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VALOMAG

2nd Seminar – Delft, the 6th December 2022

Transformation to the manufacturing of new magnets

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KOLEKTOR

liten ceatech

SUMMARY

1. Powders production for the bonded magnet manufacturing route
2. Bonded magnets manufacturing
3. Sintered magnet manufacturing route

POWDERS PRODUCTION FOR THE BONDED MAGNET MANUFACTURING ROUTE

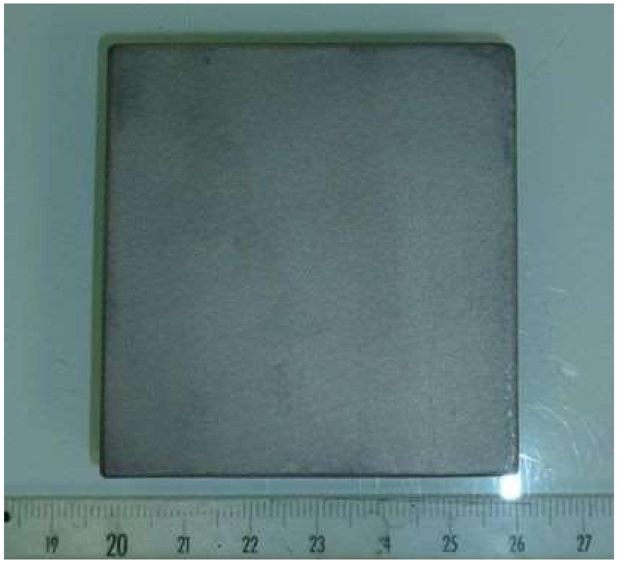
- Hydrogen Decrepitation (HD) to transform magnets into coarse powder
- Hydrogenation Disproportionation Desorption Recombination (HDDR) to obtain powders with good magnetic properties
- Objectives : Production of several kilograms of powder to check whether this powder can be processed for manufacturing bonded magnets

This route has been experimented on different magnet sources

1) N38 magnets : relatively clean batch of large magnets
2) Hard Disk Drives magnets : batch of small magnets with organic residues

POWDERS PRODUCTION FOR THE BONDED MAGNET MANUFACTURING ROUTE

N38 magnets
Epoxy coating removed
6 cm × 6.3 cm - 380 g
1 composition

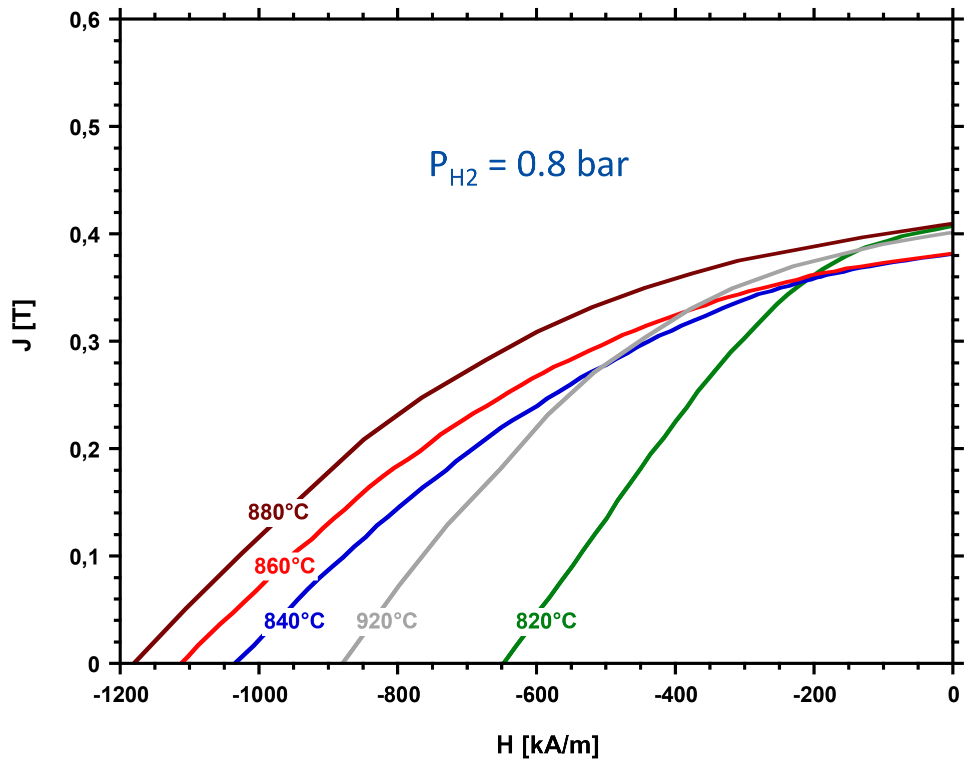


HDD magnets
Metallic coating to be removed
Small magnets, residues, …
Different compositions

POWDERS FOR THE BONDED MAGNET MANUFACTURING ROUTE : N38 MAGNETS

- Small sample of N38 magnets – P_{H2} = 0.8 bar
- Powders sieved at 200 µm
- Best magnetic properties : HDDR process at 880°C, but the powders are difficult to deagglomerate
- HDDR process at 840°C : good magnetic properties and easy to deagglomerate

T (°C)	Br [T]	Hcj (kA/m)	Powder Loading rate	Br (T) Extrapolated
820	0,41	650	0,50	0,81
840	0,38	**1040**	0,50	0,76
860	0,38	**1110**	0,49	0,79
880	0,41	**1180**	0,54	0,76
920	0,40	880	0,55	0,73



