

Project acronym: **PASSENGER**

Project title: “**Pilot Action for Securing a Sustainable European Next Generation of Efficient RE-free magnets**”

Grant agreement number: **101003914**

Start date of project: **1 May 2021**, Duration: 48 months



Deliverable No. 1.1

Fabrication of τ -phase Mn-Al-C loose powder (obtained by annealing the ϵ -phase powder) with target values: remanence $B_r = 3.0$ kG; coercivity $jH_c = 2.5$ kOe

Due date of deliverable	30/04/2023
Submission date	22/05/2023
File Name	D1.1 PASSENGER_Fabrication of τ -phase Mn-Al-C loose powder (obtained by annealing the ϵ -phase powder) with target values: remanence $B_r = 3.0$ kG; coercivity $jH_c = 2.5$ kOe
Organisation Responsible of Deliverable	METALPINE
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Revision number	12
Status	Final ¹
Dissemination Level	PU ²

¹ Document will be a draft until it is approved by the coordinator

² PU: Public, PP: Restricted to other programme participants (including the Commission Services), RE: Restricted to a group specified by the consortium (including the Commission Services), CO: Confidential, only for members of the consortium (including the Commission Services)



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REVISION HISTORY

Version	Date	Modified by	Comments
01	27.4.2023	Anna Köll, Martin Dopler (METALPINE)	Writing
02	28.04.2023	Guixiang Qin (LCM)	Contribution
03	29.04.2023	Andrés Martín-Cid (IMDEA)	Revision and edition
04	01.05.2023	Alberto Bollero (IMDEA)	Revision and edition
05	03.05.2023	Anna Köll, Martin Dopler (METALPINE)	Revision and edition
06	04.05.2023	Guixiang Qin and Nik Tankov (LCM)	Revision and edition
07	06.05.2023	Alberto Bollero (IMDEA)	Revision and edition
08	08.05.2023	Anna Köll (METALPINE)	Revision and edition
09	08.05.2023	Alberto Bollero (IMDEA)	Revision and edition
10	12.05.2023	Ignacio Torres (IMDEA)	Format edition
11	19.05.2023	Enrico Forlin	Revision and edition
12	21.05.2023	Alberto Bollero	Revision and Final version

ACKNOWLEDGEMENT AND DISCLAIMER



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement no. 101003914.

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LIST OF ACRONYMS

Abbreviation	unit	Meaning
Br, T	[Am ² kg ⁻¹], [kG], [T]	Remanence
jHc	[kA/m], [kOe]	Coercivity
M@1600 kA/m	[Am ² kg ⁻¹]	Saturation at 1600 kA/m
M _r / M@1600 kA/m	-	Squareness factor
HEBM	-	High energy ball milling
SEM	-	Scanning electron microscope
EDX	-	Energy Dispersive Spectroscopy
ECC	-	Energy channelling contrast
VSM	-	Vibrational sample magnetometer



SUMMARY

To ensure that the material has ferromagnetic properties, two different routes were taken to produce τ -MnAlC phase powder. METALPINE's task in this project is to atomize the MnAlC material to obtain powder with a crystallographic structure based on the ϵ -phase (precursor). Subsequent heat treatment and investigations by IMDEA revealed successful transformation to almost pure τ -MnAlC phase. LCM produced the MnAlC alloy by casting, which was subsequently crushed and thus processed into powder. After initial difficulties with comminution, IMDEA has demonstrated the validity of its self-developed “flash-milling” method to improve permanent magnet properties on the crushed MnAlC powder. A subsequent heat treatment influences the magnetic properties of the material, so the aim is to find a compromise between milling time and annealing time to achieve the highest possible remanence and coercivity (considering that typically for permanent magnets the increase in one of these properties is accompanied by a decrease in the second one). MBN applied its HEBM technology to replicate the “flash-milling” effect at pilot scale, towards a process industrialization. As can be seen in Table 1 the target value for this deliverable for the remanence was nearly achieved while the value of the coercivity has significantly exceeded the target value (in more than 6%).

Table 1 Comparison of the magnetic target values with achieved values

		Target values D1.1	Achieved values
Remanence [$\text{Am}^2\text{kg}^{-1}$]	Br	47,8 ($\approx 3,0$ kG)	41
Coercivity [kA/m]	jHc	199 (≈ 2.5 kOe)	212.5

The sample with the best magnetic properties so far was selected to aim for larger scale production and to further optimise the annealing process.



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INTRODUCTION

The aim of this deliverable is the production of τ -MnAlC phase powder with remanence of $B_r > 2.0$ kG and a coercivity of $jH_c > 3.5$ kOe. Keeping consistency with the magnetic units used for M18 technical report, and considering a calculated density of 5 g/cm^3 for the MnAlC alloy, the objectives of this deliverable are $M_r > 47.8 \text{ Am}^2\text{kg}^{-1}$ and $jH_c > 199 \text{ kAm}^{-1}$.

According to the project proposal, two different routes will be followed to synthesize the permanent magnet phase τ -MnAlC: gas-atomized (**METALPINE**) and as-cast (**LCM**) and ball milled powder (**MBN** and **IMDEA**).

The challenges are to reach the only ferromagnetic phase of the Mn-Al-C-system (the τ -MnAlC phase), which may be directly formed during the synthesis (depending on the technique used) or it may require a post-processing step to manage the transformation from the ϵ to the τ phase. An additional challenge is to minimize the content of secondary phases (namely, the γ_2 and β -Mn phases), since the highest content of these phases present in our material, the lowest the magnetization will be.

Interestingly, it is also important to consider in the development of this work that the synthesis of a Mn-Al alloy consisting solely of pure τ -MnAlC phase guarantees a high magnetization saturation, but it is typically accompanied by a low coercivity (< 1.5 kOe, i.e. far from PASSENGER's goal). For this purpose, previous studies carried out by **IMDEA** [1-3] have demonstrated that achieving an optimized coexistence of the τ -MnAlC and the β -Mn phases is beneficial to achieve a good balance of both magnetization and coercivity. The τ -MnAlC phase is providing magnetization while the β -Mn phase leads to an enhancement in coercivity (by acting as pinning centers during the magnetization reversal). Milling of the alloy followed by an optimized annealing is an efficient procedure to achieve this result. These are the main concepts driving the achievement of this deliverable.

