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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

PASSENGER
FOR SUSTAINABLE AND EFFICIENT RE-FREE MAGNETS

Deliverable No. 1.2

Fabrication of high-coercive Mn-Al-C loose powder (obtained by milling and annealing ε-phase powder) with target values: coercivity jHc> 3.5 kOe; threshold for remanence Br> 2.0 kG.

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MBN Nanomateralia SPA (MBN)
MATRES Material Research & Design (MATRES)
Technical University Darmstadt (TUDA)
Less Common Metals Ltd (LCM)

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LIST OF ACRONYMS

Abbreviation	unit	Meaning
Br, T	[Am2kg-1], [kG], [T]	Remanence
jHc	[kA/m], [kOe]	Coercivity
$M_{@1600\ kA/m}$	[Am2kg-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 atomise 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 of cast ingots, IMDEA have developed a ball milling method based on IMDEA's self-developed "flash-milling", that makes it possible to produce powders with a size of less than 300µm. 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 achieved when starting from τ-phase synthesis, while the value of the coercivity is approx. 3% lower than target. When starting from ε-phase synthesis, approx. 90% of target values have been achieved.

Table 1 Comparison of the magnetic target values with achieved values

		Target values D1.2	Achieved values from ε-phase synthesis	Achieved values from τ-phase synthesis
Remanence [Am^2kg^{-1}]	**Br**	**31,8** (≈2,0 kG)	**30.0**	**30.7**
Coercivity [kA/m]	**jHc**	**279** (≈3.5 kOe)	**247**	**280**

The sample with the best magnetic properties so far was selected to aim for larger scale production and to further optimise the annealing process. MnAlC τ-phase powder material has been already obtained from scale-up activities and delivered for initial magnet manufacturing tests to WP2 partners.

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1. INTRODUCTION

The aim of this deliverable is the production of τ-MnAlC phase powder with remanence of Br > 2.0 kG and a coercivity of jHc > 3.5 kOe. Keeping consistency with the magnetic units used for M18 technical report and former D1.1 [5], and considering a calculated density of 5 g/cm^3 for the MnAlC alloy, the objectives of this deliverable are Mr > 31.8 Am^2kg^{-1} and jHc > 279 kAm^{-1}.

According to the project proposal, two different routes have been followed to synthesize the permanent magnet phase τ-MnAlC: starting from gas-atomized (**METALPINE**) or as-cast (**LCM**) MnAlC material, with subsequent ball milling of 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.

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2. METHODOLOGY

The methodology followed for MnAlC powder production steps has been already reported in D1.1, including the following main steps:

- Gas-atomization from manganese-aluminium-carbon melts, performed by Metalpine and mostly leading to ε-phase;
- Cast alloy into copper mould, steel mould and strip casting, performed by LCM and mostly leading to τ-phase, with subsequent crushing of as-cast material;
- Improvement of powder properties by flash milling, performed at lab scale by IMDEA, starting from powder by both gas-atomization and casting;
- Improvement of powder properties by High Energy Ball Milling, performed at pilot scale by mechanical alloying equipment at MBN, in order to transfer the flash milling effect to a pre-production scale, starting from powder and ingots by casting;
- Powder annealing, performed at lab scale by IMDEA and at pilot scale by MBN, to refine magnetic properties of powder;
- Powder characterizations by XRD, SEM and VSM.

Additional powder production tests at lab scale have been performed by IMDEA employing Ultrasonic powder atomization process to obtain ε-phase material, on which subsequent process steps have been tested.

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3. RESULTS

3.1. GAS-ATOMIZED POWDER PROCESSING

As reported in previous D1.1, the annealing process on ε-phase performed by IMDEA at 600°C for 30min leads to 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 Am^2kg^{-1}, with no change in size or general morphology of the powder.

Similarly, when performing annealing step on ultrasonically atomized powder, a complete transformation into τ-phase is achieved, with coercivity up to 186 kAm^{-1} and remanence up to 39.7 Am^2kg^{-1}. Once applied flash milling, coercivity is increased to 247 kAm^{-1} and remanence decreases to 30.0 Am^2kg^{-1}, approaching the target values for this deliverable.

