A NOVEL APPROACH FOR SINTERING $Nd_2Fe_{14}B$-, $SmCo_5$- AND Sm_2Co_{17}-BASED MAGNETS BY THE HDDR PROCESS

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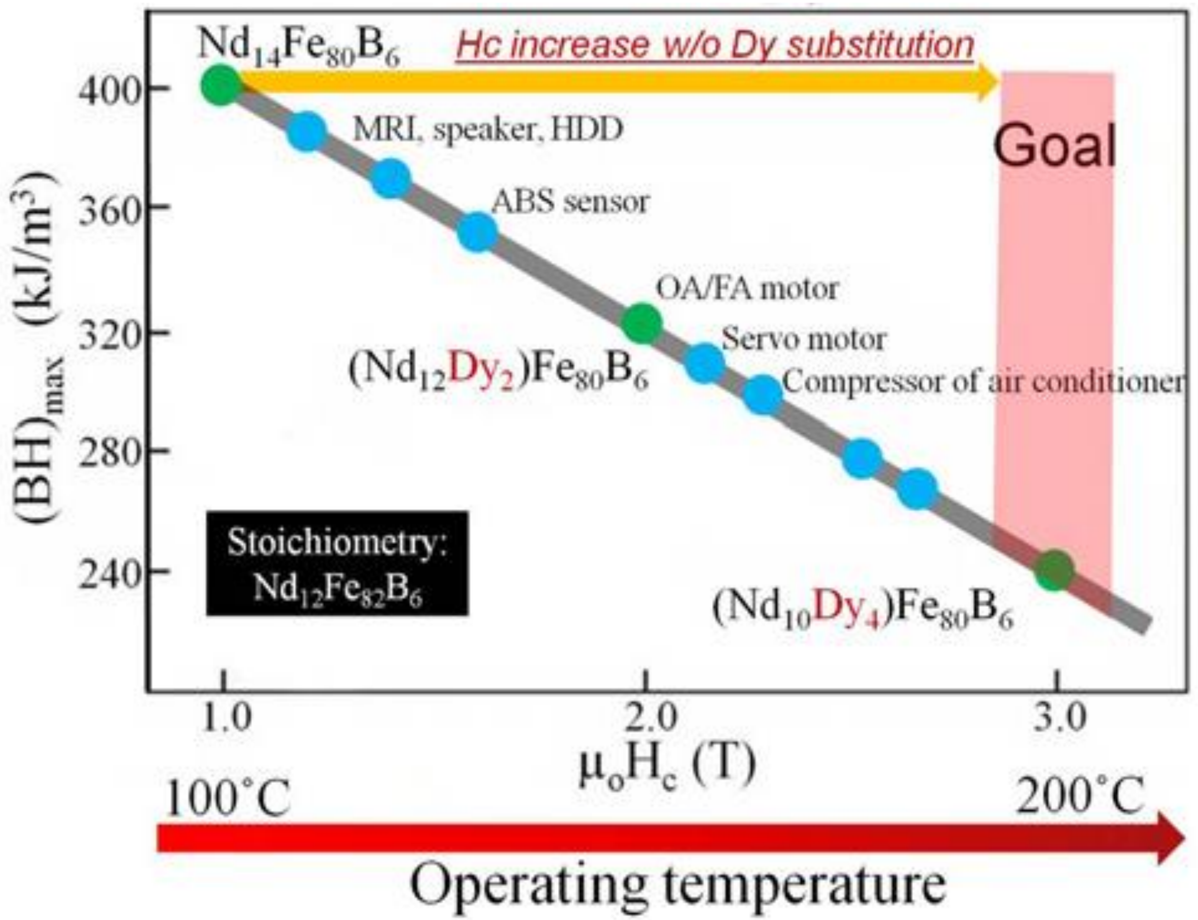
Requirements for Magnetic materials

For wind turbines and electric vehicles



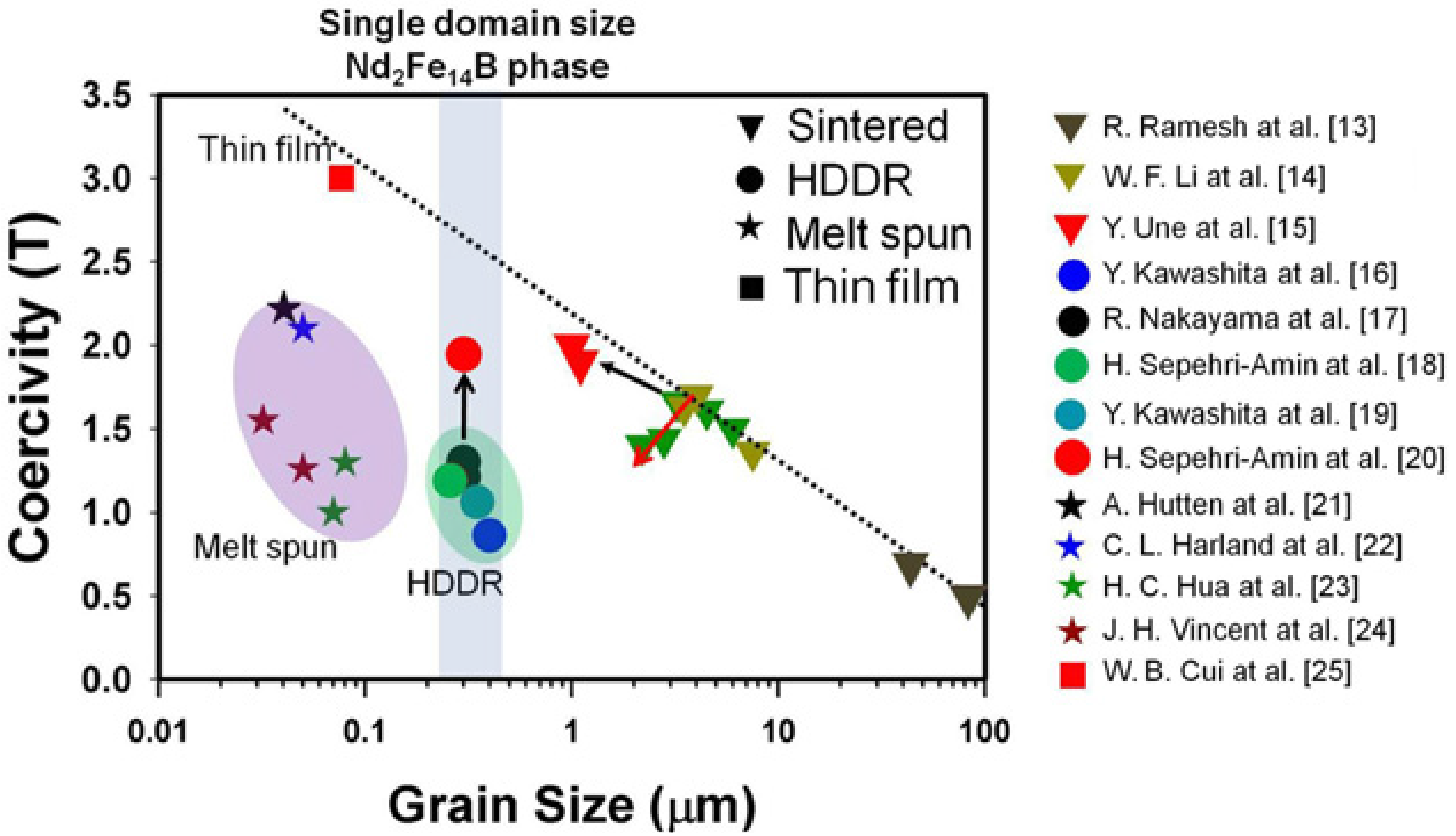
The operating temperature of the traction motors for (hybrid) electric vehicles is approximately 200 C.

Therefore, **permanent magnets suitable for use in traction motors and wind power generators must have a high coercivity of around 3 T at room temperature**.

K. Hono, H. Sepehri-Amin, Scr. Mater. 67 (2012) 530–535.

Requirements for Magnetic materials

For wind turbines and electric vehicles



the coercivity increases as the grain size decreases

We view the HDDR process as a promising method for refining the microstructure of the R-TM ferromagnetic materials type materials, particularly R-Fe-B and Sm-Co.

K. Hono, H. Sepehri-Amin, Scr. Mater. 67 (2012) 530–535.

R-TM ferromagnetic materials with fine microstructure

How can we produce **the bulk R-TM ferromagnetic materials** with fine microstructures?
Through the HDDR process.

SINTERING:
it occurs through **the diffusion** of material components

1. The HDDR process involves phase transformations through **diffusion** ⇒ the **diffusion rate** of all alloy components **increases**.

Ya.E. Geguzin, *Physics of Sintering* [in Russian], Nauka, Moscow, (1984), p. 311.
V.V. Skorokhod and S.M. Solonin, *Physical and Metallurgical Fundamentals of Powder Sintering* [in Russian], Metallurgiya, Moscow (1984), p. 159.

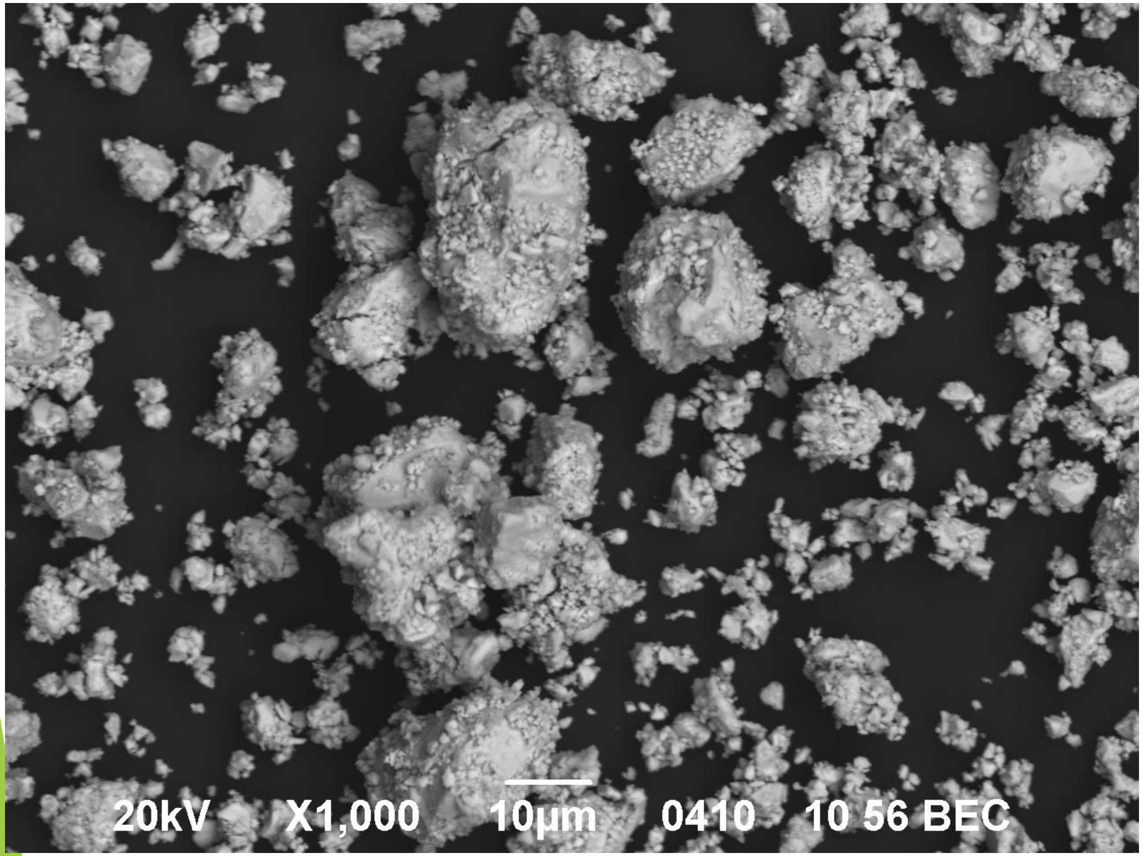
2. During HDDR, **hydrogen** is present in the alloy as a **solid solution** ⇒ The **diffusion rate** of all alloy components is **higher** than that of an alloy without a hydrogen solid solution.