METHODOLOGY

GAS-ATOMIZED POWDER PROCESSING

For gas-atomization, the melt is directed upwards into the nozzle via a rising pipe by negative pressure. There, the melt meets the atomizing gas and is thus atomized into powder. Further upstream of the nozzle, the atomized droplets spheroidise as they cool down and solidify. A schematic representation of a gas-atomization process is shown in **¡Error! No se encuentra el origen de la referencia..**



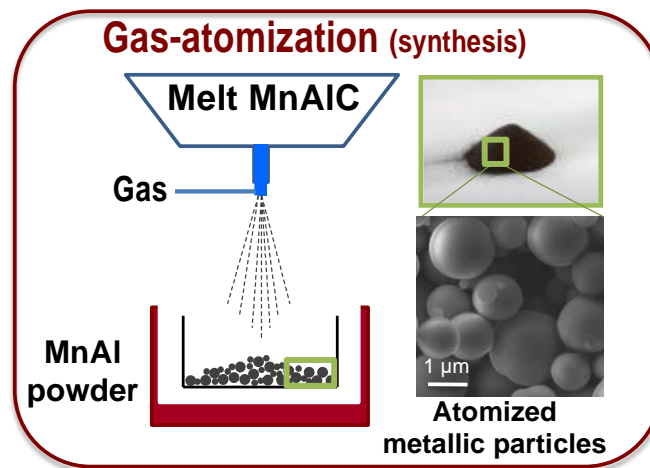


Figure 1: Schematic illustration of gas atomization

At the end of the process, the material is separated from the gas flow in a cyclone and collected below the cyclone. After successful commissioning trials, manganese-aluminium-carbon melts were atomized in small scale accompanied by number of technological challenges. Since the powder is in the epsilon phase during production, it is subsequently annealed by **IMDEA** in order to transform to the tau phase (only ferromagnetic phase in Mn-Al) in the structure. By using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and high-resolution electron channelling contrast imaging (ECC), microstructural analysis was done.

CAST ALLOY PRODUCTION

LCM has prepared MnAlC cast alloys with three different compositions:

- $(\text{Mn}_{57}\text{Al}_{43})_{98.5}\text{C}_{1.5}$ named J10229, cast into copper mould.
- $(\text{Mn}_{54}\text{Al}_{46})_{98.5}\text{C}_{1.5}$ named J10159, cast into copper mould.
- $(\text{Mn}_{55}\text{Al}_{45})_{98.5}\text{C}_{1.5}$ cast into copper and steel mould and used for strip casting.





Figure 2: Production of MnAlC alloy by LCM

LCM performed all the casts with vacuum induction melting. The raw materials used are 99.8 wt% Al, 99.8 wt% Mn, and carbon granules, loaded in the crucible building up layer by layer. Some amount of the cast alloys was sent to **TUDA** and **IMDEA** for characterization. The crushing of the as-cast material presented a big challenge for LCM and the rest of the partners involved in this task, due to the high hardness of the τ -phase. After solving this issue, it was possible to produce 7 kg ingots with nearly pure τ -phase and crush them to particle sizes under 300 μm by hammer milling (using a KEK mill at LCM) and sent to MBN and IMDEA for further processing. A total of 150 kg of cast alloys was produced at LCM. MBN and IMDEA worked on the translation of IMDEA's flash-milling method to a larger scale industrial process, using MBN's proprietary mechanical alloying process based on High Energy Ball Milling (HEBM).

Improved Properties by HEBM and flash milling

Further processing was done on LCM's milled powders to improve their magnetic properties. **IMDEA** applied its self-developed flash-milling method on powder with a mean particle size below 90 μm . The first samples in small scale were milled for six different times, between 30 and 240 seconds, and annealed at two different temperatures, 550 $^{\circ}\text{C}$ and 650 $^{\circ}\text{C}$, for 10 minutes. The following samples were milled from 120 to 840 seconds and annealed at a temperature of 550 $^{\circ}\text{C}$, which was found to be optimal for development of the magnetic properties. **MBN** applied HEBM on τ -phase MnAlC powder <300 μm directly provided by **LCM**. Different HEBM energy levels were explored at small scale to replicate the "flash milling" effect. These samples were designated T1 to T11. In a second series of experiments labelled "sp", additional energy levels were tested to optimize powder morphology and yield. These samples were designated as T5sp to T14sp. While in the first test series the powder was annealed at 2 different temperatures, the samples in the second test series were only annealed at 550 $^{\circ}\text{C}$ for 10 min. The resulting powder was evaluated by amount obtained in the 65-250 μm particle size range, crystallographic structure by XRD, and powder morphology by SEM. The powder processed by HEBM was sent to **IMDEA** for characterization (XRD, SEM and VSM). In this report only the results of samples annealed



at 550 °C are shown, in order to address this specific deliverable and make shorter and clear the document.

RESULTS

GAS-ATOMIZED POWDER PROCESSING

To evaluate the quality of the gas atomized powder produced by METALPINE, **IMDEA** carried out two trials annealing at two different temperatures, 500 °C and 600 °C, for 30 minutes to transform the ϵ -phase into τ -phase. From X-ray diffraction, and magnetic measurements, (Figure 3 and Figure 4) it is possible to see that annealing process at 500 °C results in a very small amount of τ -phase, showing a coercivity of 100.3 kAm^{-1} and a very low value of remanence of $0.26 \text{ Am}^2\text{kg}^{-1}$. However, with the annealing at 600 °C, almost full transformation into τ -phase is achieved, including a small amount of β -phase and keeping a similar coercivity of 95.5 kAm^{-1} , while increasing the remanence to $31 \text{ Am}^2\text{kg}^{-1}$ and achieving a high maximum magnetization measured at 1600 kAm^{-1} which is in good agreement with previous studies on the synthesis of a pure τ -MnAlC phase alloy [4]. The magnetic characterization of the samples obtained from LCM was carried out by using a vibrational sample magnetometer (VSM) equipped with a 1600 kA/m external magnetic field.

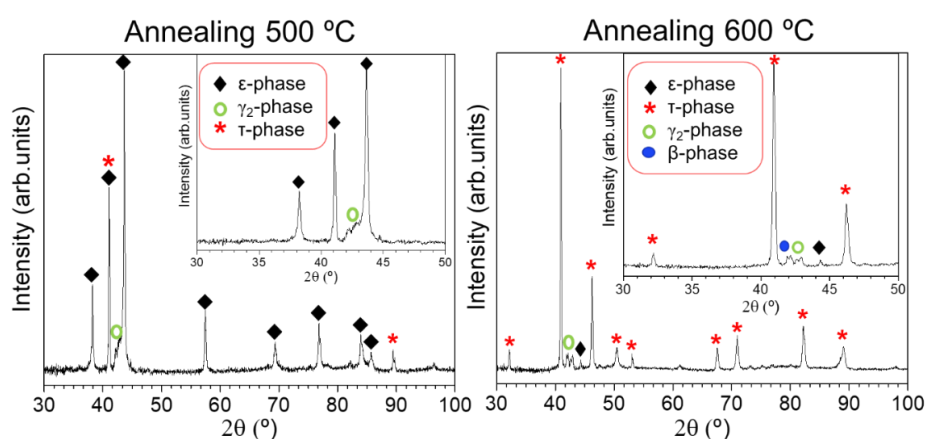


Figure 3 - X-ray diffraction patterns of the annealed gas atomized MnAlC powder at 500 °C (left) and 600 °C (right). After annealing at the lower temperature, only partial transformation of ϵ -phase to τ -phase is achieved. After annealing at the higher temperature, almost full transformation into τ -phase is achieved, with only a minor content of β -phase present.



