7. Hysteretic loop of as-quenched nanocrystalline Co$_2$Fe$_{77}$B$_{12.5}$ ribbons, $\mu_0 M_i = 1.57$ T.
where \( \mu_0 \) is the free space permeability. The anisotropy is related to directional atomic ordering along the direction of the local magnetisation to minimise the spin-orbit coupling energy [42]. The calculated anisotropy energy for the in-situ nanocrystalline alloy is 573 J/m², which is about twenty times larger than the values reported for similar amorphous alloys [3]. Furthermore, the \( M_s \) of the in-situ nanocrystalline alloy is 1.57 T. The relatively high \( M_s \) is due to the presence of the ordered Co–Fe₂ phase, which its \( M_s \) is ~4% higher than its disordered counterparts [43]. High \( M_s \) of Co–Fe₂ can also be inferred from the high hyperfine magnetic field interactions of the Fe nuclei, in the nanocrystals of Co–Fe₂ (Fig. 6b).

To understand the evolution of \( M_s \) of the alloy, it is necessary to take into account a few primary considerations concerning the electronic structure and magnetic properties of the 3D system. In this regard, the Slater–Pauling figure, which shows the relationship between the magnetic moment and the number of valence electron per atom (\( e/\alpha \)) is used. The \( e/\alpha \) is estimated for Co–Fe₂ nanocrystals, as 8.7, and for the amorphous matrix 7.72. Then, \( e/\alpha \) for the nanocomposite is calculated based on the portion of the nanocrystals in the amorphous matrix. The magnitude of the magnetic moment for \( e/\alpha \) of the nanocomposite is 1.64 \( \mu_0 \) which is slightly higher than the magnetic moment of the nanocomposite estimated based on \( M_s \), 1.47 \( \mu_0 \). This difference can be due to the hybridisation effect, as a result of SRO of boron atoms, which is observed by Mössbauer spectroscopy in Section 3.2.1.

4. Conclusions

An in-situ nanocrystallised Co₇₀Fe₇₇B₁₂.₅₅ alloy, with a tuned amorphisation capability has been designed, using a thermodynamics-based CALPHAD approach, together with a topological instability parameter. The proposed scheme works as a guideline for the tuning of AMC of alloys, to favour the formation of the desired ordered phase (Co–Fe₂) nanocrystals throughout the volume of the alloys, during the rapid quenching process. This can be achieved without any post-spinning heat treatment, which is normally required in order to grow the necessary amount of nanocrystalline phase. The XRD and TEM results confirm the formation of the Co–Fe₂ ordered phase, dispersed heterogeneously throughout the amorphous matrix. Furthermore, the local atomic order of the nanocrystalline structures and the amorphous matrix has been investigated by the distribution of hyperfine magnetic field, using Mössbauer spectroscopy. In the latter, the Warren–Cowley parameter is negative for cobalt atoms showing their tendency to form ordered structures, and it is positive for boron atoms implying that they are prone to undergo short-range order due to their size and electronegativity difference with atoms in the amorphous matrix. The proposed approach of designing in-situ nanocrystalline alloys by rapid quenching, using both thermodynamic and topological parameters, is useful for the development of functional materials for a broad range of applications. Future research on the introduction of other elements, such as Nb or Cu, in order to increase the number of crystalline nuclei in the two-phase system (melt–solid) and therefore further decrease the grain size, may also benefit from the proposed predictive modelling approach.

CRediT authorship contribution statement

Hasan Ahmadian Baghbaderani: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. Ansar Masood: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – review & editing, Project administration, Funding acquisition. Kenny L. Alvarez: Investigation, Data curation, Writing – review & editing. Cian Ó Mathúna: Supervision. Paul McCloskey: Conceptualization, Validation, Project administration, Writing – review & editing, Funding acquisition. Plamen Stamenov: Conceptualization, Validation, Project administration, Writing – review & editing, Formal analysis, Visualization, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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