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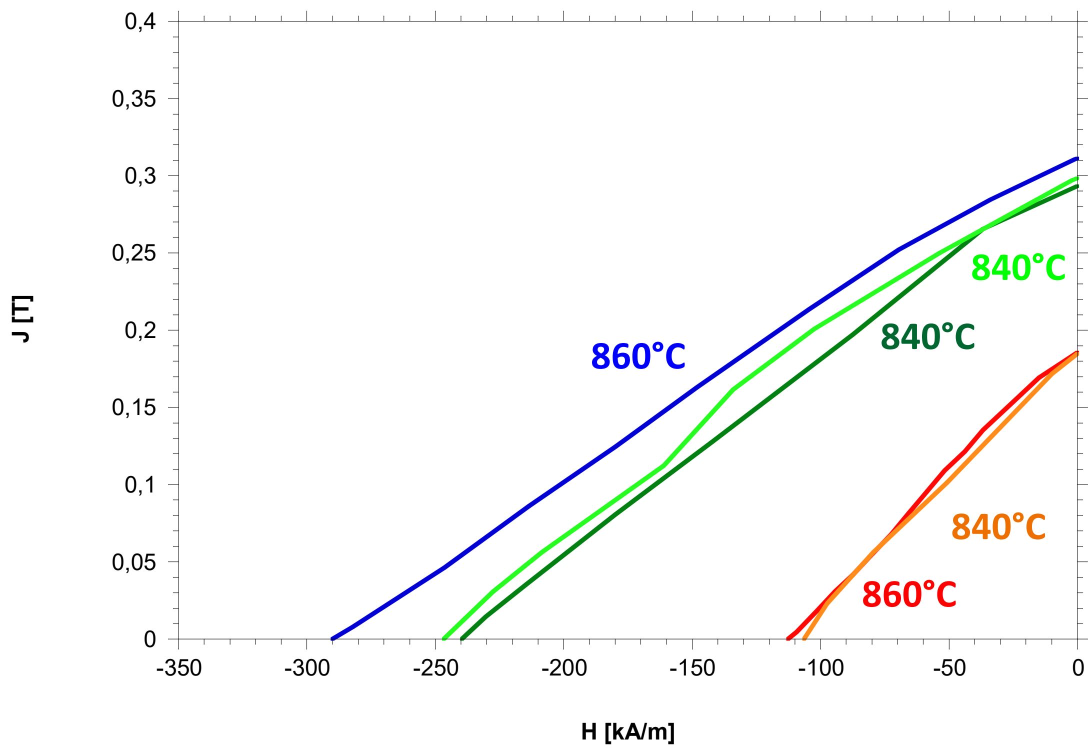
POWDERS FOR THE BONDED MAGNET MANUFACTURING ROUTE : HDD MAGNETS

- HDDR process : best process conditions determined previously with N38 magnets
- HDDR Powders from "**as received" HDD magnets** :
  840°C and 860°C
- HDDR Powders **only with HDD magnets** :
  840°C, 840°C and 860°C
- Very poor magnetic properties for as received magnets – No difference between 840°C and 860°C
- Poor magnetic properties when only magnets are selected – Small difference between 840°C and 860°C



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POWDERS FOR THE BONDED MAGNET MANUFACTURING ROUTE : HDD MAGNETS

- Very poor magnetic properties for the "as received" magnets – High contamination of the powder by O, C and S
- Poor magnetic properties with only magnets selected – High contamination of the powder by O, C and S
  but less than the "as received" magnets

	O (ppm)	C (ppm)	S (ppm)
As received magnets	5820	1340	145
Only magnets	5560	1140	85

An additional cleaning of the magnets before the HD + HDDR treatments could reduce the carbon and oxygen content in the HDDR powder

POWDERS FOR THE BONDED MAGNET MANUFACTURING ROUTE

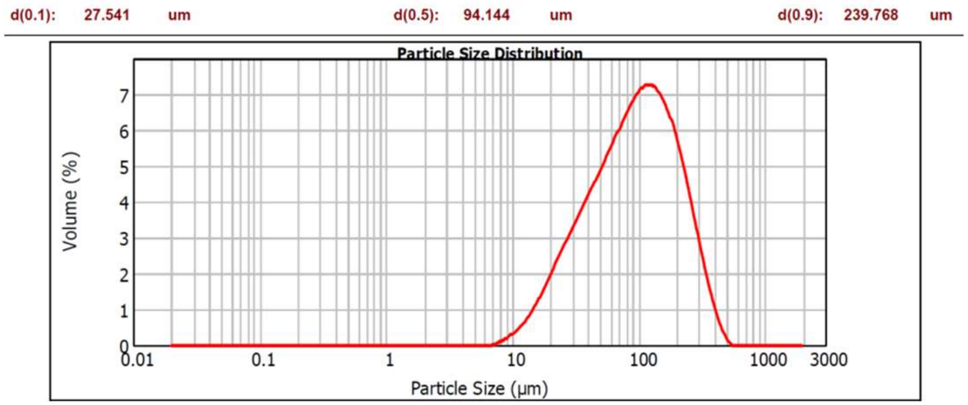
- HDDR powder for KOLEKTOR

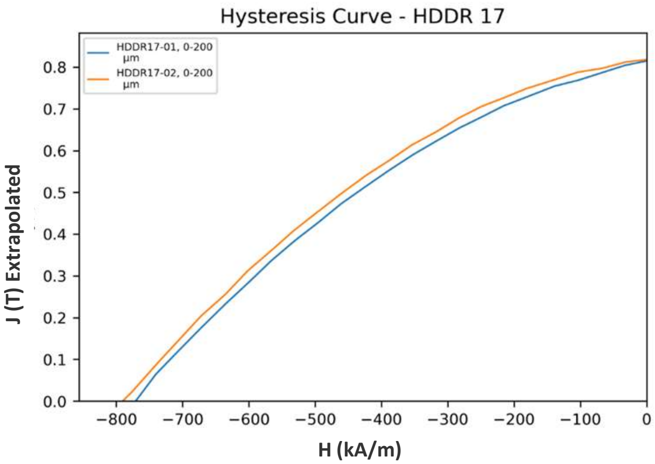
15.4 kg of used N38 magnets

6.1 kg < 200 µm

- Particle size distribution required by KOLEKTOR

- Coercivity is 30% lower than obtained, previously with small samples





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POWDERS FOR THE BONDED MAGNET MANUFACTURING ROUTE : CONCLUSIONS

- 15.4 kg of used N38 magnets and 6.1 kg < 200 µm : **40% of the powder can be recycled**
- Efficiency could be improved by grinding the powder with a grain size > 200 µm

- N38 magnetic properties : **Coercivity and squareness** could be increased by **improving the HDDR cycle**

- An **additional cleaning** of the HDD magnets before the HDDR treatment could reduce the carbon and oxygen content in the HDDR powder

BONDED MAGNETS MANUFACTURING

Work done for polymer bonded preparation (scope)