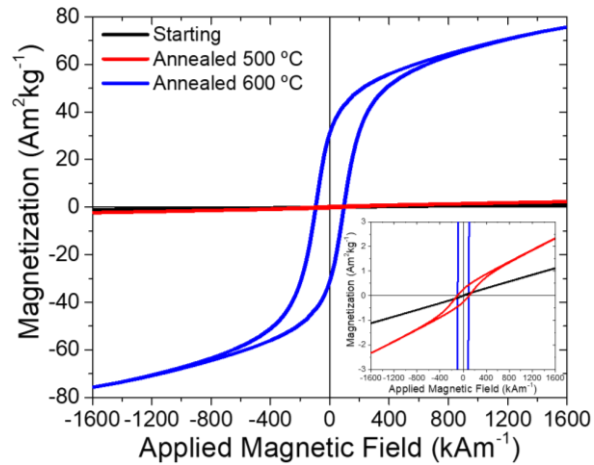


Figure 4 - Comparison of the magnetization curves of the starting gas atomized MnAlC powder (black) and annealed at 500 °C (red) and at 600 °C (blue). Inset showing the low magnetization region in detail.

SEM images from the annealed samples show no change in size or general morphology of the powder (Figure 5).

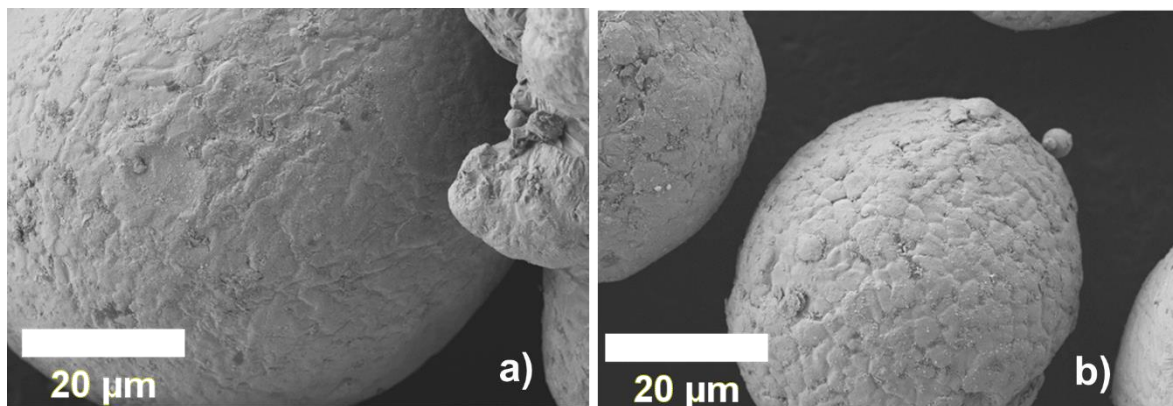


Figure 5 – SEM images of spherical particles after annealing at a) 500 °C and B) 600 °C for 30 minutes.

CAST ALLOY PRODUCTION

Analysis of the three different compositions

X-ray diffraction analysis of the cast alloys (J10229 and J10159) made by IMDEA and TUDA showed that the alloys are made of almost pure τ -phase, with a small presence of β -phase and γ_2 -phase. Table 1 Table 2 shows a summary of the volume fraction of the phases of each of the cast alloys.



Table 2 - Volume fractions and phases obtained for the cast MnAlC alloys.

Aimed Composition	τ -phase (%)	β -phase (%)	γ_2 -phase (%)
$(\text{Mn}_{54}\text{Al}_{46})_{98.5}\text{C}_{1.5}$	98.6 – 99.0	1.0 – 1.4	-
$(\text{Mn}_{57}\text{Al}_{43})_{98.5}\text{C}_{1.5}$	91.4 – 95.2	-	4.8 – 8.6

The results indicate that the samples which were produced by LCM have high phase purity together with the precise control of the chemical composition. **This is one of the highlights of the project at this stage as, to the best of our knowledge, this is the first time that τ -MnAlC phase has been produced at an industrial scale by casting technologies.**

As the microstructural features of MnAlC system play a significant role in the magnetic properties, TUDA carried out detailed microstructural analysis using high-resolution electron channelling contrast imaging (ECCI). Complementary to the BSE imaging, the ECC images give better contrast resolution for fine microstructural features like twinning, stacking faults, and dislocations, seen in Figure 6.



Figure 6 - High-resolution electron channelling contrast (ECC) images of samples which were prepared by LCM.



The temperature and magnetic field dependent magnetization measurements are shown in Figure 7.

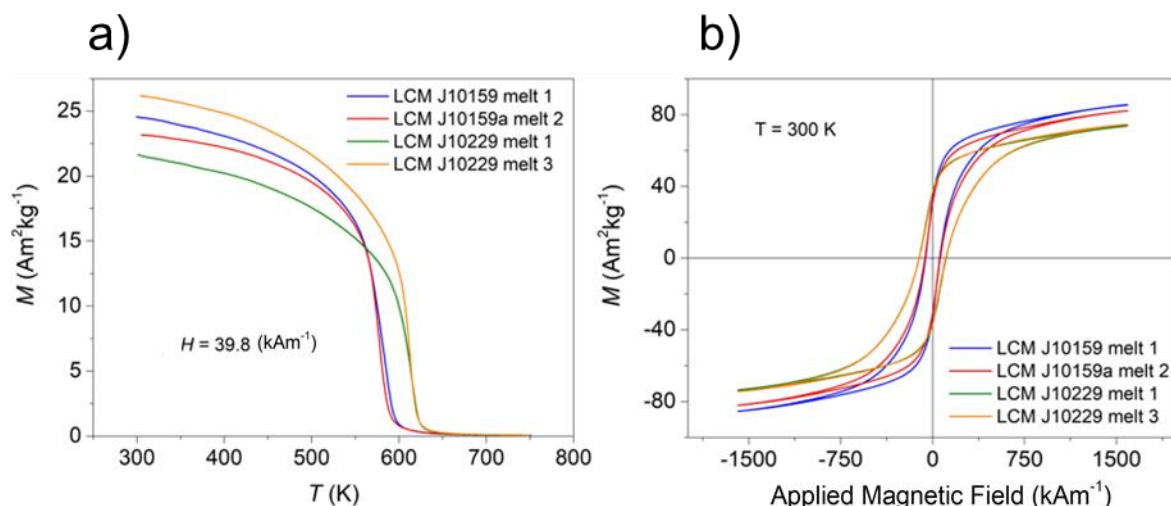


Figure 7 - Magnetic measurements of the samples prepared by LCM: a) temperature dependent magnetization and b) field dependent magnetization.