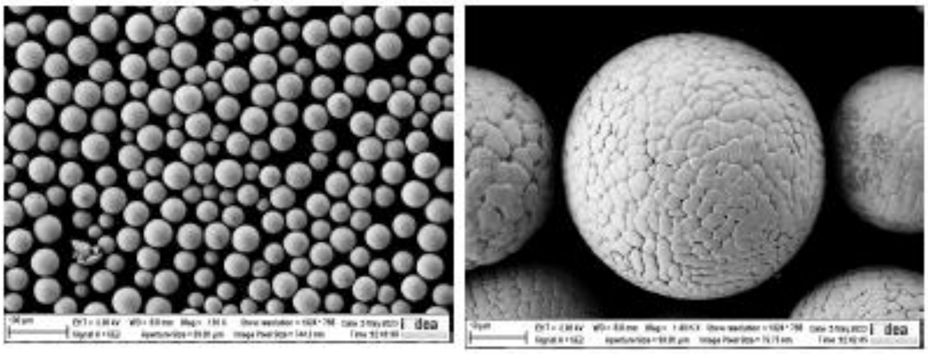

Figure 1. Ultrasonically atomized powder by IMDEA, 20-50µm size range.

3.2. CAST ALLOY PRODUCTION

As reported in previous D1.1, MnAlC materials produced by LCM have high τ-phase purity together with the precise control of the chemical composition, being already performed at a pre-industrial production scale by casting, in particular when using the copper mould.

A total of 158 kg of the alloy has been produced by casting on copper mould and 133kg of the alloy has been produced by casting on larger steel mould.

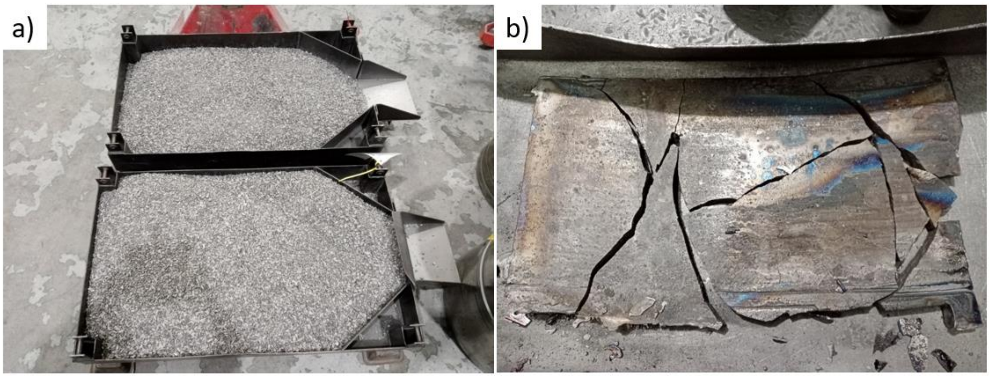

Figure 2 Crushed MnAlC pieces -158kg (a), cast by steel mould 33kg/cast (b)

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Improved properties by flash milling

As previously reported, when increasing flash milling time a reduction of remanence and an increase of coercivity is obtained on as-milled samples, due to the amorphization, microstrain, and grain size reduction during the process. A subsequent annealing allows a relaxation of the induced microstrain reduces the coercivity, while an ordering of the τ-phase enhances the magnetization.

After annealing, the coercivity tends to stabilize around 0.24 T. The remanence is recovered achieving a maximum of 35.9 Am^2kg^{-1} with 360s of milling.