- Selection of magnetic powder
- Selection of polymer
- Selection of additives Test compounding on HDDR powder (CEA powder)
- Test moulding (CEA powder)
- Measuring set up parameters for CEA powder (to define technological parameters)

Results achieved

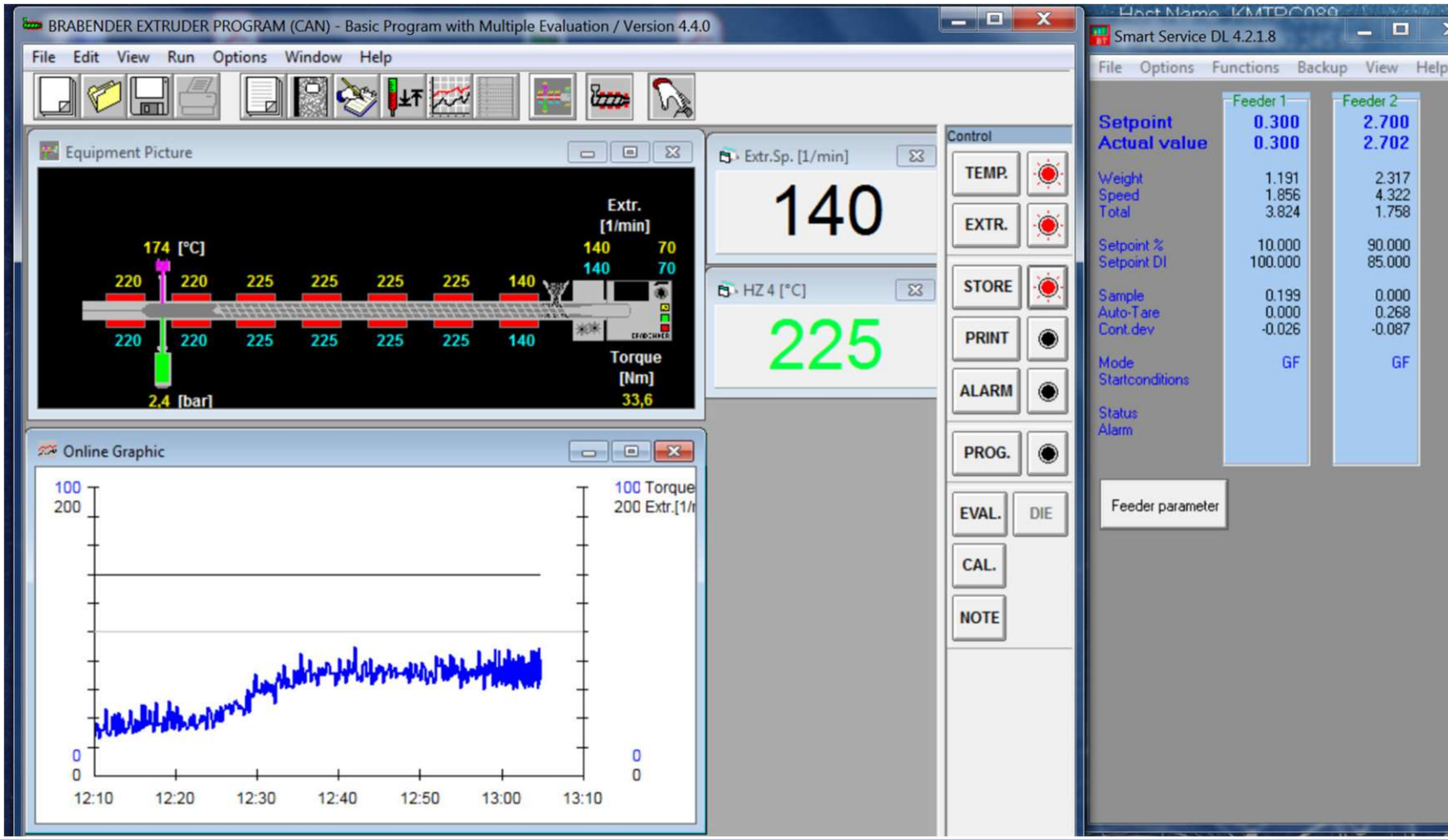
- Mechanical properties
- Magnetic properties
- Corrosion resistance

BONDED MAGNETS MANUFACTURING : COMPOUNDING PARAMETERS

- Torque: between 30 and 40 Nm (more than previous (25Nm))
- Temperature: in the range
- Pressure 2.4 bar (good)

- Moulding temp: 290°C
- Tools temp: 90°C
- Injection pressure:2400 bar (higher than previous which was 1050 to 1150 bar)
- Holding pressure:1400 bar (higher than previous, which was 900 bar)
- Field: 0 and 500 mT

- Magnetised axially
- Energy input: 12 kWs
- U = 1800 V (magnetising voltage)
- I = around 13 kA
- H = 2200 kA/m (calculated)