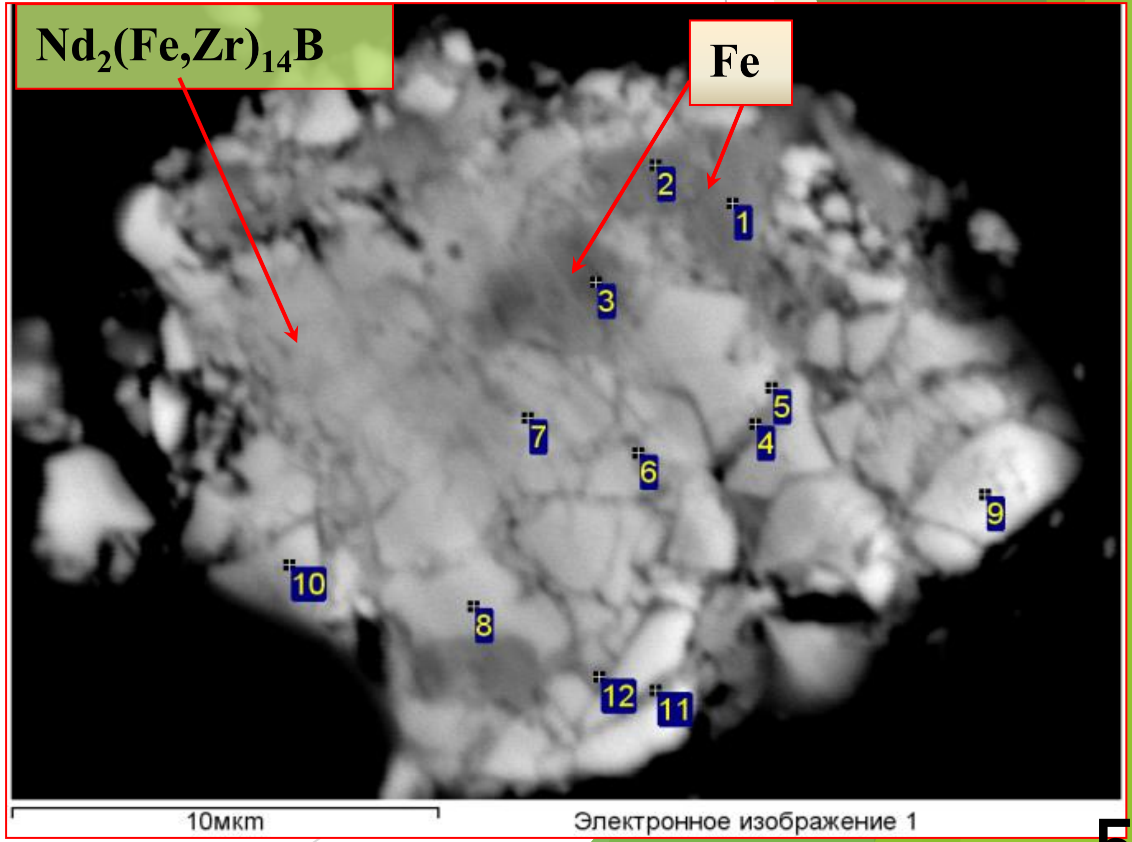
V.I. Pokhmurskii and V.V. Fedorov, *Effect of Hydrogen on Diffusion Processes in Metals* [in Ukrainian], FMI NANU, Lviv (1998), p. 206.

The morphology and microstructure of the coarse particles of the $Nd_{11.7}Fe_{81.1}Zr_{1.2}B_6$ alloy milled in hydrogen.

Milling terms: v=200 rpm, τ=1 h

Particle size: from 2-3 to 10-30 microns





I.I. Bulyk, I.V. Borukh, https://doi.org/10.1007/s11106-023-00354-9

Preliminary Results of Sintering $R_2Fe_{14}B$ Magnetic Materials Using the HDDR Process

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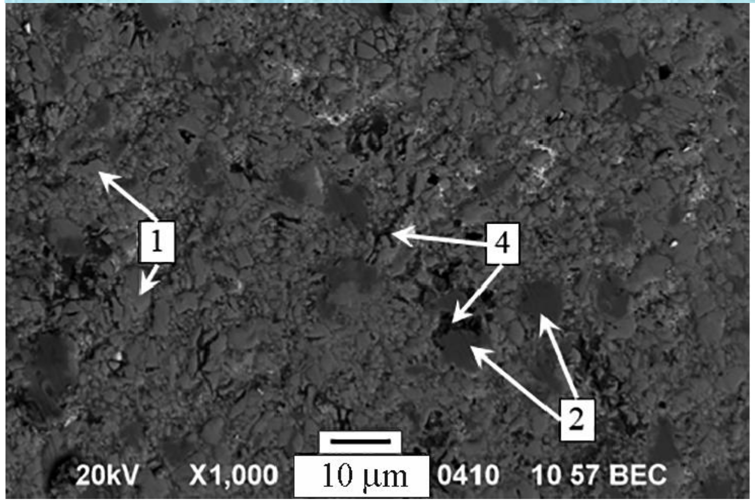
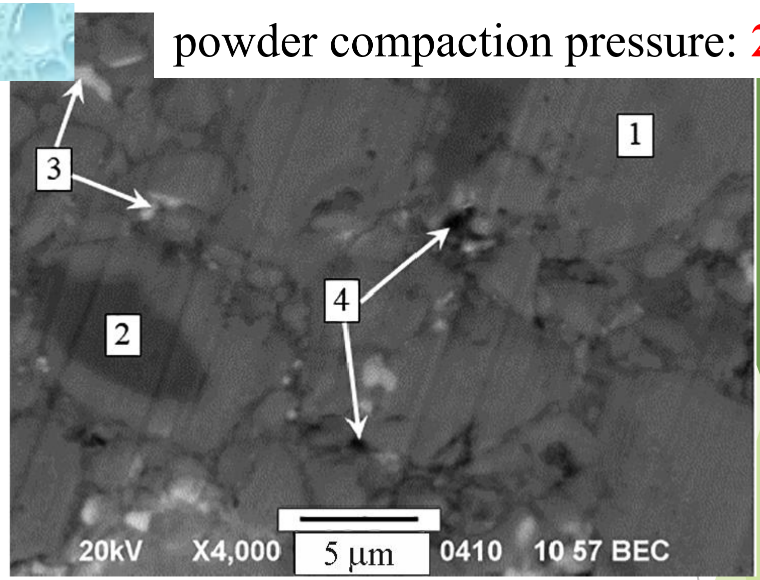
The microstructure of the sintered through the HDDR process **$Nd_{11.7}Fe_{81.1}Zr_{1.2}B_6$** alloy

powder compaction pressure: **2 t/cm²**

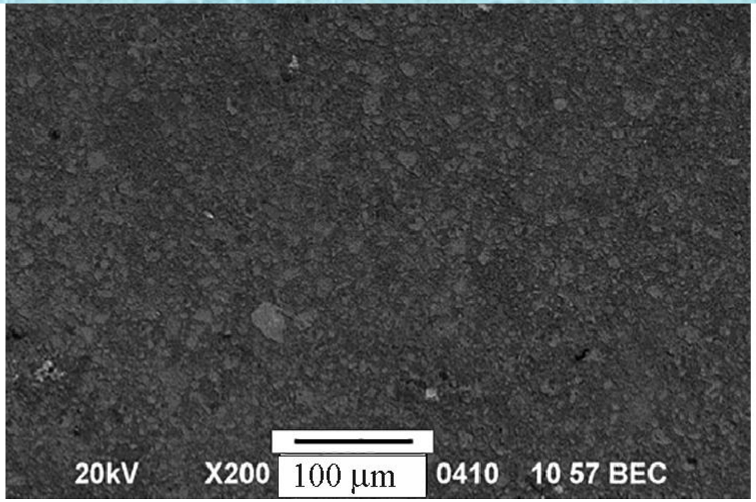
T_{DR} = 850°C

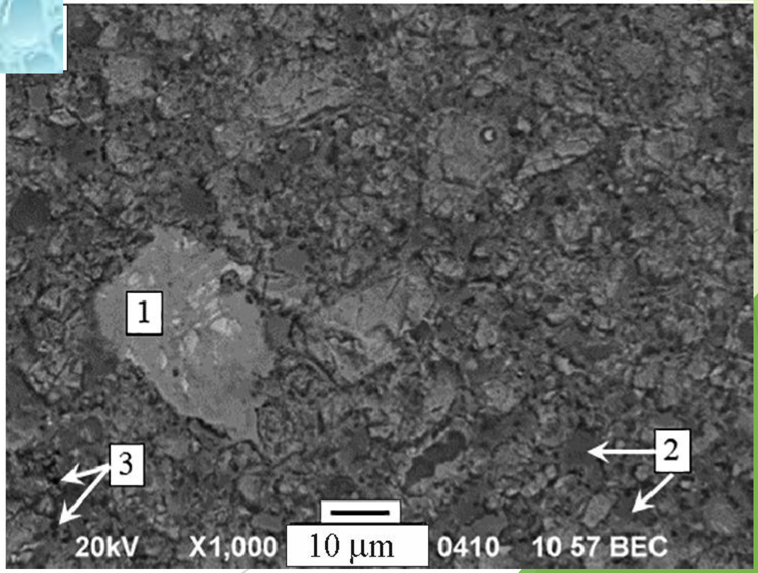




1) $Nd_2(Fe, Zr)_{14}B$ phase;
2) α-Fe-based solid solution;
3) Nd-rich phase;
4) pores