For the third composition cast at LCM ($(\text{Mn}_{55}\text{Al}_{45})_{98.5}\text{C}_{1.5}$), the analysis of the as-cast materials showed a full τ -phase structure present when using the copper mould, and around 96% of τ -phase content present with the steel mould. LCM carried out hammer milling using a KeK mill, and some amount of powder was sent to IMDEA and TUDA for characterization, confirming that this milling procedure can reduce the particle size of the τ -phase without significantly affecting the microstructure and magnetic properties of the as-cast alloy.

For scaling up, LCM made further 23 casts with the same melting cycles as before and the resulting phase was still a complete τ -phase. **This produced a total of 158 kg of the alloy as can be seen in Figure 8 a).** However, due to the size limitation of water-cooled system on ISP furnace, the resulting cast weight was just around 7 kg. By steel mould (without water cooled system) in GNB furnace, the resulting cast weight can be around 33 kg for MnAlC alloy as shown in Figure 8 b). There were **4 castings done resulting in a total of 133 kg of the alloy.** However, the cooling rate by steel mould is slower than that by copper mould, samples have been sent to TUDA and IMDEA for phase ID to see if full τ -phase can be achieved.



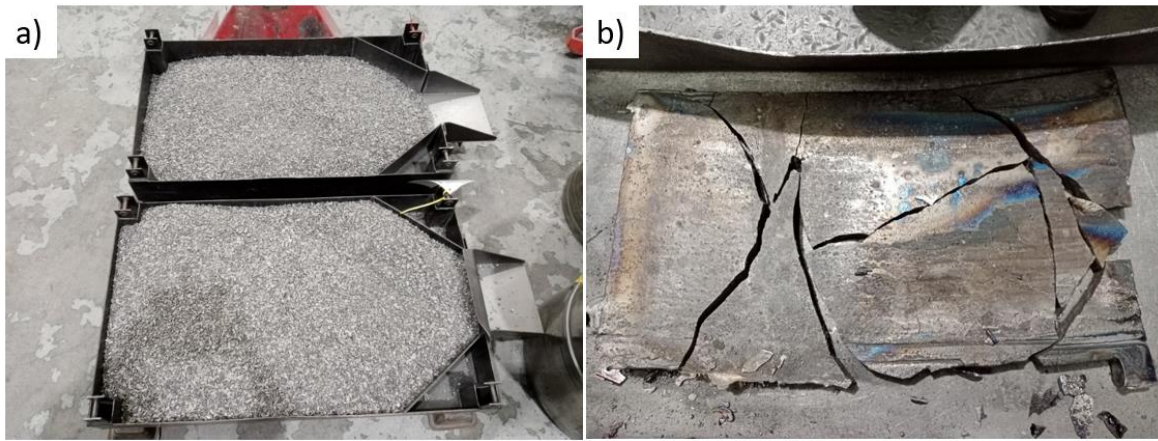


Figure 8 Crushed MnAlC pieces -158kg (a), cast by steel mould 33kg/cast (b)

Despite the good properties of the powder obtained by the milling process using the hammer mill, the overall process is still not optimised for efficient up-scaled industrial production (at present the process is time consuming as it requires a major strip down and cleaning after each use, and safety operation routes need to be established).

Improved properties by flash milling

Magnetic measurements of the as-milled samples show an increased coercivity after applying the flash-milling method with also an increased remanence for all the milling times, while the magnetization at 1600 kA m^{-1} is greatly reduced as can be seen in Figure 9. As seen in Figure 10, SEM images show that the morphology of the particles is not affected by the flash-milling process, while there is a minimal change on the particle size for the 240s milled sample.

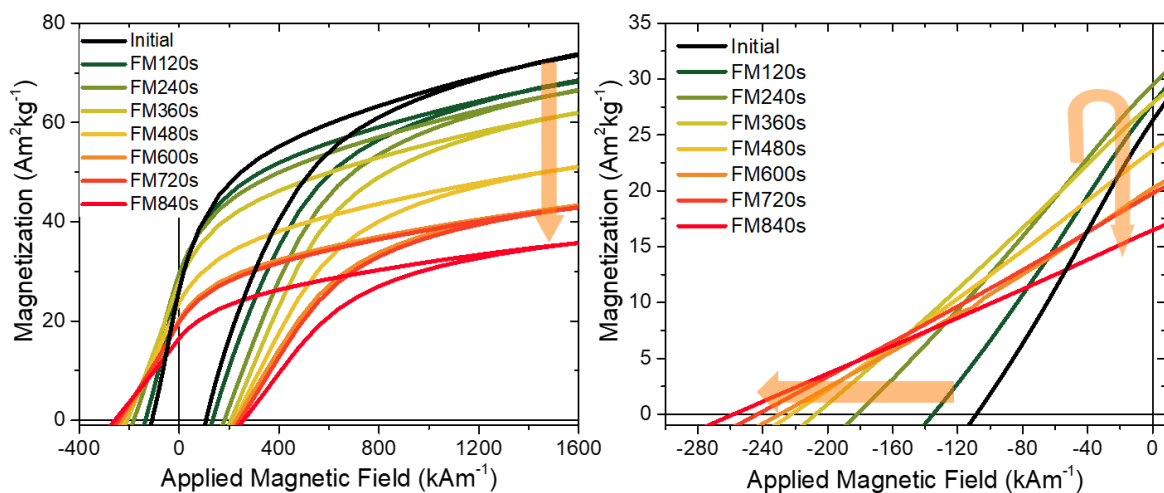


Figure 9 - Magnetization curves evolution with milling time of IMDEA's flash-milling processed powder. Arrows indicate the trend of



magnetization at 1600 kA/m, remanence and coercivity with the flash milling time.

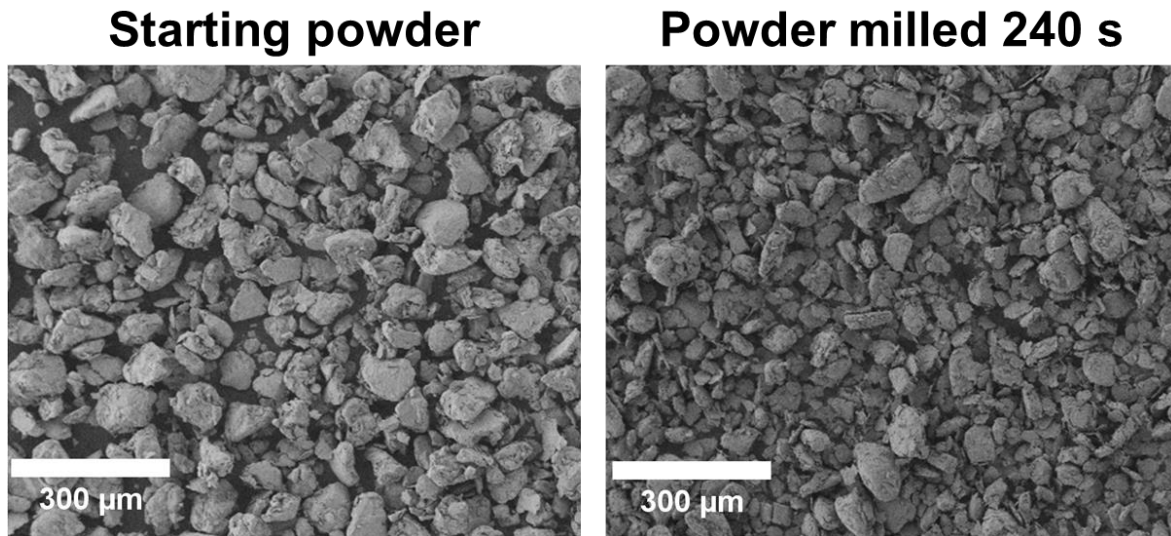


Figure 10 - SEM images of the starting powder and powder processed by IMDEA's flash-milling for an intermediate time of 240 s.