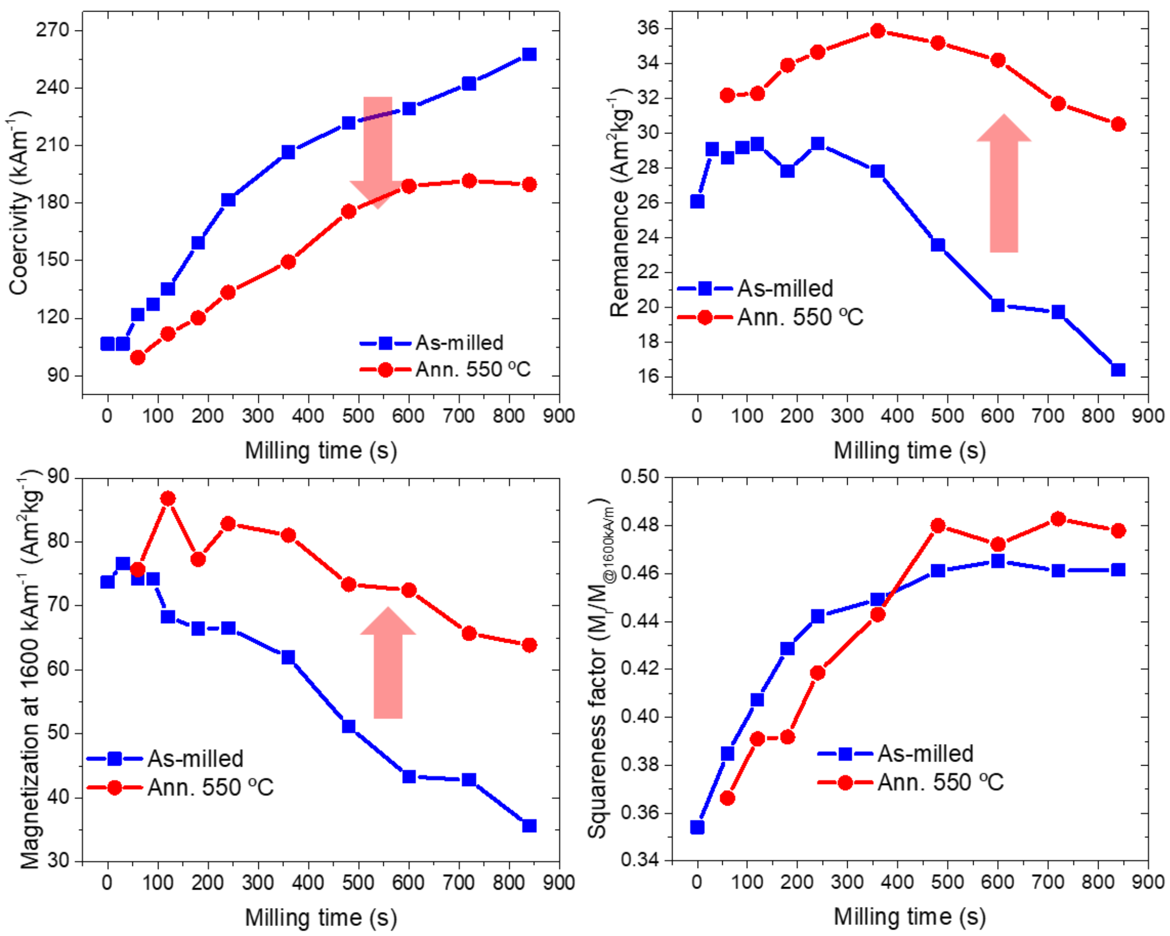

Figure 3 - Magnetic properties evolution with milling time before and after annealing for flash-milled samples.

Improved properties by HEBM

As previously reported, magnetic measurements of the as milled samples show an increased coercivity with the increase of HEBM process energy, with also an increased remanence. The evolution of the magnetic properties for the different process energy has a behaviour almost identical to the flash-milled and annealed flash-milled samples, when starting from τ-phase MnAlC powder produced by LCM. After HEBM, there is an increase

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of the coercivity and a diminishing of the magnetization, due to the amorphization, microstrain and grain size reduction during the process. After annealing (HT), a relaxation of the induced microstrain reduces the coercivity, while an ordering of the τ-phase enhances the magnetization. In general, the coercivity, remanence and squareness have a stabilization trend after the "T11" step of HEBM.

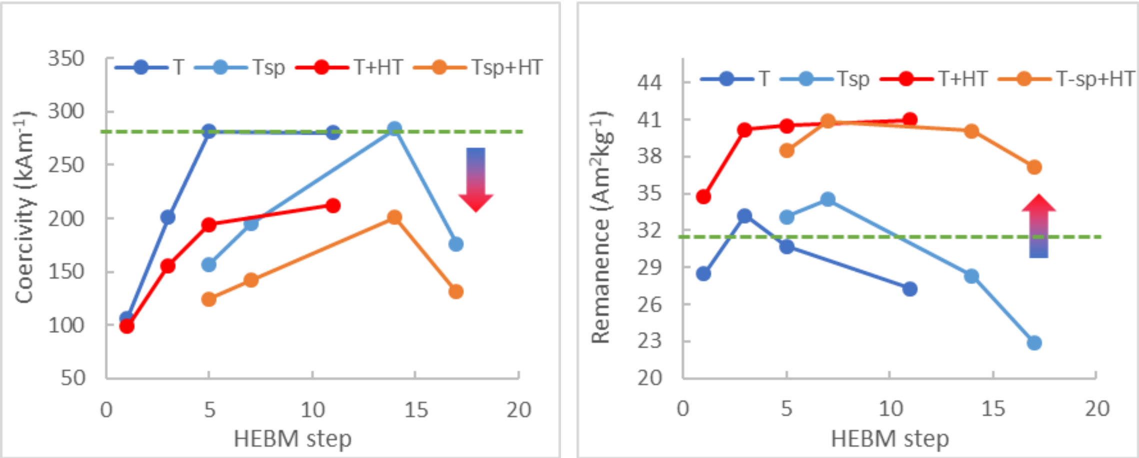

Figure 4. Magnetic properties of powder by HEBM method from small scale tests, measurements by IMDEA. D1.2 target values are reported as green dotted lines for reference.