T_{DR} = 950°C





1) $Nd_2(Fe, Zr)_{14}B$ phase;
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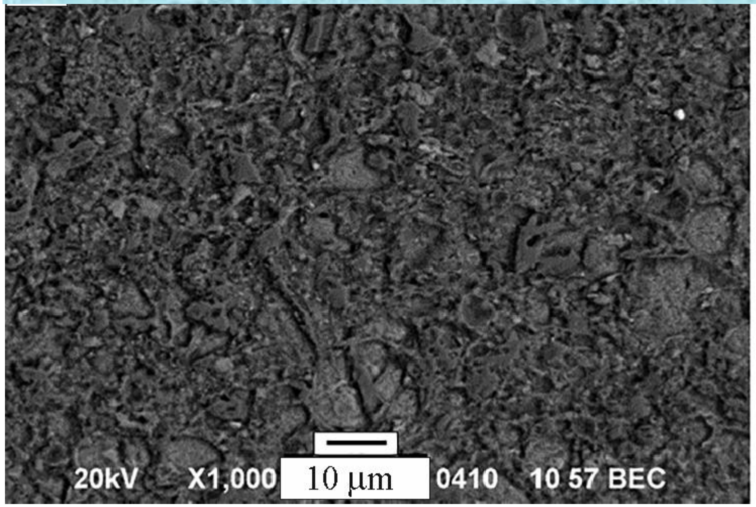
I.I. Bulyk, I.V. Borukh, https://doi.org/10.1007/s11106-023-00354-9

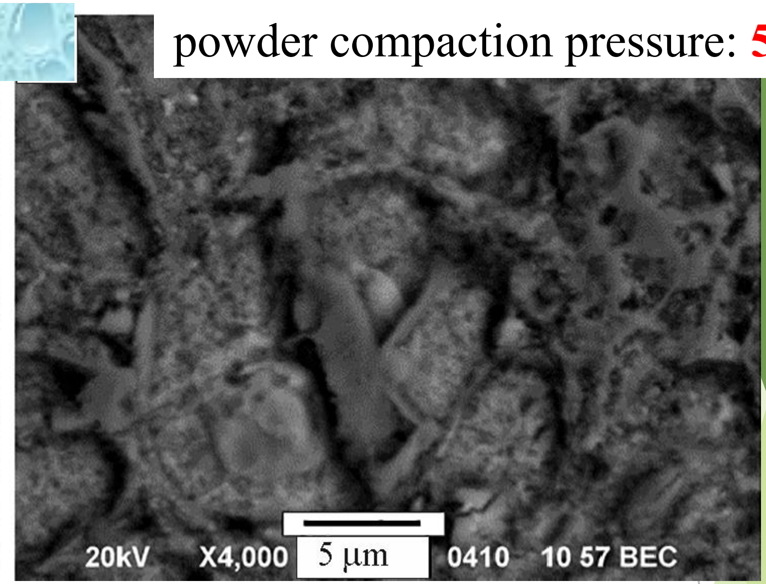
Preliminary Results of Sintering $R_2Fe_{14}B$ Magnetic Materials Using the HDDR Process

The microstructure of the sintered through the HDDR process **$Nd_{11.7}Fe_{81.1}Zr_{1.2}B_6$** alloy

***T*DR = 850°C**

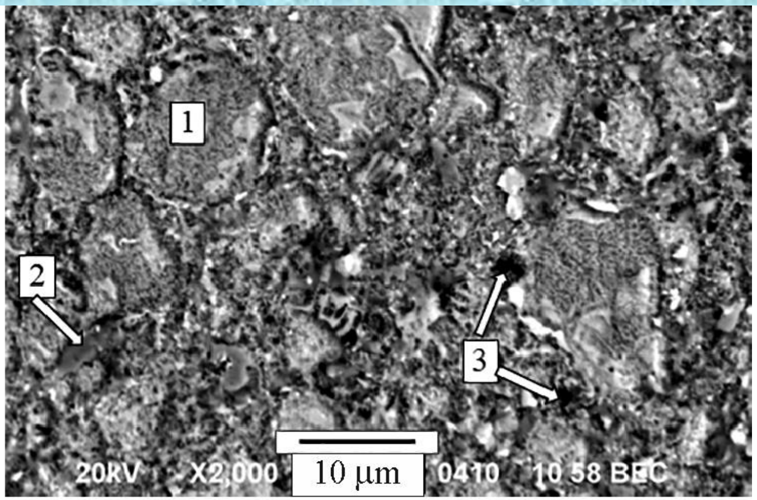
powder compaction pressure: **5 t/cm²**

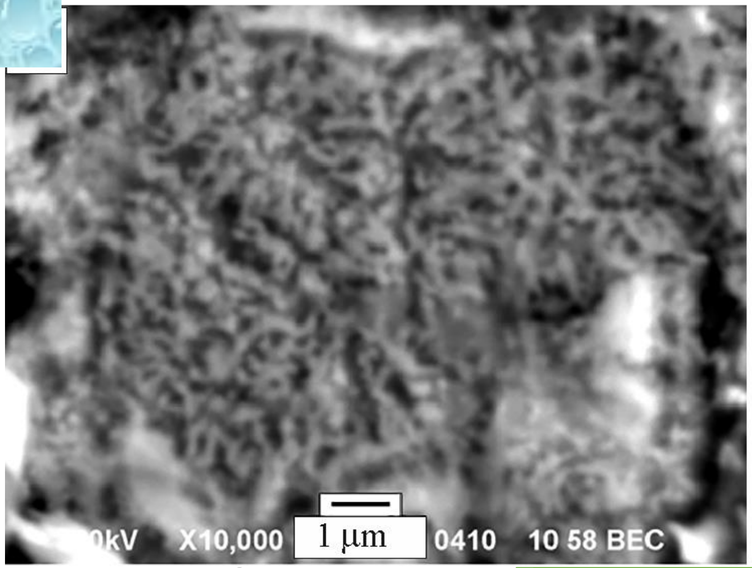




***T*DR = 950°C**

1) $Nd_2(Fe, Zr)_{14}B$ phase;
2) α-Fe-based solid solution;
3) pores



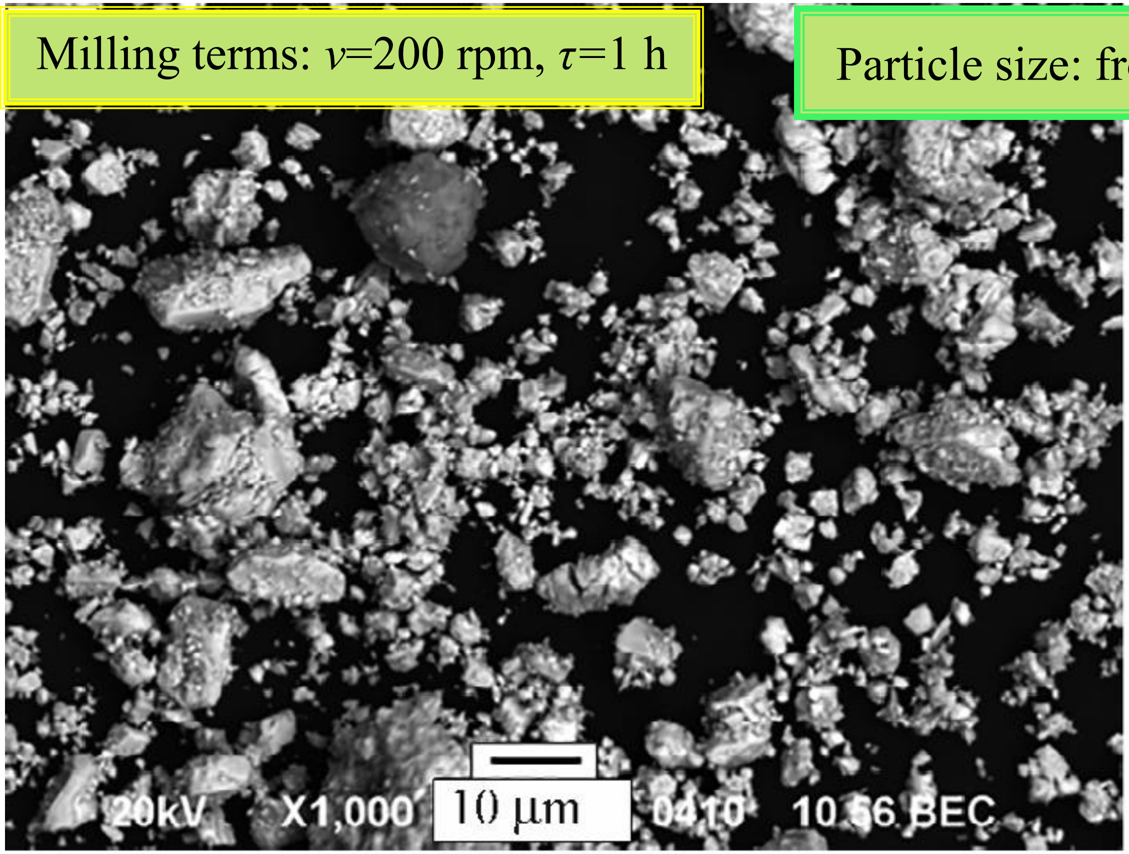


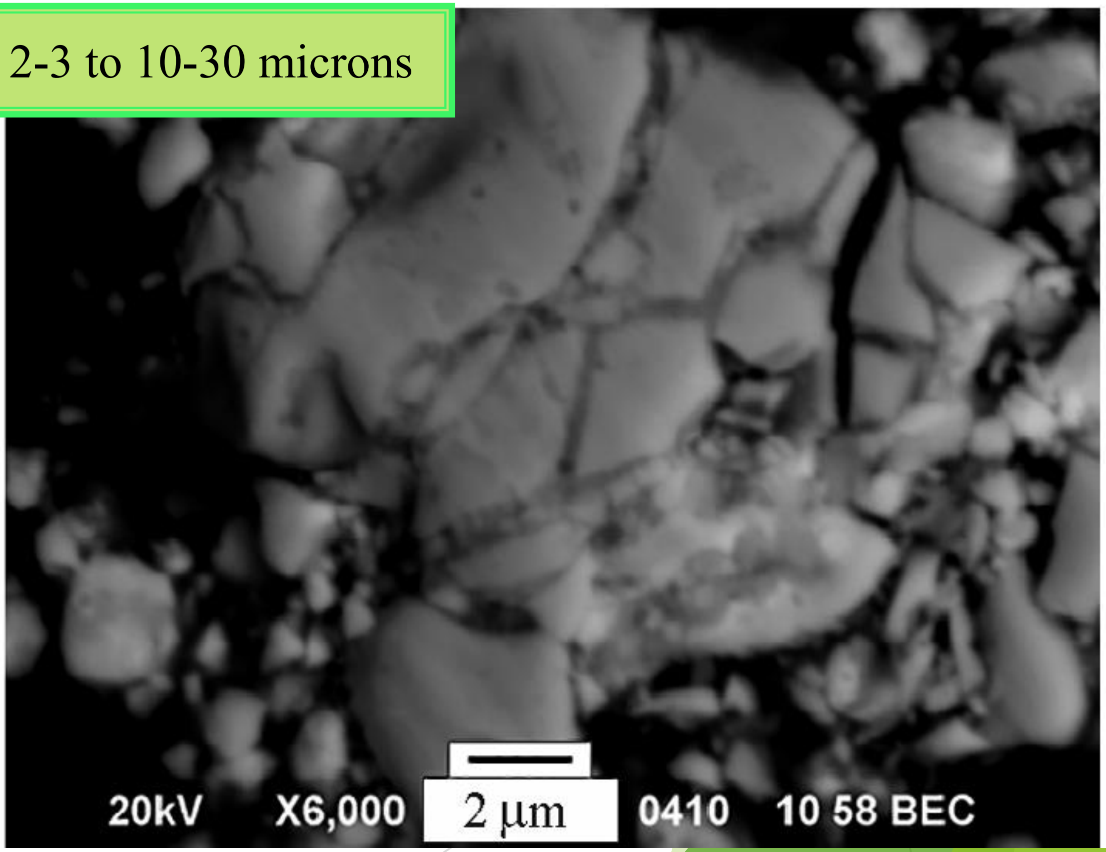
I.I. Bulyk, I.V. Borukh, https://doi.org/10.1007/s11106-023-00354-9