After annealing at 550 °C, the X-ray diffraction patterns show narrower peaks corresponding to the τ -phase, and an increase of the β -phase peaks intensity. While the amount of γ_2 -phase remains very small for all the milling durations, the β -phase has a clear upward trend with milling time after annealing. Figure 11 shows the evolution of the magnetic properties for the different flash milling times. After milling, there is an increase of the coercivity and a diminishing of the magnetization, due to the amorphization, microstrain, and grain size reduction during the process. After annealing, a relaxation of the induced microstrain reduces the coercivity, while an ordering of the τ -phase enhances the magnetization.

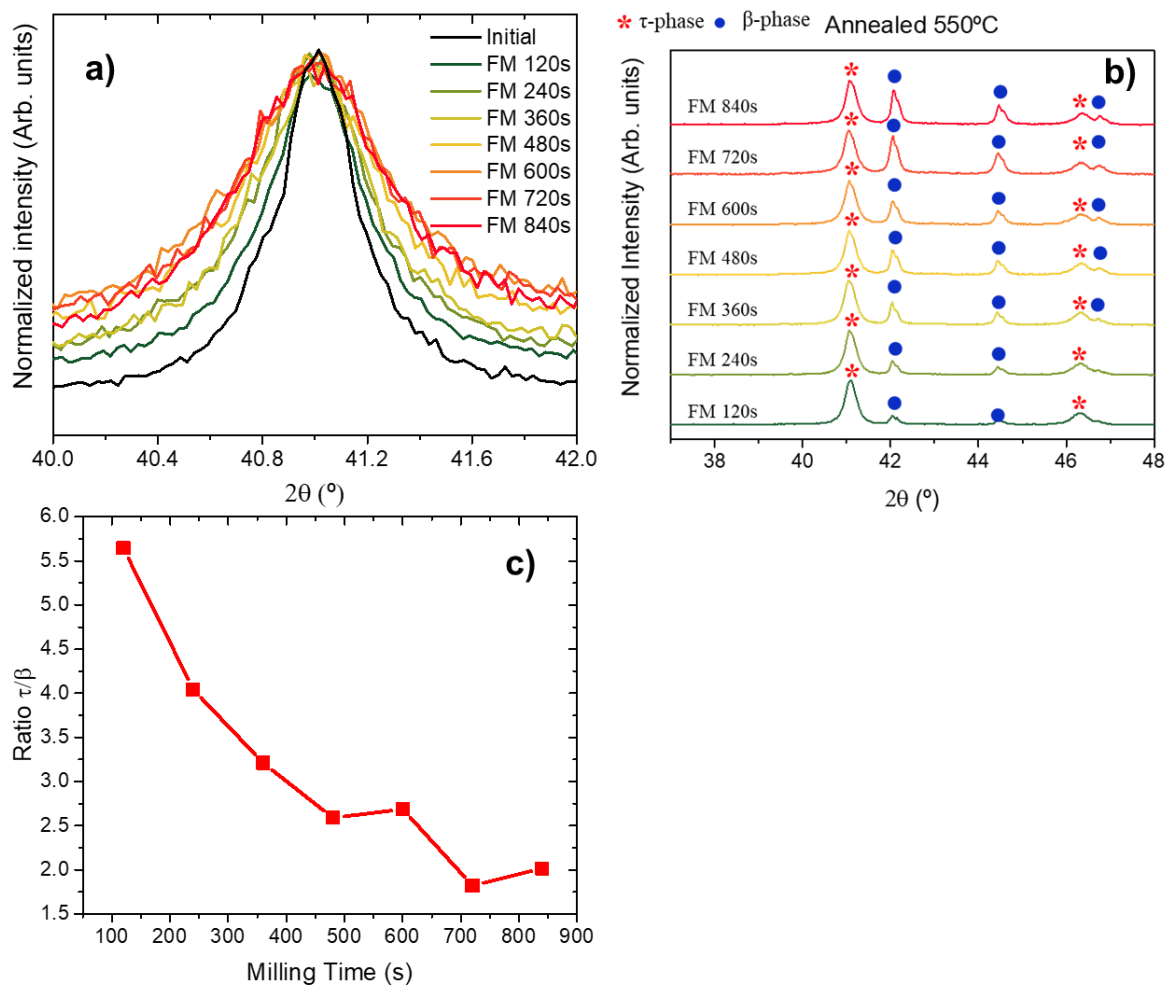


Figure 11 - Evolution of a) the broadening of the τ -phase XRD peak with milling time, b) the XRD peaks after annealing and c) the ratio of τ -phase to β -phase after annealing.

Furthermore, the magnetization at 1600 kAm^{-1} decreases slightly, while the remanence increases slightly with milling time, showing a small enhancement of the squareness of the demagnetization, defined as the remanence divided by the magnetization at 1600 kAm^{-1} . In general, the coercivity, remanence and squareness have an upward trend after just 240 s of milling, which means that a small increase in the milling time used when applying IMDEA's flash-milling method can still lead to a significant increase in coercivity.

With increased flash milling times, there is a further broadening of the τ -phase XRD peaks, remaining approximately constant after 480s while the amount of β -phase has a stabilization trend for longer milling times as can be seen in Figure 11. Regarding the magnetic properties, the coercivity keeps an increasing trend, but the remanence changes from an increasing trend to a decreasing trend after 360s of milling. After annealing, the coercivity tends to stabilize around 0.24 T. The remanence is recovered achieving a maximum of $35.9 \text{ Am}^2\text{kg}^{-1}$ with 360s of milling, as can be seen in Figure 12.