Considering the targets values of magnetic properties for this D1.2, the powder material obtained by small scale process at "T5" conditions in form of as-milled powder has the combination of magnetic properties properties basically matching the target values: coercivity 280 kAm^{-1} and remanence 30.7 Am^2kg^{-1}.

When applying the second set of HEBM process conditions "sp", at small scale conditions, 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). In this case, the measured remanence is lower than target values: coercivity 284 kAm^{-1} and remanence 27.3 Am^2kg^{-1}. Remanence values exceeding the target can be achieved by annealing the material, but with too high decrease of coercivity.

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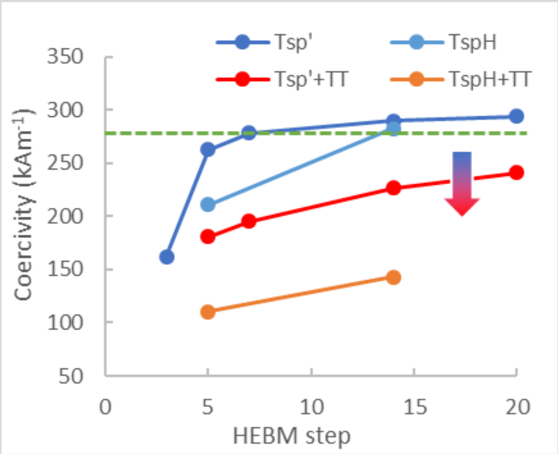

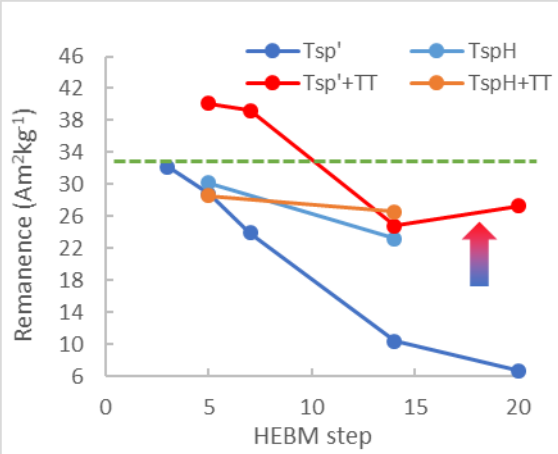

Figure 5. Magnetic properties of powder by HEBM method from scale-up tests, measurements by IMDEA. D1.2 target values are reported as green dotted lines for reference.

These two conditions (T5 and T14sp) have been selected as reference for initial scale-up tests of HEBM process on MnAlC powder by casting production, towards higher productivity of powder. Starting from such powder processing conditions, the refinement of HEBM parameters and of subsequent annealing step, both at pilot scale, is currently in progress at MBN, targeting improvements in productivity, batch-to-batch quality consistency and finer tuning of powder particle size as well as magnetic properties. At present, the powder obtained by scale up tests of HEBM with the combination of properties closer to D1.2 targets is identified by T5sp' conditions "as-milled": coercivity 263 kAm^{-1} and remanence 28.8 Am^2kg^{-1}.

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4. CONCLUSIONS

The target values for the D1.2 are defined with the following values:

- Remanence Br>2.0 kG (≈31.8 Am^2kg^{-1})
- Coercivity jHc=3.5 kOe (≈279 kA/m)

Presently, the produced sample with the magnetic properties closest to the objective values is τ-phase MnAlC powder produced by casting at LCM and processed by HEBM by MBN at "T5" conditions, reaching remanence values up to 30.7 Am^2kg^{-1} and coercivity values up to 280kA/m, i.e. very close to the targeted values.

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.

Scale up steps for HEBM have been performed and are currently in progress, based on identified conditions at small pilot scale and transferring them to larger equipment, in line with productivity of currently available casting process for MnAlC, with possibility to tune the final magnetic properties. As a first results of such scale-up steps, "T5sp'" and "T5spH" conditions have been applied to HEBM equipment with larger productivity, obtaining first powder batches for sintering and compounding tests within the project activities on MnAlC.

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