The morphology and microstructure of the coarse particles of the $Nd_{16}Fe_{73.9}Zr_{2.1}B_8$ alloy milled in hydrogen

Milling terms: v=200 rpm, τ=1 h

Particle size: from 2-3 to 10-30 microns





I.I. Bulyk, I.V. Borukh, https://doi.org/10.1007/s11106-023-00354-9

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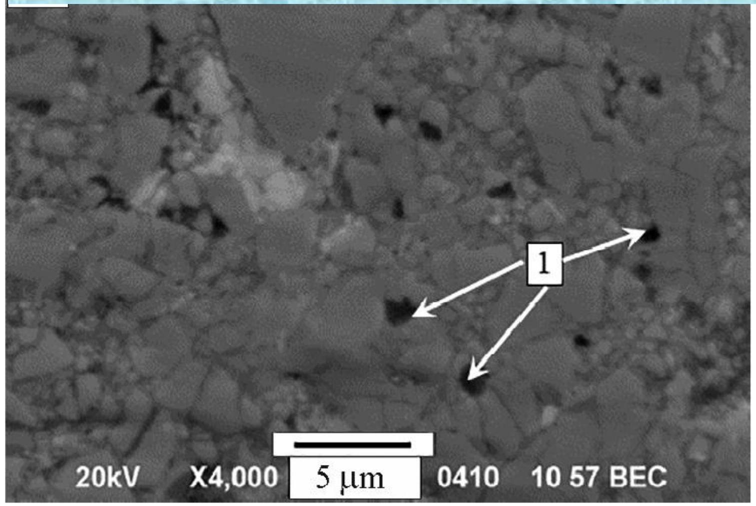
Preliminary Results of Sintering $R_2Fe_{14}B$ Magnetic Materials Using the HDDR Process

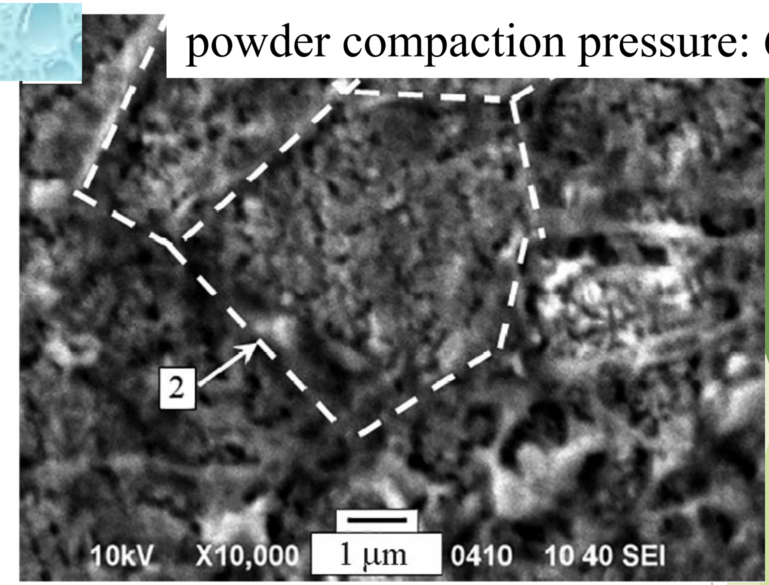
The microstructure of the sintered through the HDDR process the $Nd_{16}Fe_{73.9}Zr_{2.1}B_8$ alloy

unetched section, 1) pores; etched section, 2) boundaries between sintered particles