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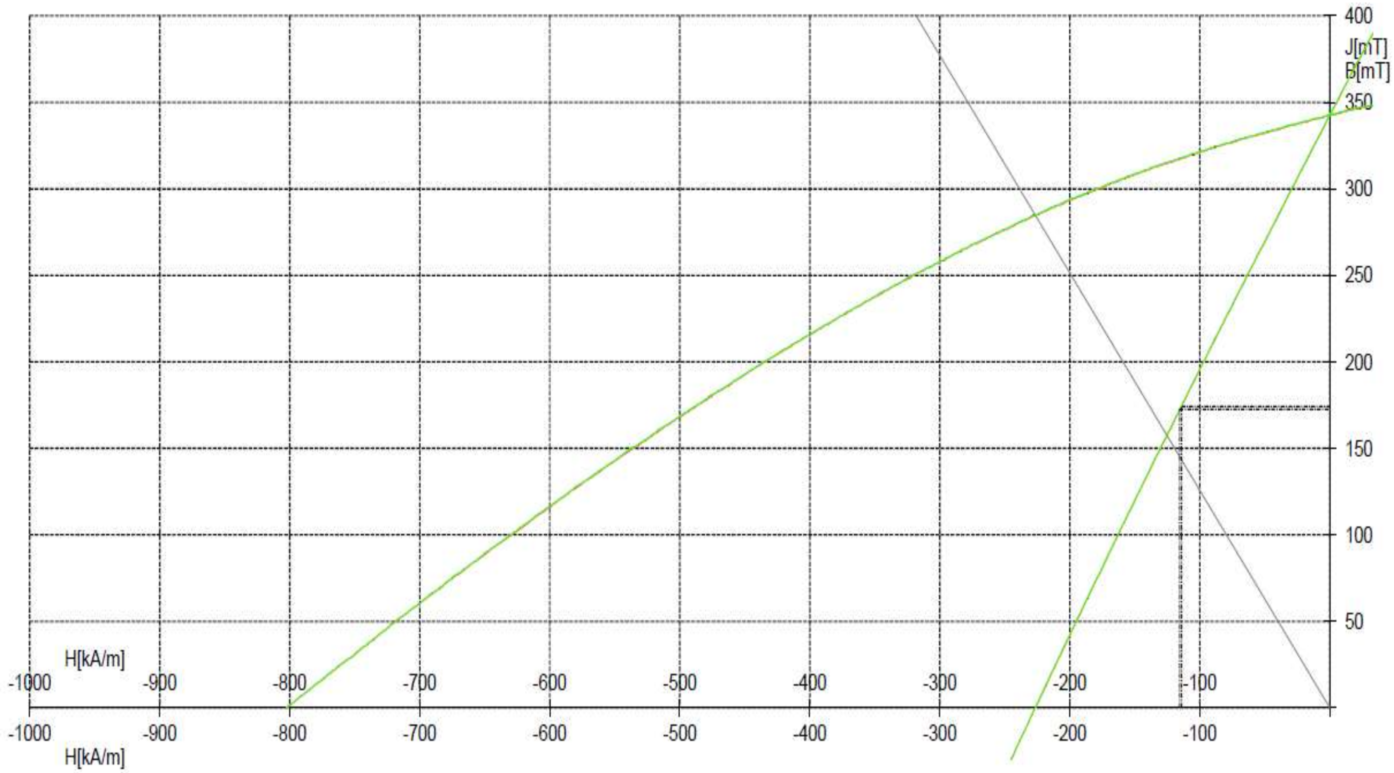
BONDED MAGNETS MANUFACTURING : DEMAG CURVES

Isotropic:

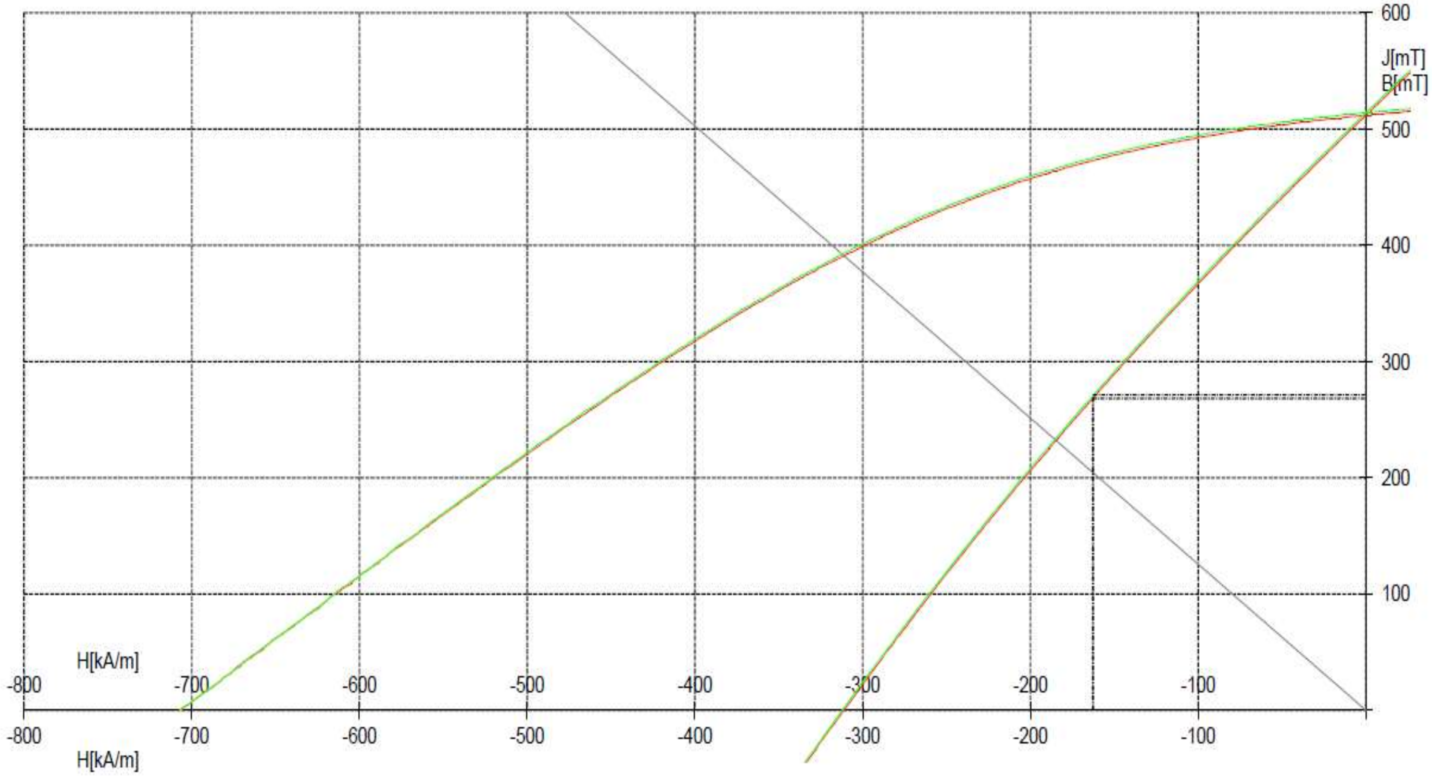
	1	2	Average	
B_r	= 342.6	343.0	342.8	mT
$(BH)_{max}$	= 19.89	19.95	19.92	kJ/m³
H_{cB}	= 227	227	227	kA/m
H_{cJ}	= 803	802	803	kA/m
B_a	= 0.174	0.173	0.173	T
H_a	= 114	116	115	kA/m
J_k	= 0.308	0.309	0.309	T
H_k	= 150	150	150	kA/m
H_{max}	= 1269	1270	1270	kA/m
T	= 24	24	24	°C