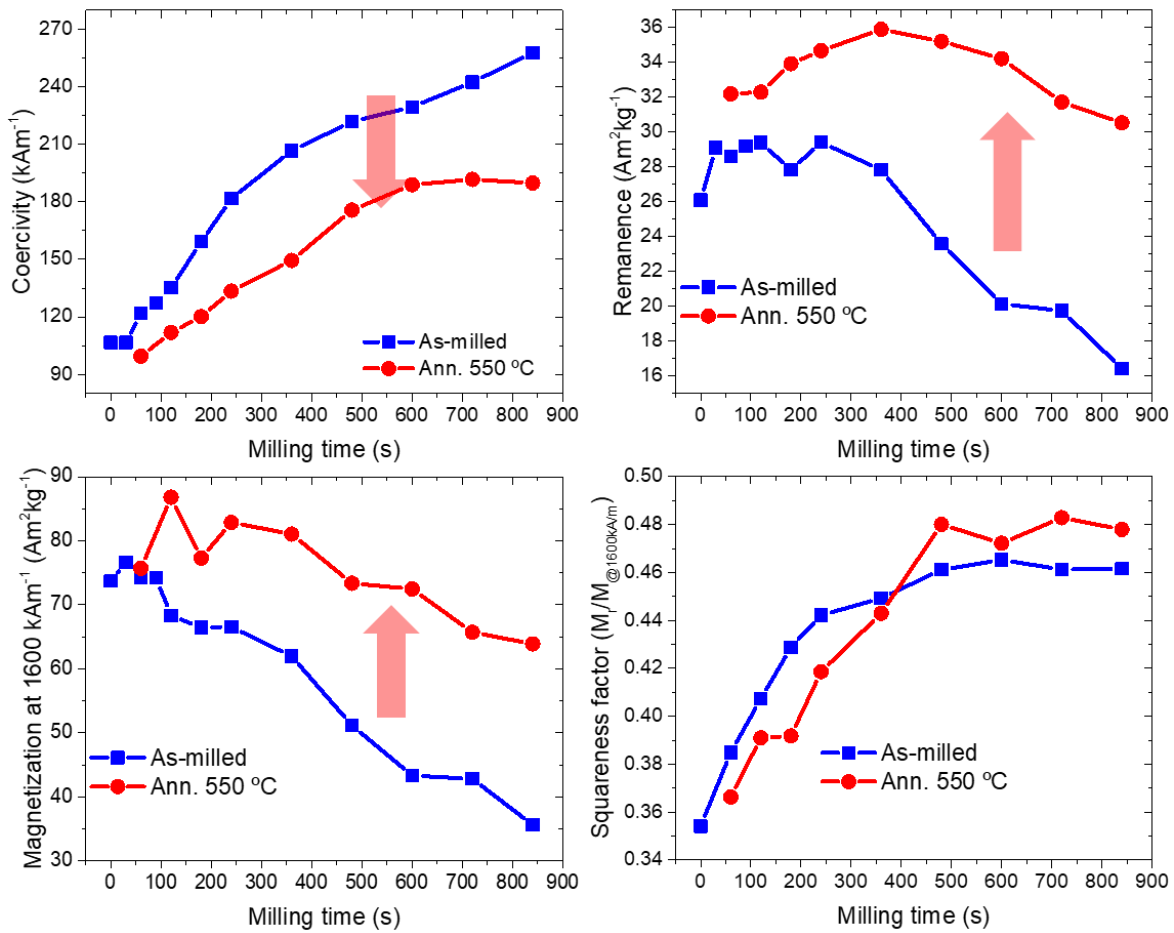


Figure 12 - Magnetic properties evolution with milling time before and after annealing for flash-milled samples.

Improved properties by HEBM

Magnetic measurements of the as milled samples show an increased coercivity with the increase of HEBM process energy, with also an increased remanence, while the magnetization at 1600 kAm⁻¹ is greatly reduced as can be seen in Figure 13. As seen in Figure 14, SEM images show that there is a reduction of the particle size with the HEBM process.



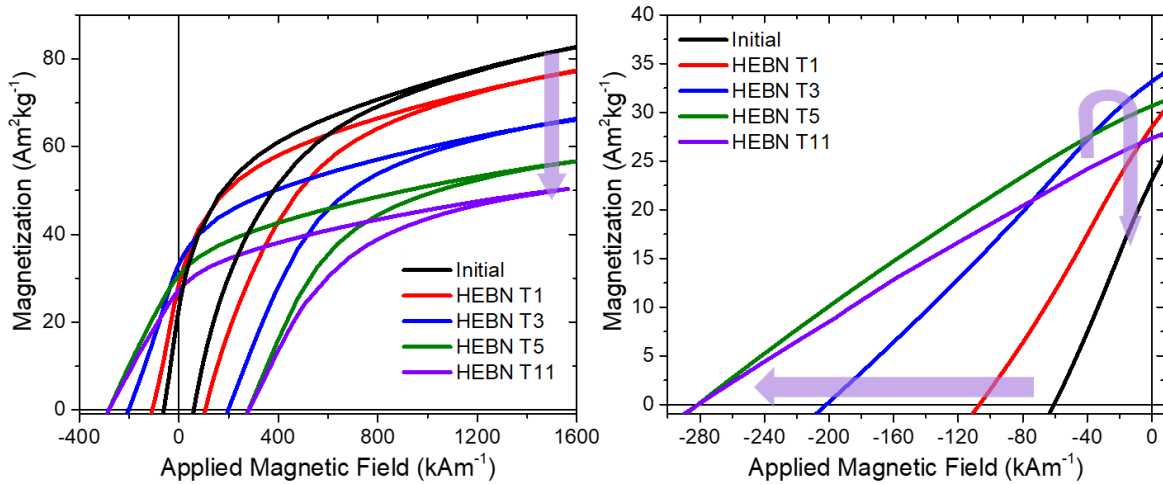


Figure 13 - Magnetization curves evolution with milling time of the processed powder by High Energy Ball Milling (HEBM) performed by MBN. Arrows indicate the trend of magnetization at 1600 kA/m, remanence and coercivity with the process energy.

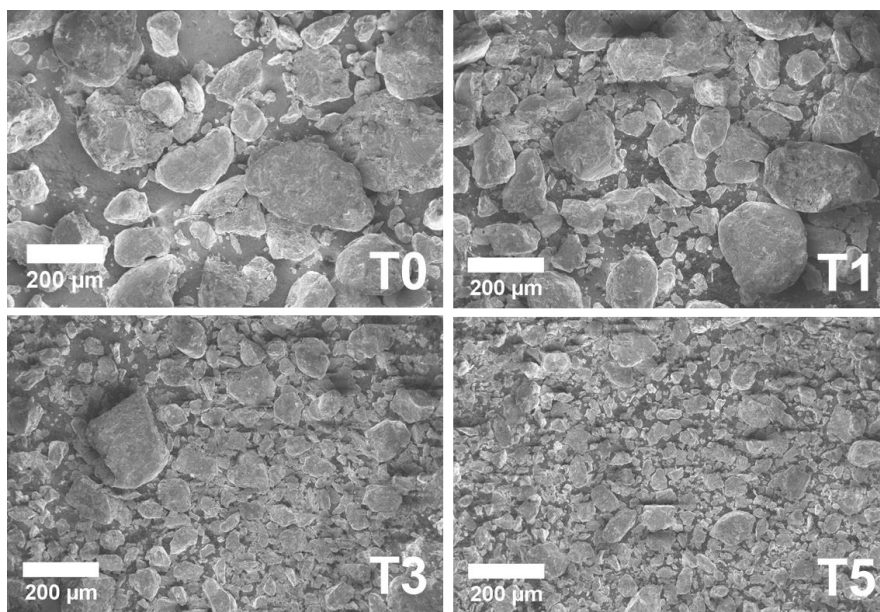


Figure 14 - SEM images of the initial powder (T0) and of powders ball-milled for different process energies (T1, T3 and T5) by MBN using High Energy Ball Milling (HEBM).