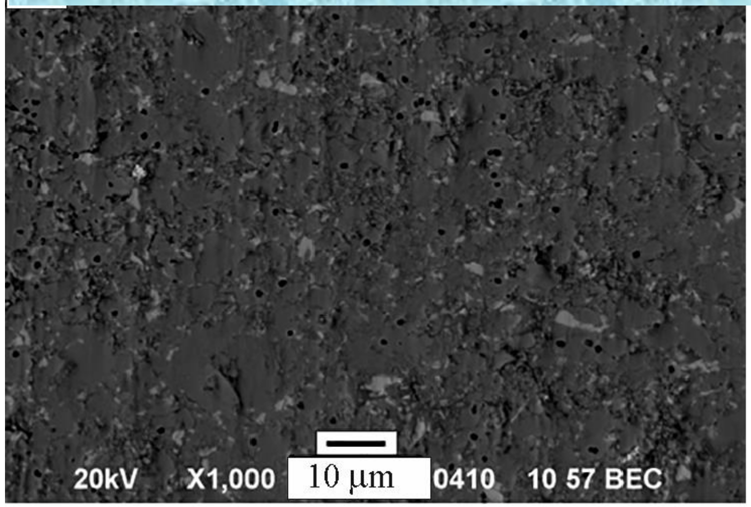
T_{DR} = 850°C

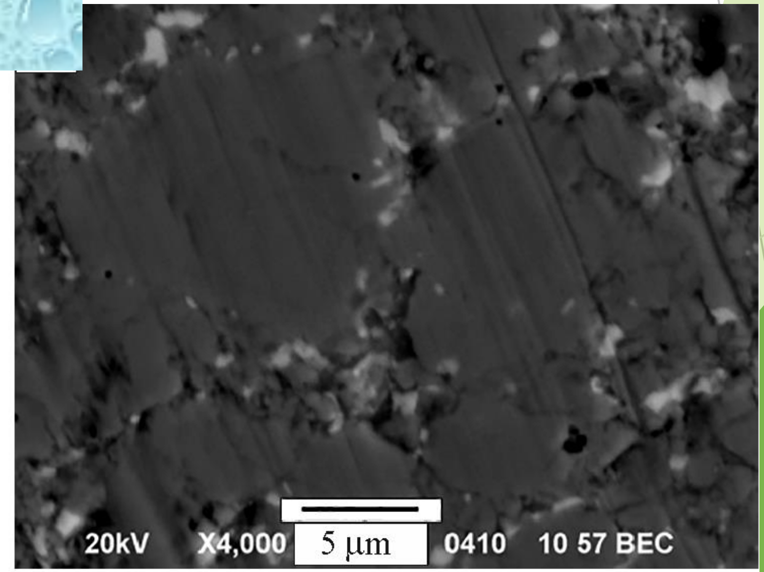
powder compaction pressure: **6 t/cm²**





T_{DR} = 950°C

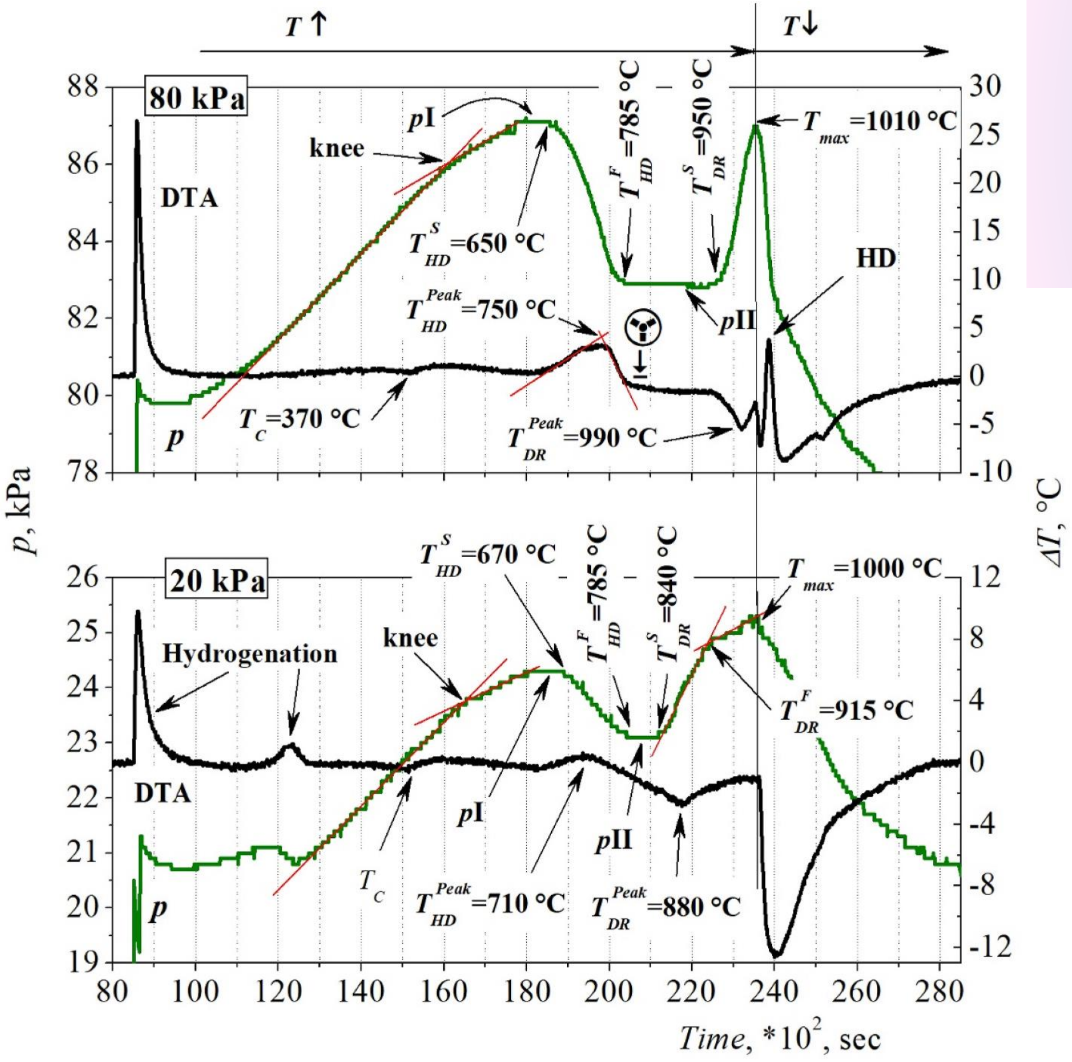




I.I. Bulyk, I.V. Borukh, https://doi.org/10.1007/s11106-023-00354-9

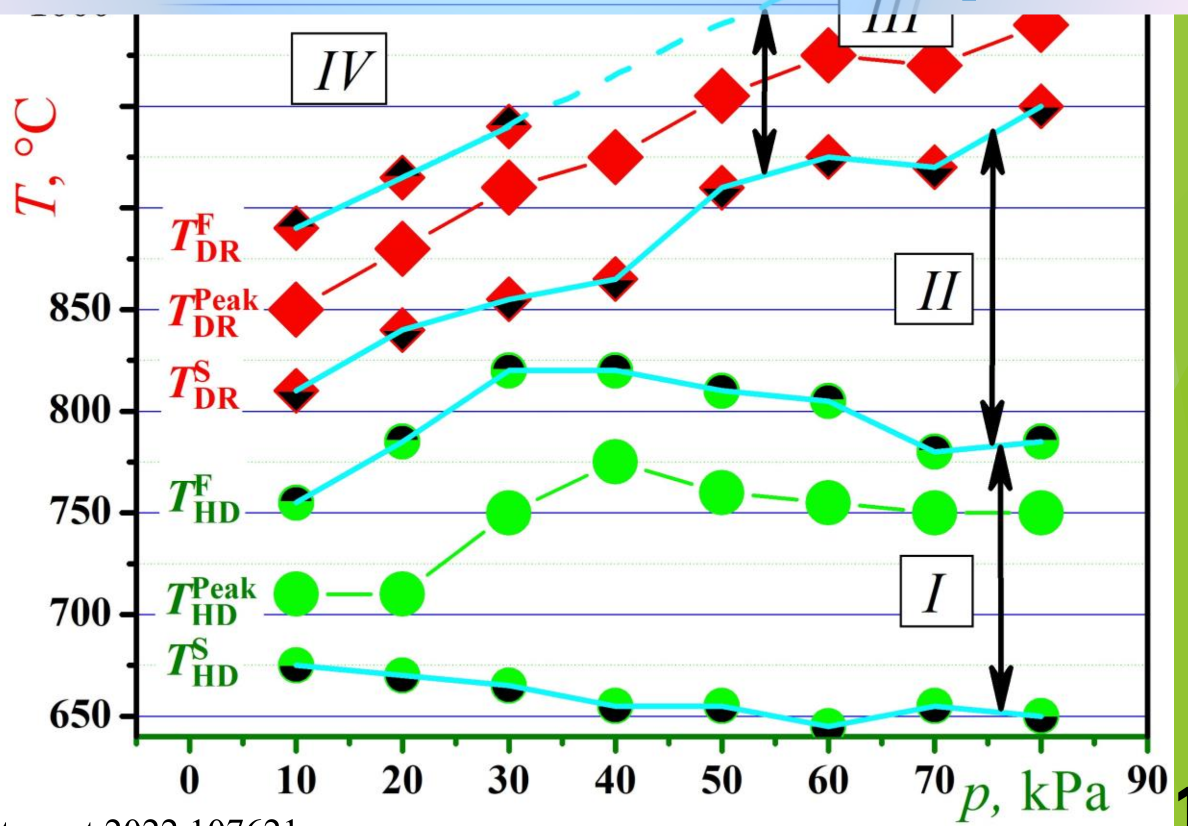
Preliminary Results of Sintering $R_2Fe_{14}B$ Magnetic Materials Using the HDDR Process

Sintering $R_2Fe_{14}B$ magnetic materials using the HDDR process:



Next step:

Preparing a **P**ressure – Phase **C**omposition – **T**emperature diagram to use as a basis for choosing HDDR parameters



Ihor I. Bulyk, et al., Intermetallics 148 (2022) 107621. https://doi.org/10.1016/j.intermet.2022.107621.

HDDR PROCESS IN $SmCo_5$ MATERIALS

LITERATURE DATA ABOUT HDDR IN $SmCo_5$ ALLOYS

HD
H_2 ≥570-620 °C

$$SmCo_5 \rightleftharpoons SmH_{2+\delta} + Co$$

DR
Vacuum ≤950 °C

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Preliminary Results of Sintering $SmCo_5$ Magnetic Materials Using the HDDR Process

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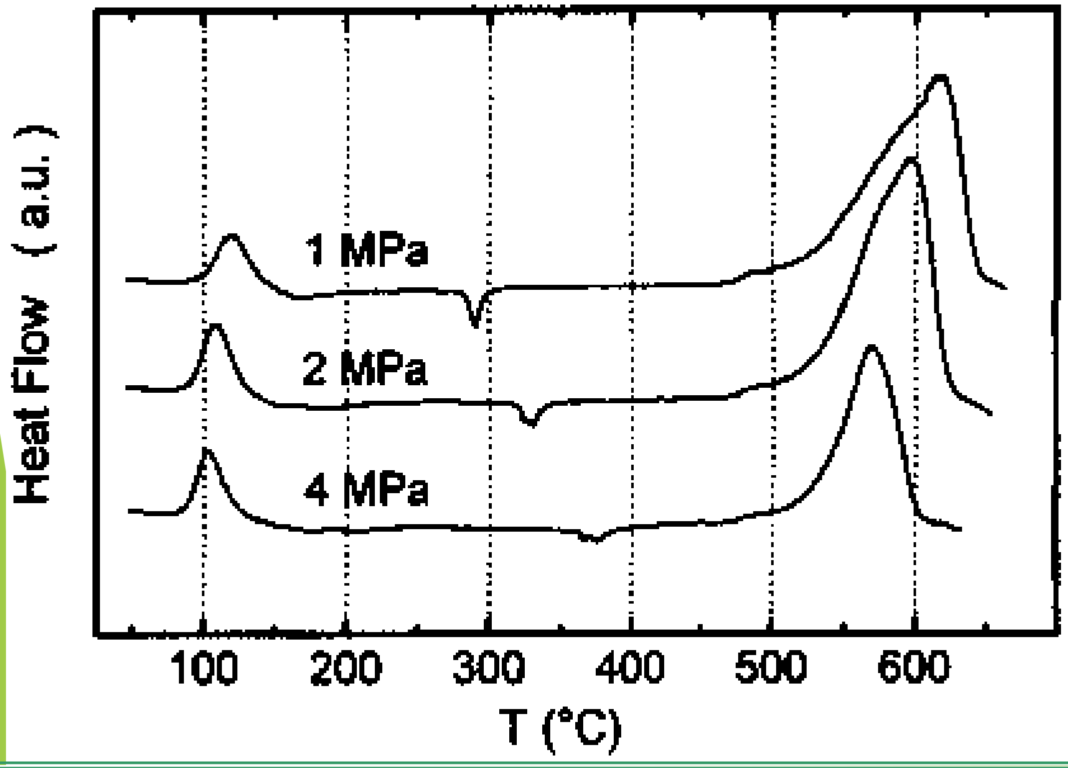
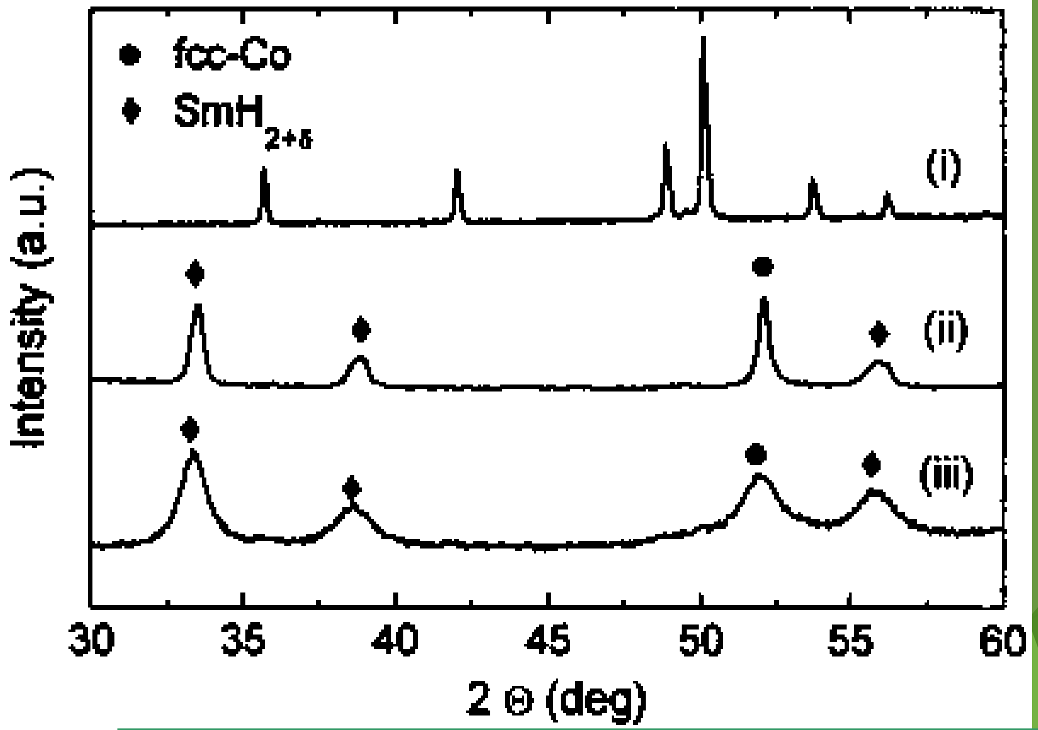
HDDR PROCESS IN $SmCo_5$ MATERIALS

DSC curves for $SmCo_5$ under different hydrogen pressures



LITERATURE DATA



XRD patterns for $SmCo_5$ alloy:
(i) starting alloy;
(ii) (ii) after HD under 2 MPa;
(iii) (iii) reactive milling in hydrogen.

M. Kubis, A. Handstein, B. Gebel, 0. Gutfleisch, K.-H. Muller, and L. Schultz, J.Appl.Phys. 85 (1999) 5666-5668. https://doi.org/10.1063/1.369834

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*Preliminary Results of Sintering **$SmCo_5$** Magnetic Materials Using the HDDR Process*