BONDED MAGNETS MANUFACTURING : DEMAG CURVES

Anisotropic:

	1	2	Average	
B_r	= 512.0	514.2	513.1	mT
$(BH)_{max}$	= 43.72	44.09	43.91	kJ/m³
H_{cB}	= 311	312	312	kA/m
H_{cJ}	= 707	707	707	kA/m
B_a	= 0.268	0.271	0.270	T
H_a	= 163	163	163	kA/m
J_k	= 0.461	0.463	0.462	T
H_k	= 193	193	193	kA/m
H_{max}	= 1267	1265	1266	kA/m
T	= 23	23	23	°C

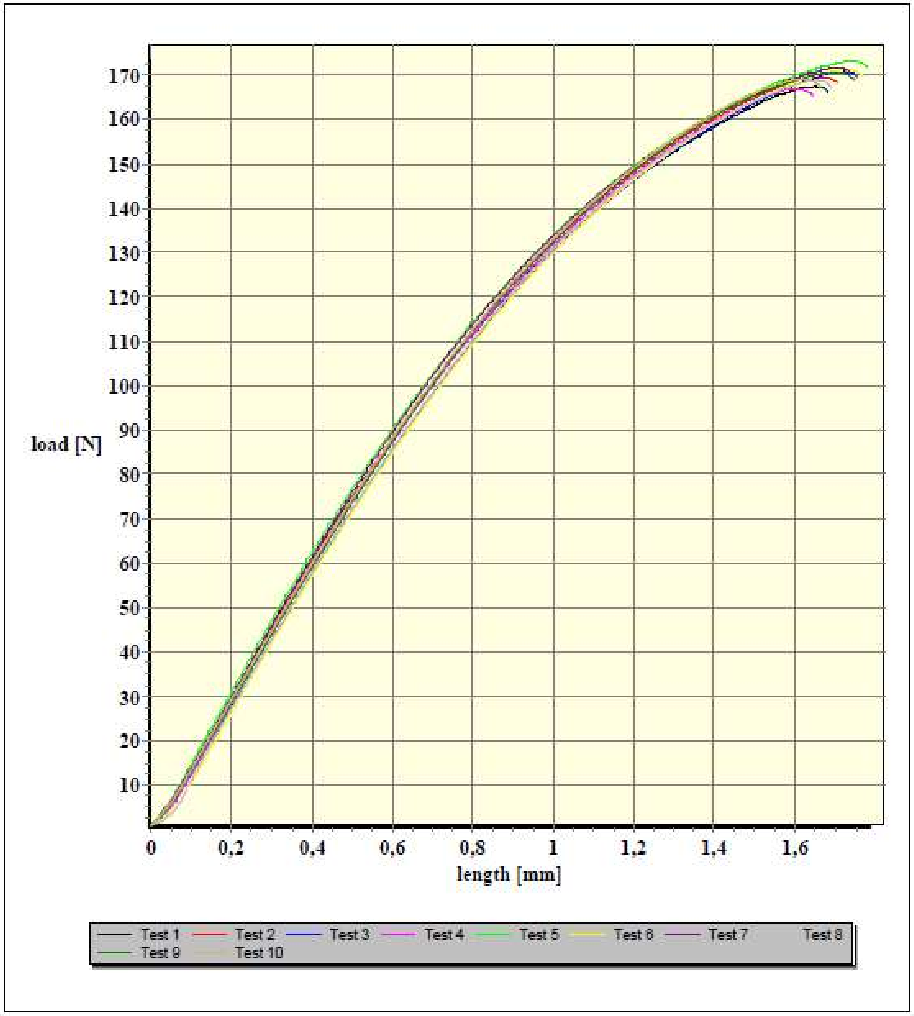


BONDED MAGNETS MANUFACTURING : MECHANICS

Mechanics (bending):

name	Fm [N]	sFmax [mm]	h [mm]	b [mm]	l [mm]	σfB [MPa]	E(b) [MPa]
Test 1	166,137	1,683	3,07	10,09	80,00	104,821	7189,991
Test 2	168,212	1,707	3,07	10,09	80,00	106,131	6780,015
Test 3	169,449	1,757	3,07	10,09	80,00	106,911	6839,373
Test 4	165,355	1,648	3,07	10,09	80,00	104,328	7607,831
Test 5	171,452	1,784	3,07	10,09	80,00	108,175	7575,759
Test 6	169,821	1,771	3,07	10,09	80,00	107,146	7684,205
Test 7	170,104	1,744	3,07	10,09	80,00	107,324	7059,406
Test 8	167,163	1,691	3,07	10,09	80,00	105,469	7536,835
Test 9	168,944	1,749	3,07	10,09	80,00	106,592	6836,466
Test 10	167,313	1,664	3,07	10,09	80,00	105,563	7248,407

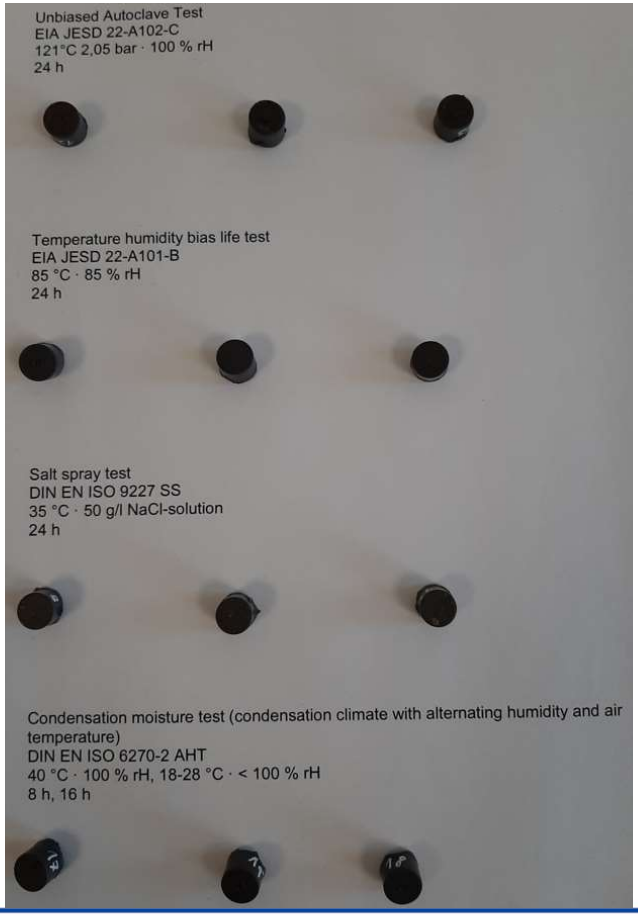
name	Fm [N]	sFmax [mm]	h [mm]	b [mm]	l [mm]	σfB [MPa]	E(b) [MPa]
MW	168,395	1,720	3,07	10,09	80,00	106,246	7235,829
s	1,908	0,047	0,00	0,00	0,00	1,204	350,143
MIN	165,355	1,648	3,07	10,09	80,00	104,328	6780,015
MAX	171,452	1,784	3,07	10,09	80,00	108,175	7684,205