After annealing at 550 °C, the X-ray diffraction patterns show narrower peaks corresponding to the τ -phase, and an increase of the β -phase peaks intensity (Figure 15). While the amount of γ_2 -phase remains very small for all the samples, the β -phase has a clear upward trend with process energy after annealing, a very similar behaviour to the flash-milled

samples. Figure 16 shows the evolution of the magnetic properties for the different process energy, with a behaviour almost identical to the flash-milled and annealed flash-milled samples. After HEBM, there is an increase of the coercivity and a diminishing of the magnetization, due to the amorphization, microstrain and grain size reduction during the process. After annealing, a relaxation of the induced microstrain reduces the coercivity, while an ordering of the τ -phase enhances the magnetization.

Furthermore, the magnetization at 1600 kAm^{-1} decreases slightly while the remanence increases slightly with process energy, showing a small enhancement of the squareness of the demagnetization. In general, the coercivity, remanence and squareness have a stabilization trend after the T11 step of HEBM.

When applying the second set of HEBM process conditions “sp”, the evolution of the magnetic properties follows a similar trend as with the previous HEBM and producing a slightly improved squareness factor at the highest energy (T14sp).

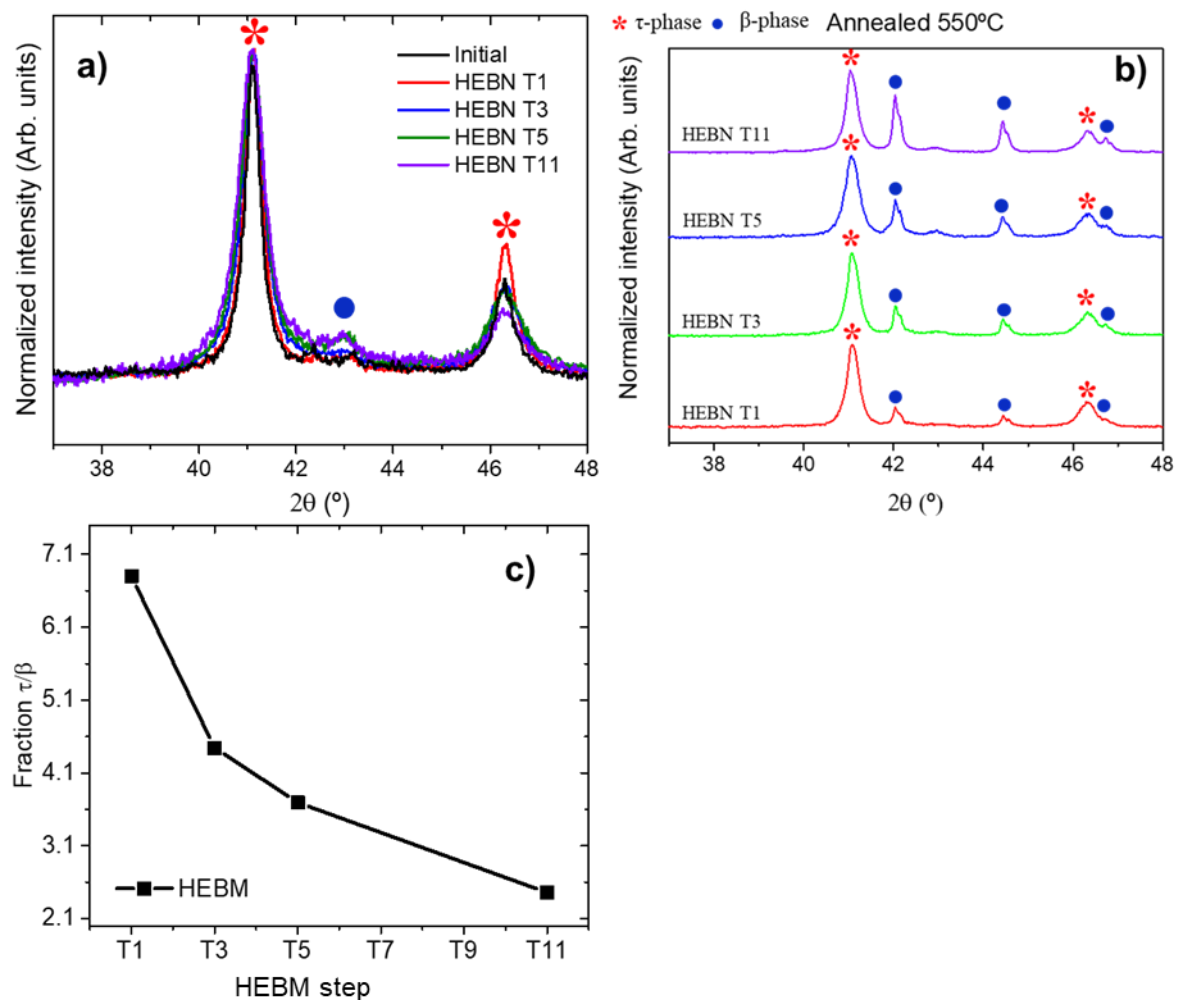


Figure 15 - Evolution of a) the broadening of the τ -phase XRD peak with milling time, b) the XRD peaks after annealing and c) the ration of τ - to β -p hase after annealing.