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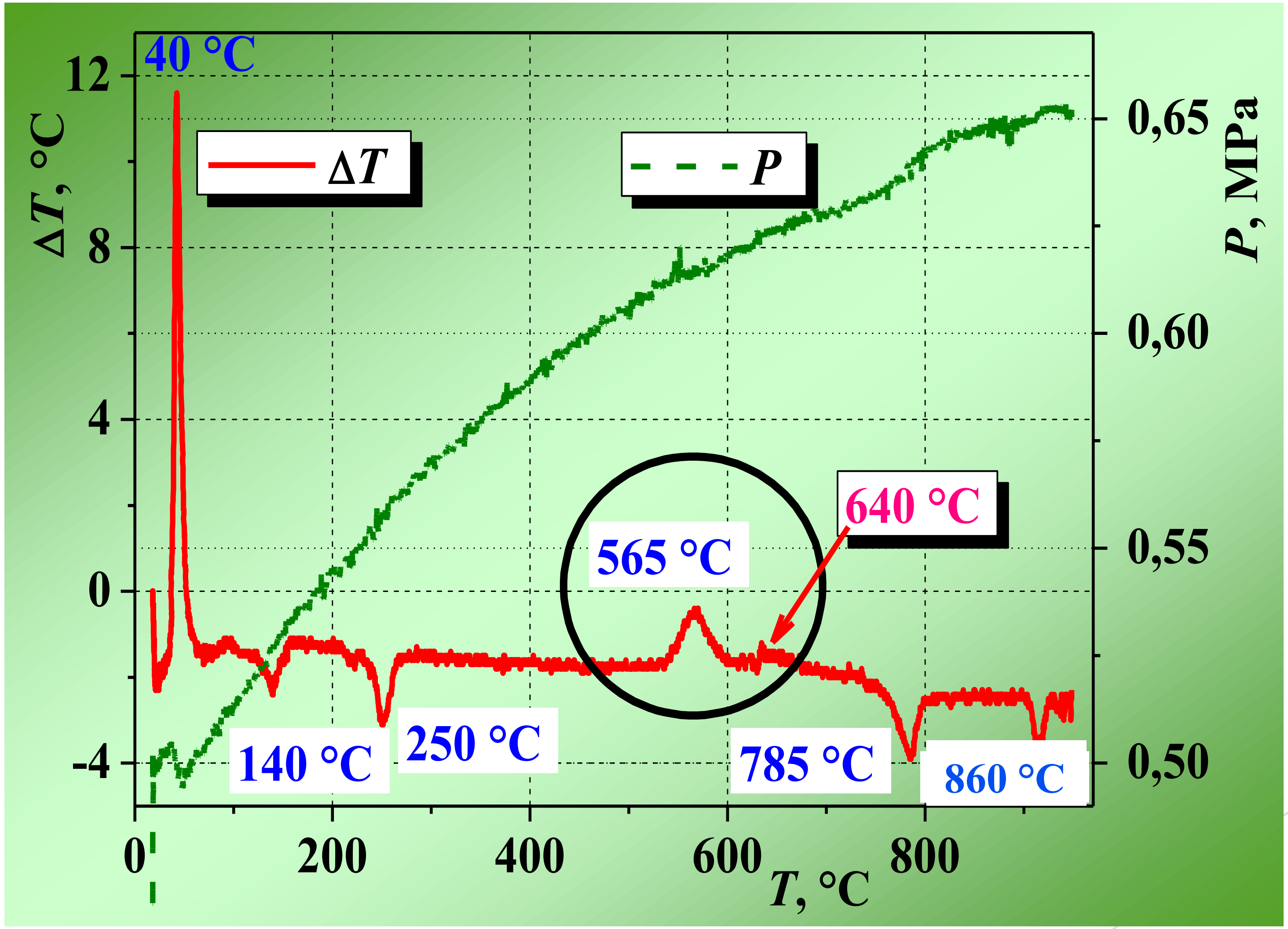
TERMS OF THE HDDR PROCESS IN $SmCo_5$ ALLOY



DTA curves for $SmCo_5$–H_2 under hydrogen pressures of 0.5 MPa

I.I. Bulyk, et al. Materials Science. 43 (2007) 102-108. http://rd.springer.com/article/10.1007/s11003-007-0011-6.

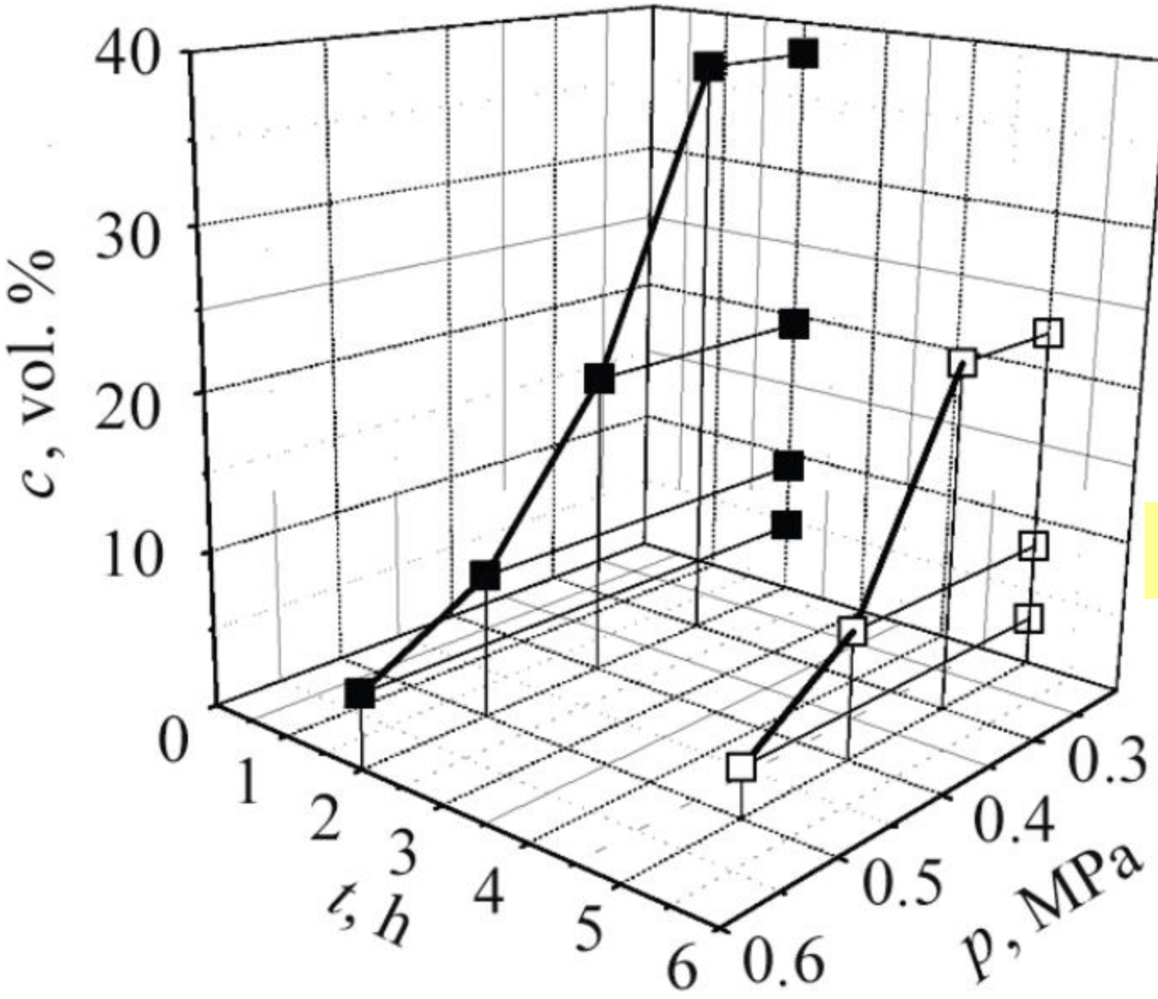
*Preliminary Results of Sintering **$SmCo_5$** Magnetic Materials Using the HDDR Process*

TERMS OF THE HDDR PROCESS IN $SmCo_5$ ALLOY

(*c*) amount of the $SmCo_5$ phase

(*p*) hydrogen pressure

(*t*) duration of reaction



Conventional HD (640 °C)

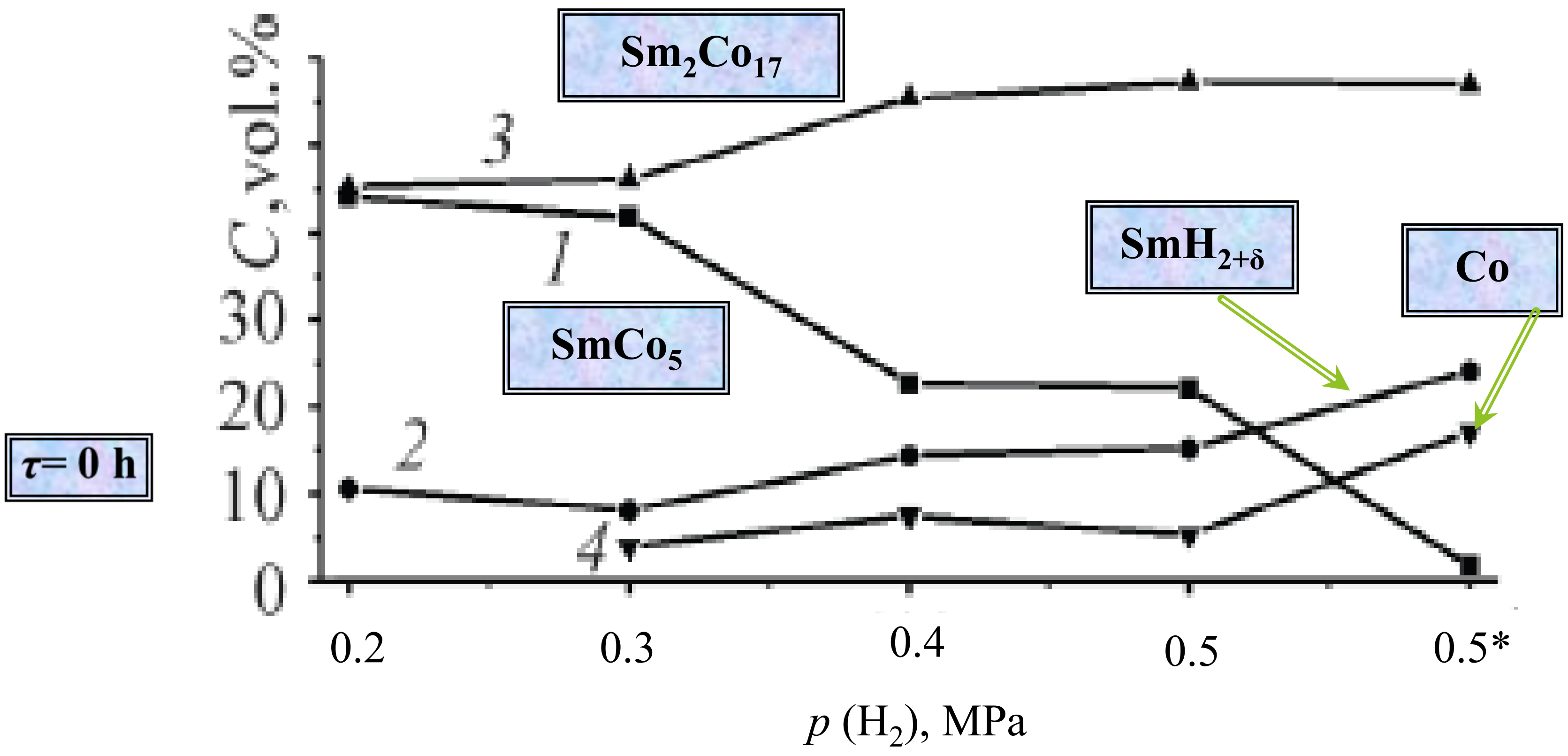
$$SmCo_5 \Rightarrow SmH_{2+\delta} + Co$$

Bulyk I.I., Panasyuk V.V., Materials Science. 48 (2012) 1-11. http://rd.springer.com/journal/11003/48/1.