BONDED MAGNETS MANUFACTURING : CORROSION RESISTANCE RELATED

Magnetic flux:

Injection moulded HDDR + PA									
Tests	Std	Conditions	duration	I mass s (g)	I flux s (10-6 Vscm)	I mass e (g)	d mass (%)	I flux e (10-6 Vscm)	d flux (%)
Unbiased Autoclave Test	EIA JESD 22-A102-C	121 °C · 2,05 bar · 100 % rH	24 h	2,71	14,72	2,72	100,36	14,27	96,94
Temperature humidity bias life test	EIA JESD 22-A101-B	85 °C · 85 % rH	24 h	2,73	14,74	2,71	99,26	14,31	97,08
Salt spray test	DIN EN ISO 9227 SS	35 °C · 50 g/l NaCl-solution	24 h	2,71	14,71	2,72	100,36	14,7	99,93
Condensation moisture test (condensation climate with alternating humidity and air temperature)	DIN EN ISO 6270-2 AHT	40 °C · 100 % rH, 18-28 °C · < 100 % rH	8 h, 16 h	2,69	14,72	2,7	100,37	14,73	100,06



BONDED MAGNETS MANUFACTURING
CONCLUSIONS

- Magnetics – for first tests surprisingly good
- On a parr with isotropic standard NdFeB
- Mechanics completely comparable to standards
- Processes well (extrusion and injection moulding)
- Corrosion properties comparable to regular

Suggestion: Shift demag curve towards higher Hk

SINTERED MAGNET MANUFACTURING ROUTE

- Melting EOL magnets
- Casting of an ingot
- Production of new ribbons incorporating the recycled ingot + virgin materials to correct composition shift
- Sintered magnet fabrication following the standard route

This route has been experimented on two magnet sources

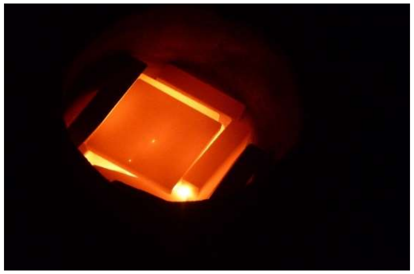
1. N38 magnets : relatively clean batch of large magnets
2. Hard Disk Drives magnets : batch of small magnets with residues

SINTERED MAGNET MANUFACTURING ROUTE : MELTING OF N38 MAGNETS

Induction furnace : 12 kg of magnets in the crucible

↓

Heating up



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Molten alloy

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Casting in a mold

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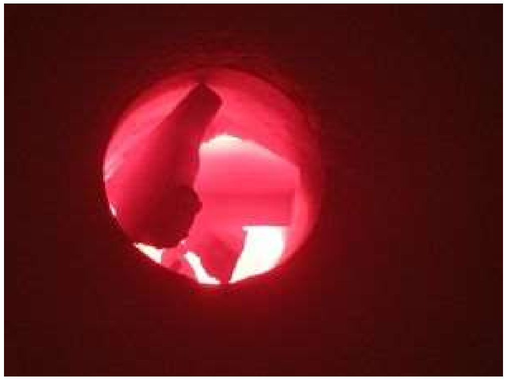
Analysis of the chemical composition of the SC42 ingot

SINTERED MAGNET MANUFACTURING ROUTE : RECYCLED N38 ALLOY



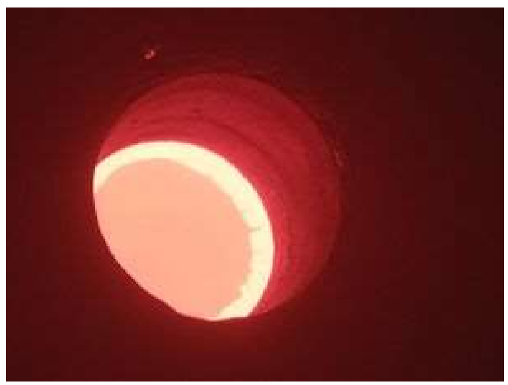
Induction furnace : 15 kg

Composition : N38 magnets

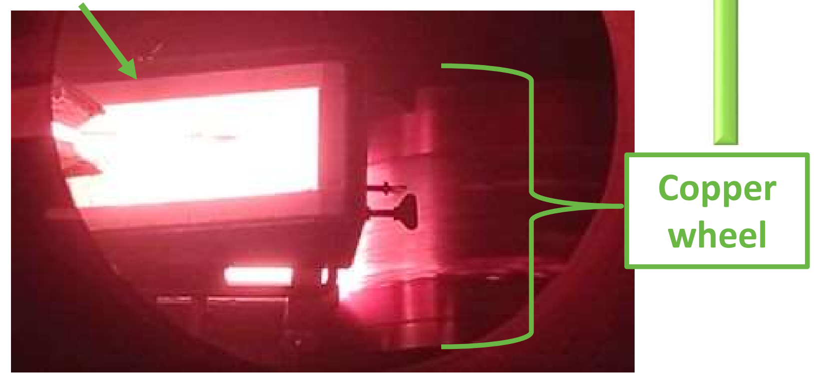
- **Recycled materials (SC42 ingot) : 6.5 kg (43%)**
- **New materials : 8.5 kg (57%)**