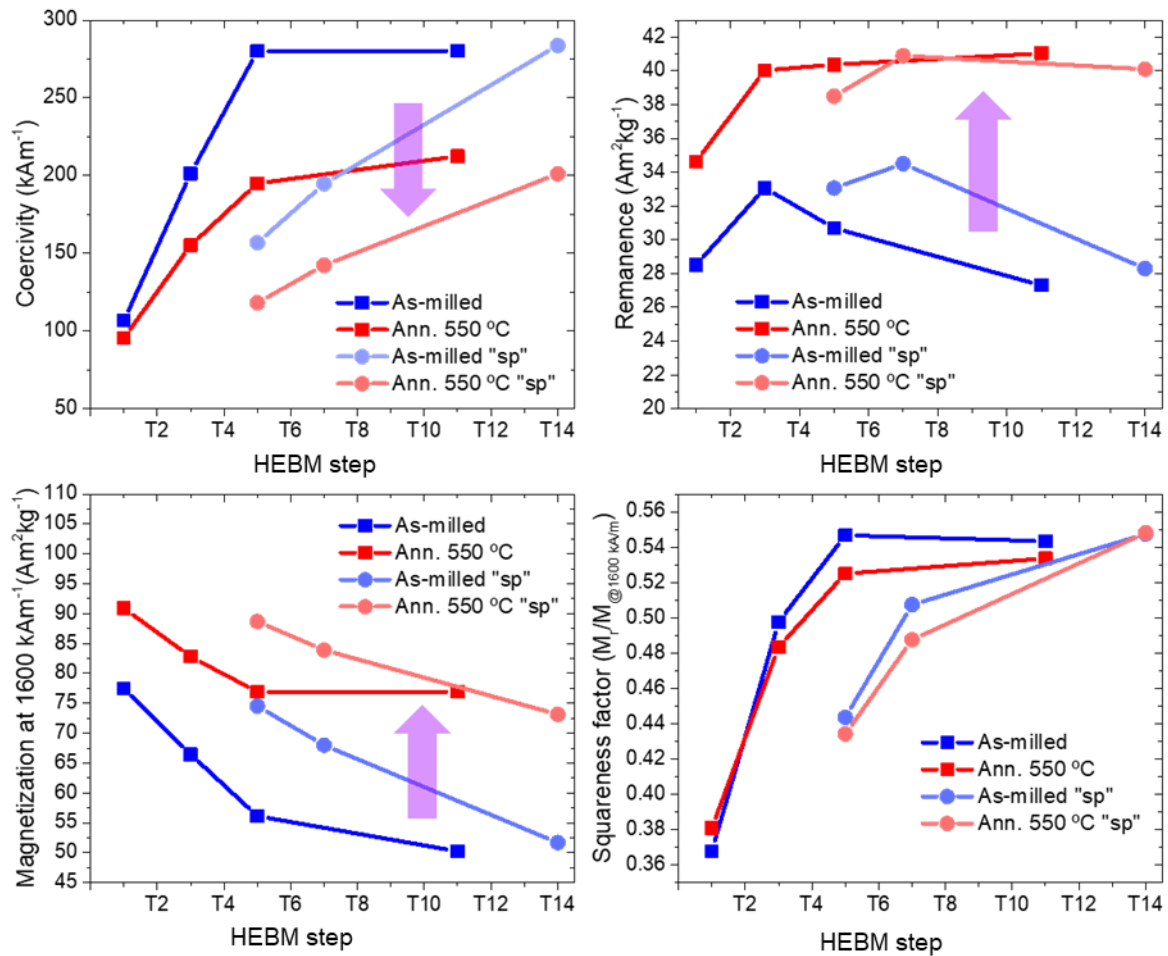


Figure 16 - Magnetic Properties HEBM method

A summary of the magnetic properties obtained by IMDEA's flash milling method and by MBN's proprietary HEBM (taking as starting point - results obtained by IMDEA's flash milling and annealing) can be found in Table 3. In this table, the samples with the best combination of magnetic properties (coercivity and remanence) obtained by the scalable HEBM method are marked in blue, for the first set of parameters of HEBM, and red, for the "sp" set of parameters of HEBM. Also, the red numbers represent the values that fulfil the objective of this deliverable.

Table 3 - Results for Remanence and Coercivity for various process steps before and after heat treatment

Sample	Milling Step		H _c (kA/m)	M _r (Am ² kg ⁻¹)	M _{@1600 kA/m} (Am ² kg ⁻¹)	M _r /M _{@1600 kA/m}
LCM	T0	As made	61.3	23.1	82.62	0.28
		HT550	62.9	24.5	88.10	0.28
HEBM	T1	As milled	106.6	28.5	77.5	0.37
		HT550	95.5	34.6	90.9	0.38
	T3	As milled	201.3	33.1	66.4	0.50
		HT550	155.2	40.0	82.8	0.48
	T5	As milled	280.1	30.7	56.1	0.55
		HT550	195.0	40.4	76.9	0.53
	T11	As milled	280.1	27.3	50.3	0.54
		HT550	212.5	41.0	76.9	0.53
HEBM "sp"	T5sp	As milled	156.8	33.1	74.5	0.44
		HT550	124.9	38.5	88.7	0.43
	T7sp	As milled	194.7	34.5	68.0	0.51
		HT550	142.3	40.9	83.9	0.49
	T14sp	As milled	283.7	28.3	51.7	0.55
		HT550	201.1	40.1	73.2	0.55

CONCLUSIONS

The target values for the D1.1 are defined with the following values:

- Remanence Br=3.0 kG (≈47.8 Am²kg⁻¹)
- Coercivity Hc=2.5 kOe (≈199 kA/m)

Presently, the produced samples with the magnetic properties closest to the objective values are T11 and T14sp reaching remanence values up to 41 Am²kg⁻¹ after annealing, i.e. near the targeted value, while the targeted coercivity is well exceeded, by reaching values up to 212.5 kA/m after annealing. This has been possible based on the following highlights:

- I. To the best of our knowledge, this is the first time that τ-MnAlC phase has been produced at an industrial scale (158 kg) by casting technologies (at LCM's premises).
- II. IMDEA's self-developed "flash-milling" process (and annealing) has been successfully translated by MBN to a larger scale production process for MnAlC powder with suitable permanent magnet properties, to be used in a later stage as precursor for MnAlC magnets fabrication.



The sample selected for the following scale-up steps was decided to be T14sp, due to its better as-milled magnetic properties and the possibility to further optimize the annealing process to tune the final magnetic properties.

REFERENCES

- [1] C. Muñoz-Rodríguez, L. Feng, E.M. Palmero, T. Mix, J. Rial, F. Olsson, B. Skårman, H. Vidarsson, P.-O. Larsson, T.G. Woodcock, and A. Bollero, Fabrication of bulk τ MnAl–C magnets by hot-pressing from ϵ -phase gas-atomized and milled powder, *J. Alloys Compd.* 847, 156361 (2020).
- [2] J. Rial, E.M. Palmero, and A. Bollero, Efficient nanostructuring of isotropic gas-atomized MnAl powder by rapid milling (30 s), *Engineering* 6 (2), 173-177 (2020).
- [3] J. Rial, P. Švec, E.M. Palmero, J. Camarero, P. Švec Sr., and A. Bollero, Severe tuning of permanent magnet properties in gas-atomized MnAl powder by controlled nanostructuring and phase transformation, *Acta Mater.*, 157, 42-52 (2018).
- [4] V. Øygarden, J. Rial, A. Bollero, and S. Deledda, Phase-pure τ -MnAlC produced by mechanical alloying and a one-step annealing route, *J. Alloys Compd.* 779, 776-783 (2019).