TERMS OF THE HDDR PROCESS IN $SmCo_5$ ALLOY

The phase composition of the $SmCo_5$-based alloy after disproportionation in hydrogen

Solid HD, 700 °C, holding time is 2 h



*** - the holding time is 5 h**

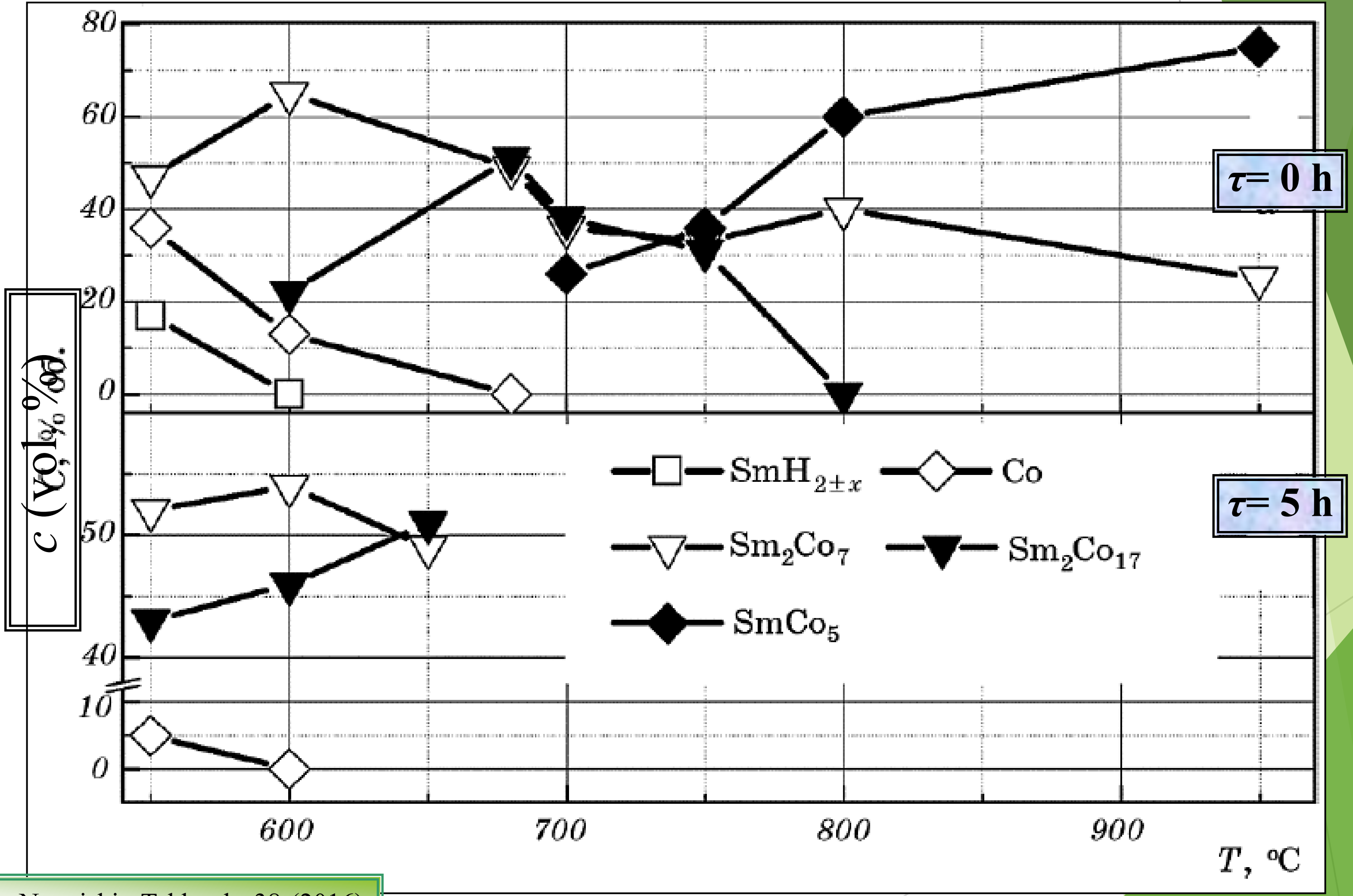
Bulyk I.I., Panasyuk V.V. Materials Science. 48 (2012) 1-11. http://rd.springer.com/journal/11003/48/1.

Preliminary Results of Sintering $SmCo_5$ Magnetic Materials Using the HDDR Process

TERMS OF THE HDDR PROCESS IN $SmCo_5$ ALLOY

Phase composition of $SmCo_5$-based alloy after recombination

Conventional HDDR,
***HD*: 0.5 MPa, 640 °C, 5 h**



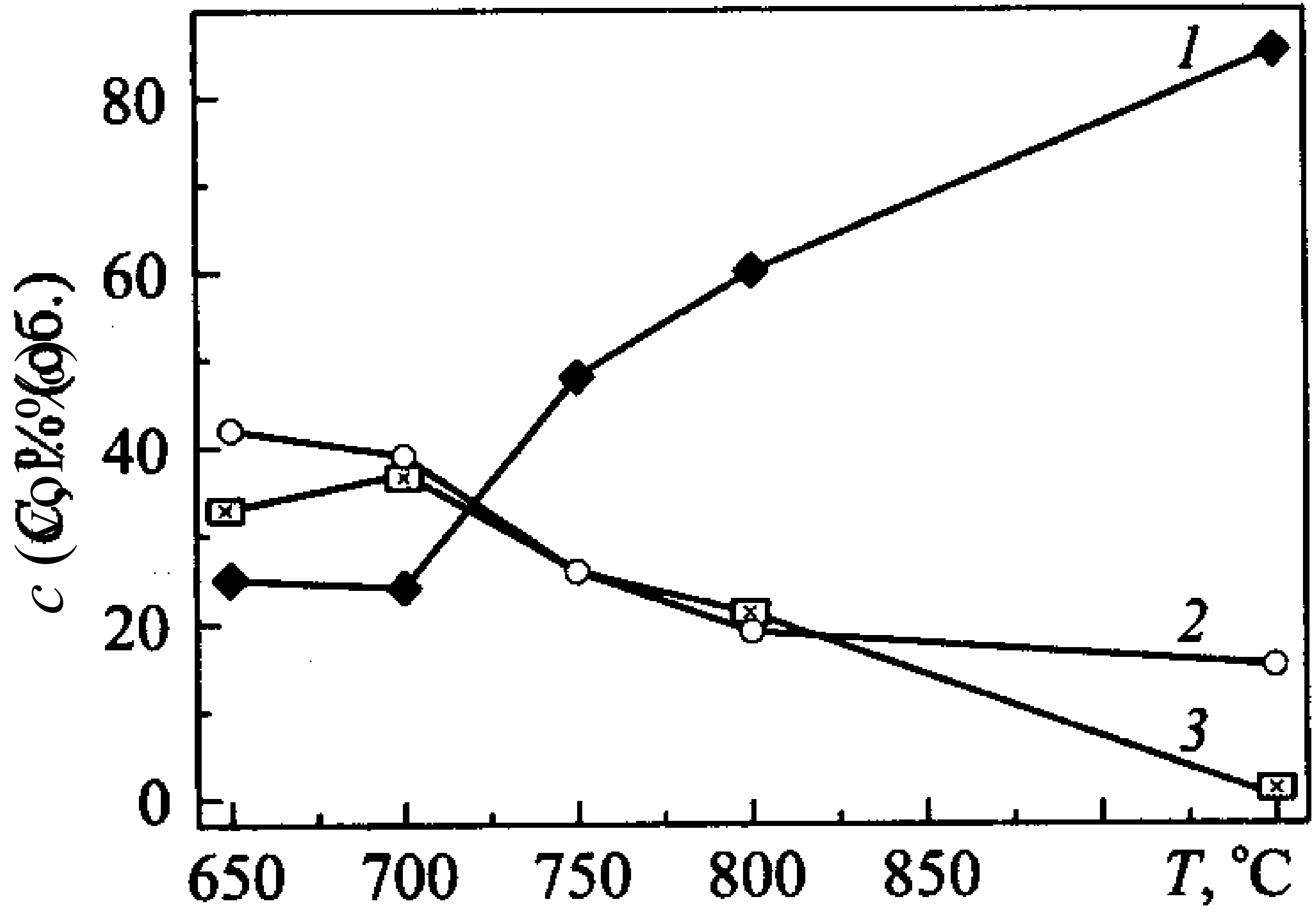
I.I. Bulyk and A.M. Trostianchyn, Metallofiz. Noveishie Tekhnol., 38 (2016) 511—519 (in Ukrainian), https://doi.org/10.15407/mfint.38.04.0511.

Preliminary Results of Sintering $SmCo_5$ Magnetic Materials Using the HDDR Process