SC46 ribbons

the alloy is completely melted



Casting on a copper wheel



SINTERED MAGNET MANUFACTURING ROUTE : MAGNETIC PROPERTIES

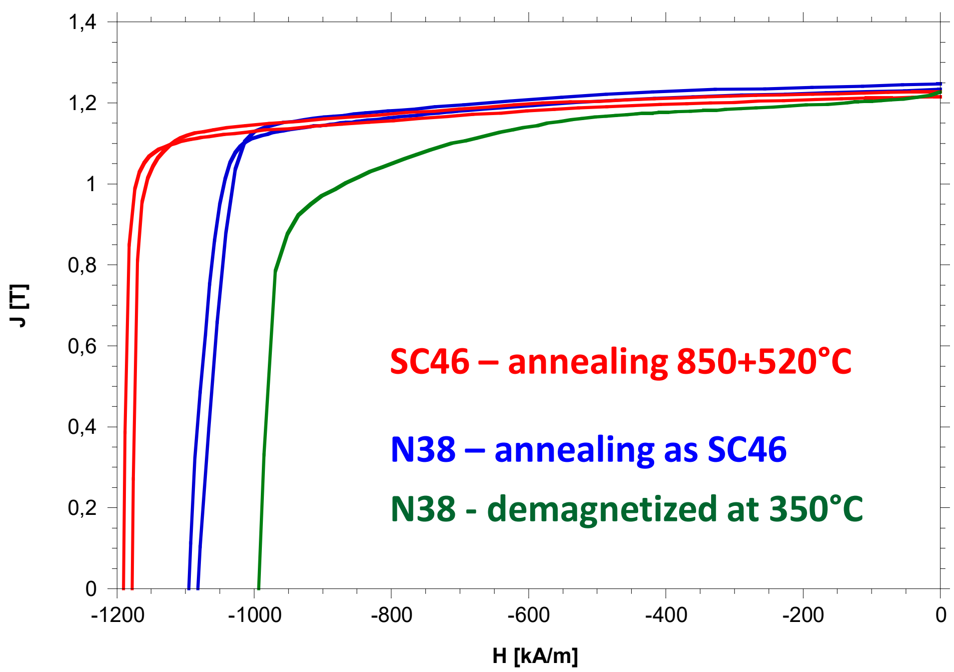
SC46 ribbons → powder (5 µm particle size)

Sintering : 4h – 1050°C

Annealing : 2h 850°C – 2h 520°C

Comparison SC46/N38

- Same Remanence
- Coercivity of N38 depends on TT
- S46 coercivity 10% higher



SINTERED MAGNET MANUFACTURING ROUTE : CHARACTERIZATIONS

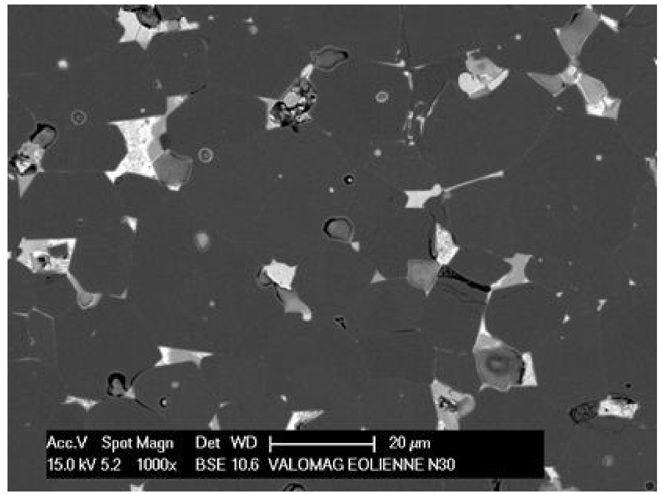
IGA analysis

	O (ppm)	C (ppm)
N38 magnet	**3400**	**840**
SC46 ribbons	**70**	**400**
SC46 magnet	**3000**	**740**

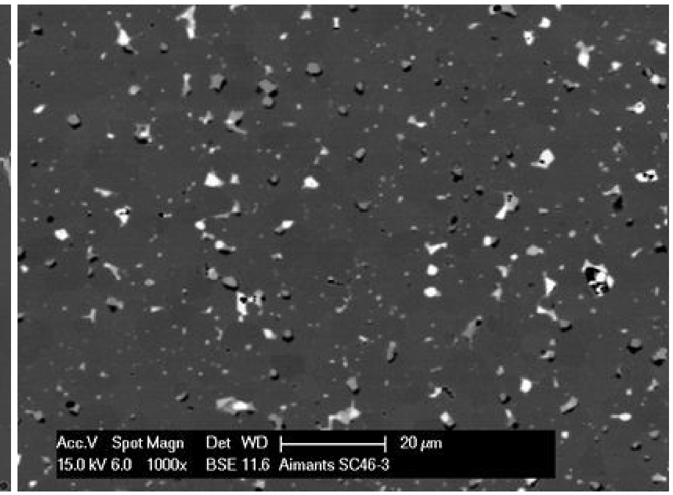
SC46 ribbons : 43% of recycled magnets
Strong reduction of O content but **no reduction of C content**

C and O magnet contents close to N38 magnet contents

Microstructure



N38 magnet : grain size > 10 µm



SC46 magnet : small grain size < 10 µm

Better coercivity for SC46 magnets could be explained by the microstructure difference

SINTERED MAGNET MANUFACTURING ROUTE : HDD MAGNETS

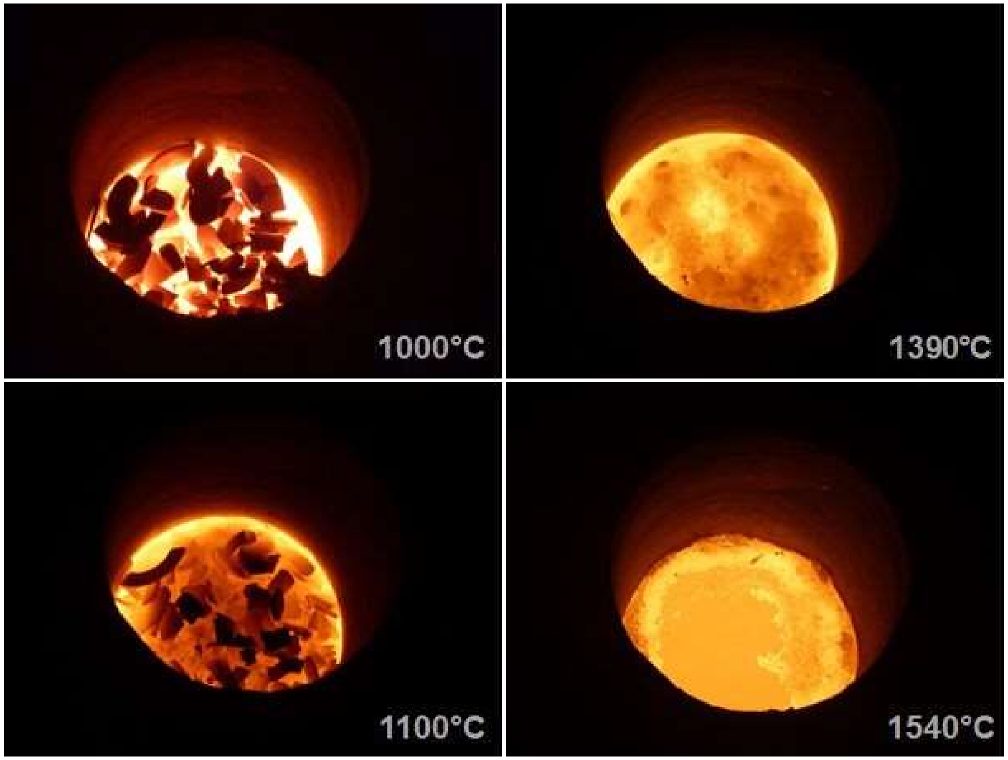
"As received" HDD magnets

Thermal pyrolysis of organic materials

***Clean* magnets after removal of carbon formed during thermal pyrolysis**

SINTERED MAGNET MANUFACTURING ROUTE : MELTING OF HDD MAGNETS

Melting of HDD clean magnets in the strip-casting furnace : SC52



SINTERED MAGNET MANUFACTURING ROUTE : MASS BALANCE AND IGA

	After casting	
Crucible	3.30 kg	28 %
Tundish	0.30 kg	3 %
Ingot	8.06 kg	69 %
Total weight	11.65 kg	100 %

IGA	O (ppm)	N (ppm)	C (ppm)
Crucible	15200	470	880
Spout	980	26	900
SC52 Ingot	280	20	880

SINTERED MAGNET MANUFACTURING ROUTE

Reference = Industrial NdFeB alloy : **43UH-1**

1. Jet Milling and sintering
2. Magnetic properties and chemical analysis of magnets

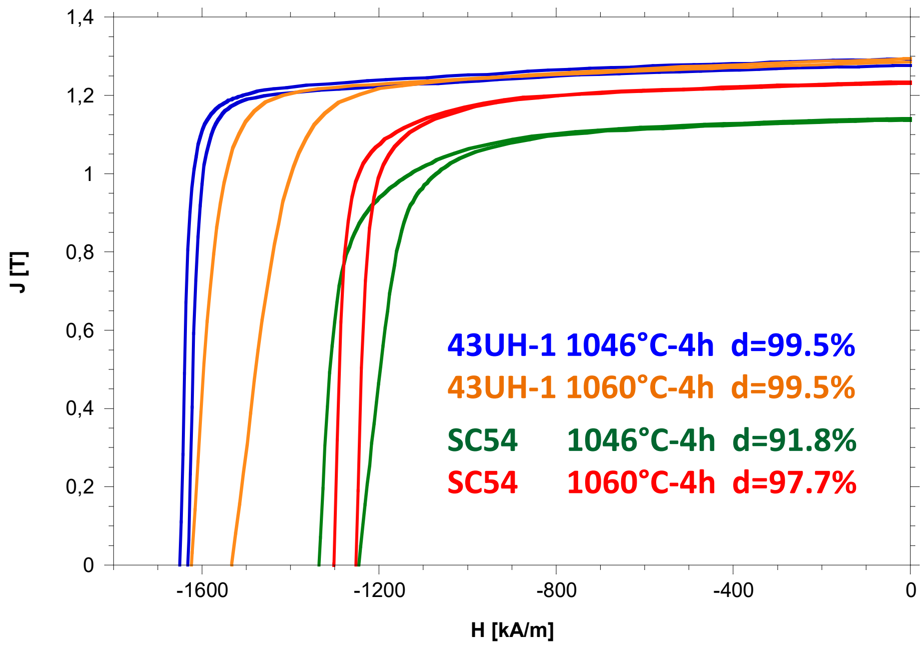
CEA NdFeB alloy : we targeted the 43UH-1 composition

1. Chemical analysis (ICP and IGA) of **SC52** ingot from HDD magnets
2. 50% Recycled magnets (6 kg SC52 ingot) + 50% new materials (6 kg)
3. Strip-casting **SC54** : ribbons
4. Jet Milling and Sintering
5. New magnets : Magnetic properties and chemical analysis

43UH-1 COMPOSITION	%
TRE	30.76
Nd	21.73
Pr	5.47
Dy	3.53
B	0.98
Co	0.90
Cu	0.07
Al	0.23
Ti	0.05
Ga	0.15
Zr	0.02
Fe	66.84

SINTERED MAGNET MANUFACTURING ROUTE

43UH-1 and SC54 magnets : magnetic properties and chemical analysis



ICP	Fe (wt %)	RE (wt %)
43UH-1	66.9	30.8
SC54	67.5	30.2

IGA		O (ppm)	C (ppm)
43UH-1	1046°C - 4h	2950	530
43UH-1	1060°C - 4h	2820	580
SC54	1046°C - 4h	3210	880
SC54	1060°C - 4h	3400	870

- Insufficient densification for SC54 magnets : lack of rare earths + more impurities
- The percentage of end-of-life magnets (50%) should be reduced

SINTERED MAGNET MANUFACTURING ROUTE
CONCLUSIONS

- We have demonstrated that it is possible **to manufacture sintered magnets from end-of-life magnets** using **industrial processes** or that can easily become industrial processes.
- Two types of magnets were treated.
- **The melting process reduces the amount of oxygen** that is trapped as rare-earth oxide in the crucible. The RE oxides can be recycled using the hydrometallurgic route.
- The problem of **high carbon content** in recycled magnets from HDD magnets can be solved by:
  1) a better cleaning of the magnets
  2) reducing the proportion of end-of-life magnets to produce new NdFeB alloy
  3) increasing the amount of rare earth in the NdFeB alloy

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