TERMS OF THE HDDR PROCESS IN $SmCo_5$ ALLOY

Phase composition of $SmCo_5$-based alloy after recombination

***Solid HDDR, HD*: 0.4 MPa, 650°C, 2 h**



$SmCo_5$

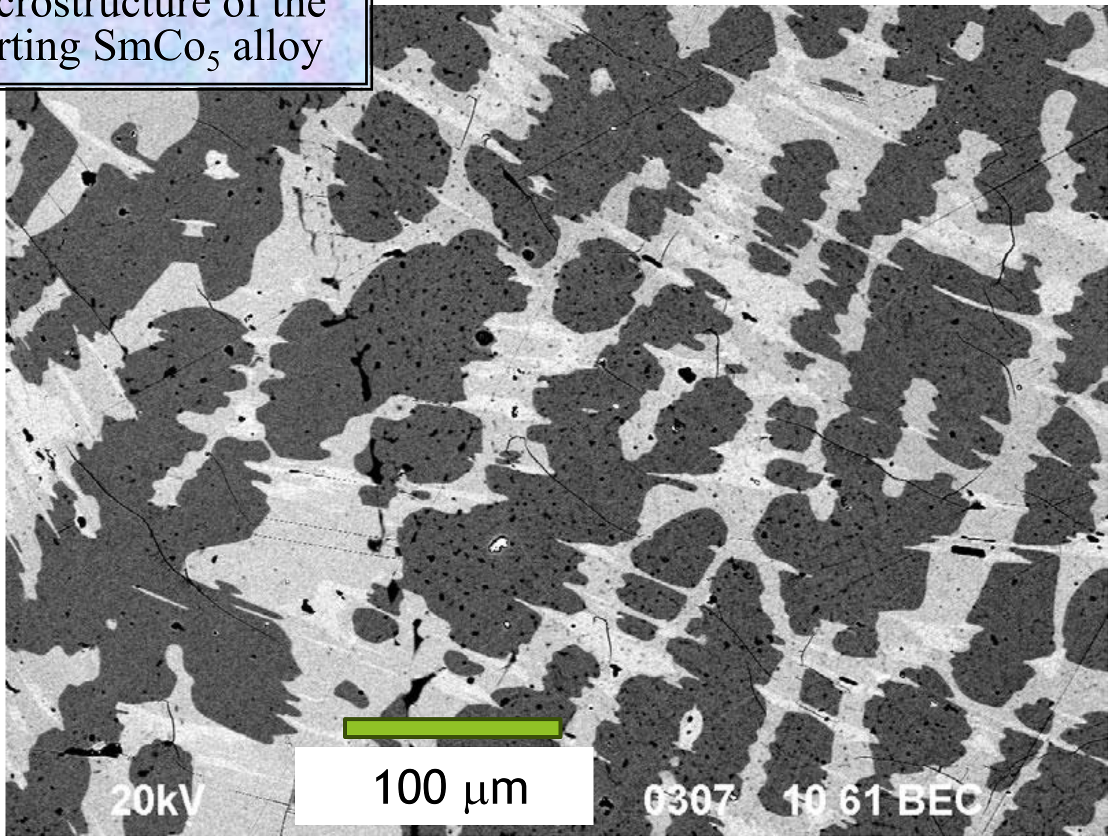
Sm_2Co_7

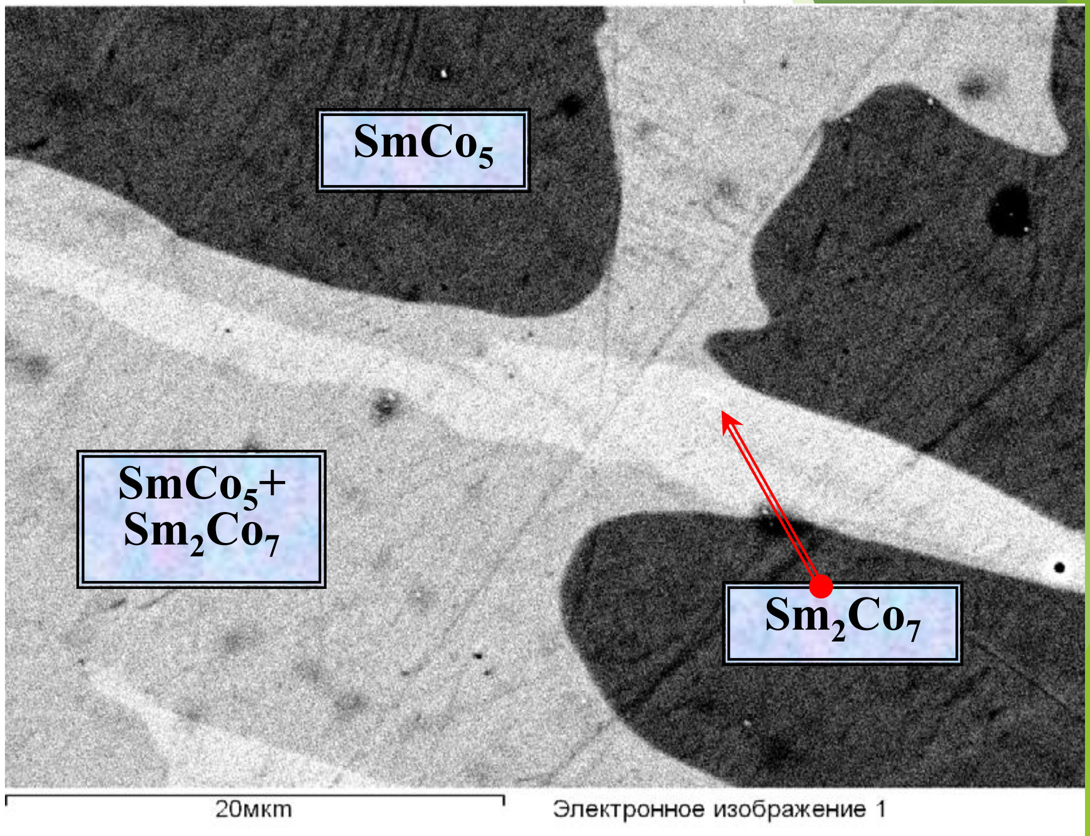
Sm_2Co_{17}

I.I. Bulyk, et al., Powder Metall. Met. Cer
http://link.springer.com/article/10.1007/s11106-014-9556-8.

FEATURES OF THE MICROSTRUCTURE OF THE $SmCo_5$ ALLOY DURING HDDR

Microstructure of the starting $SmCo_5$ alloy



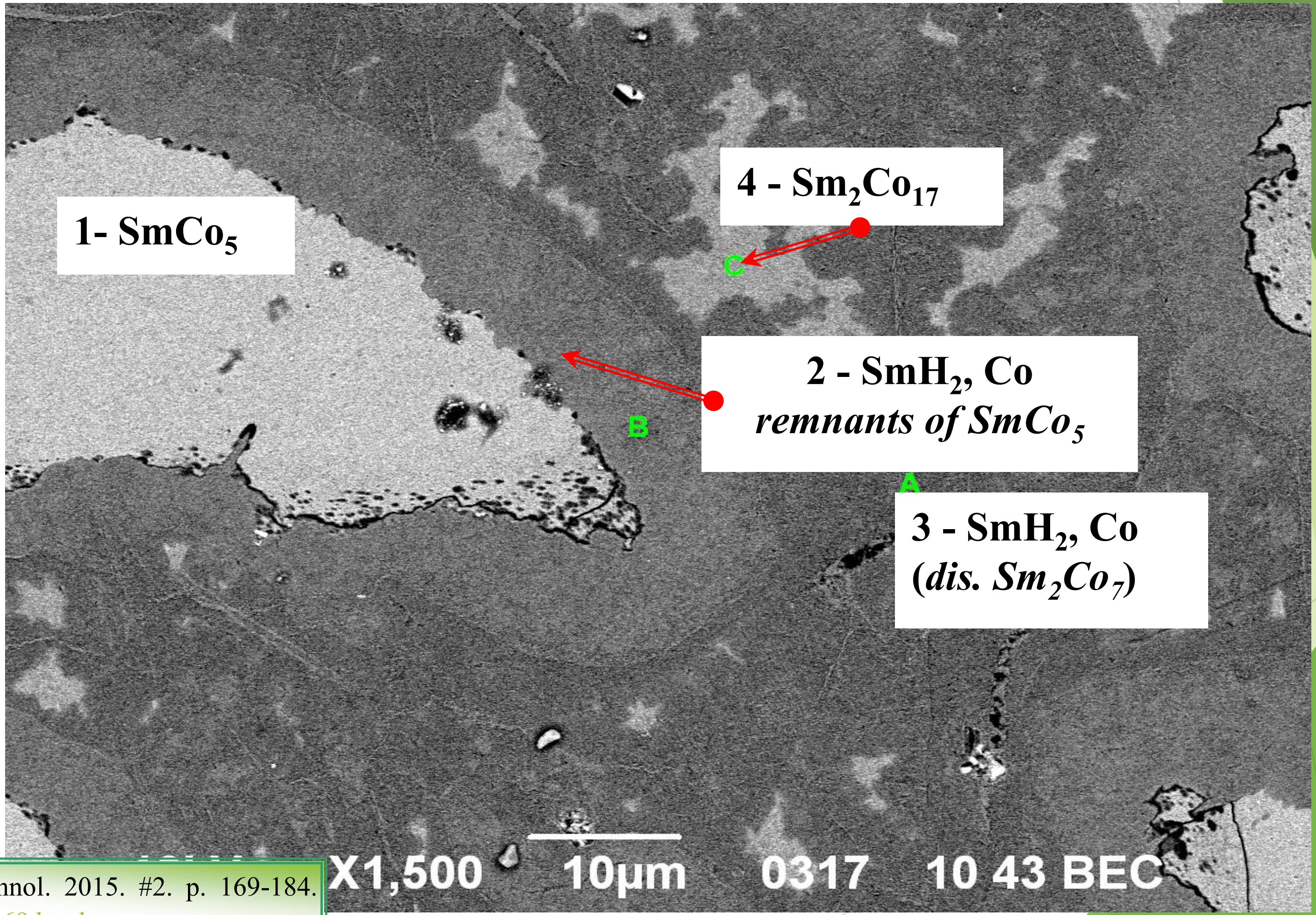


I.I. Bulyk, et al, Metallofiz. Noveishie Tekhnol. 2015. #2. p. 169-184. http://mfint.imp.kiev.ua/ua/abstract/v37/i02/0169.html.

FEATURES OF THE MICROSTRUCTURE OF THE $SmCo_5$ ALLOY DURING HDDR

$SmCo_5$ ALLOY AFTER solid HD
partially disproportionated

solid-HD: 0.5 MPa, 640 °C, 5 h.

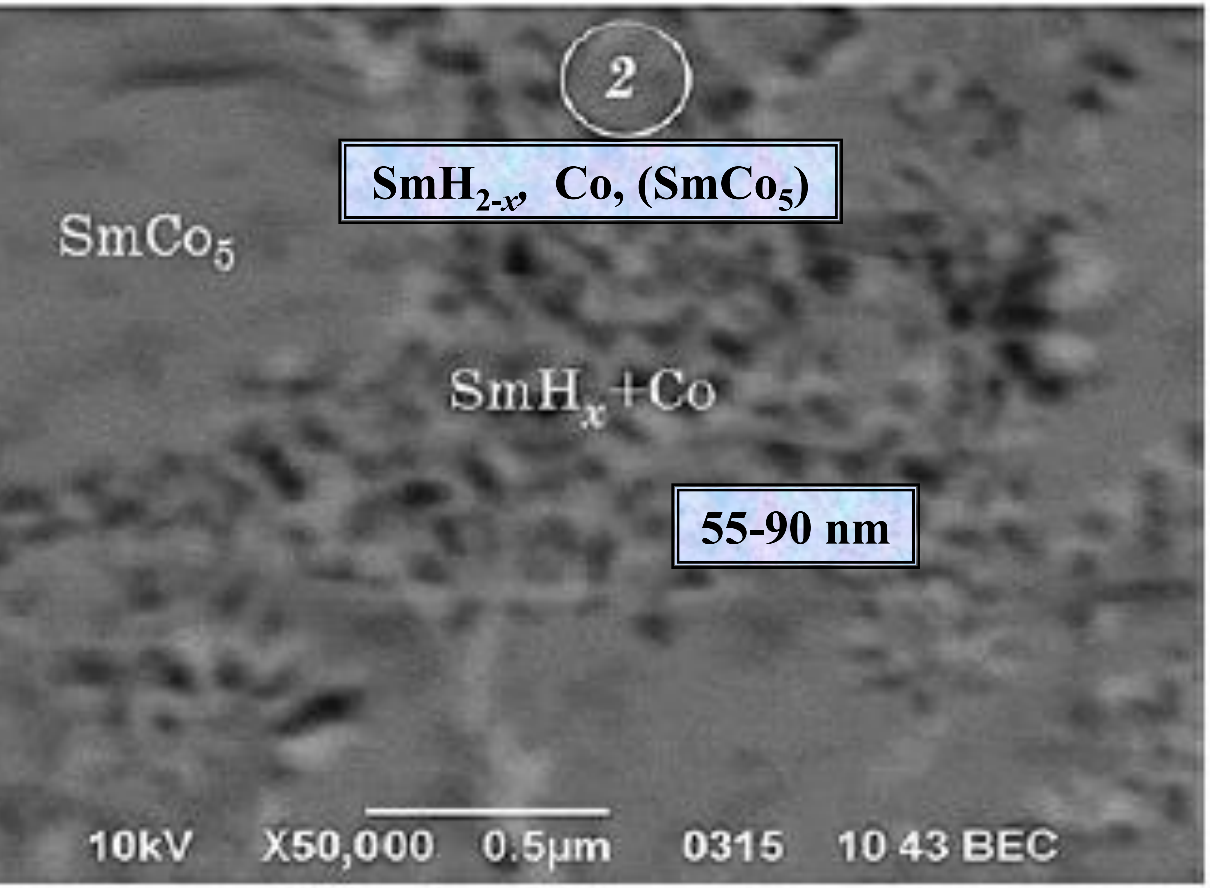


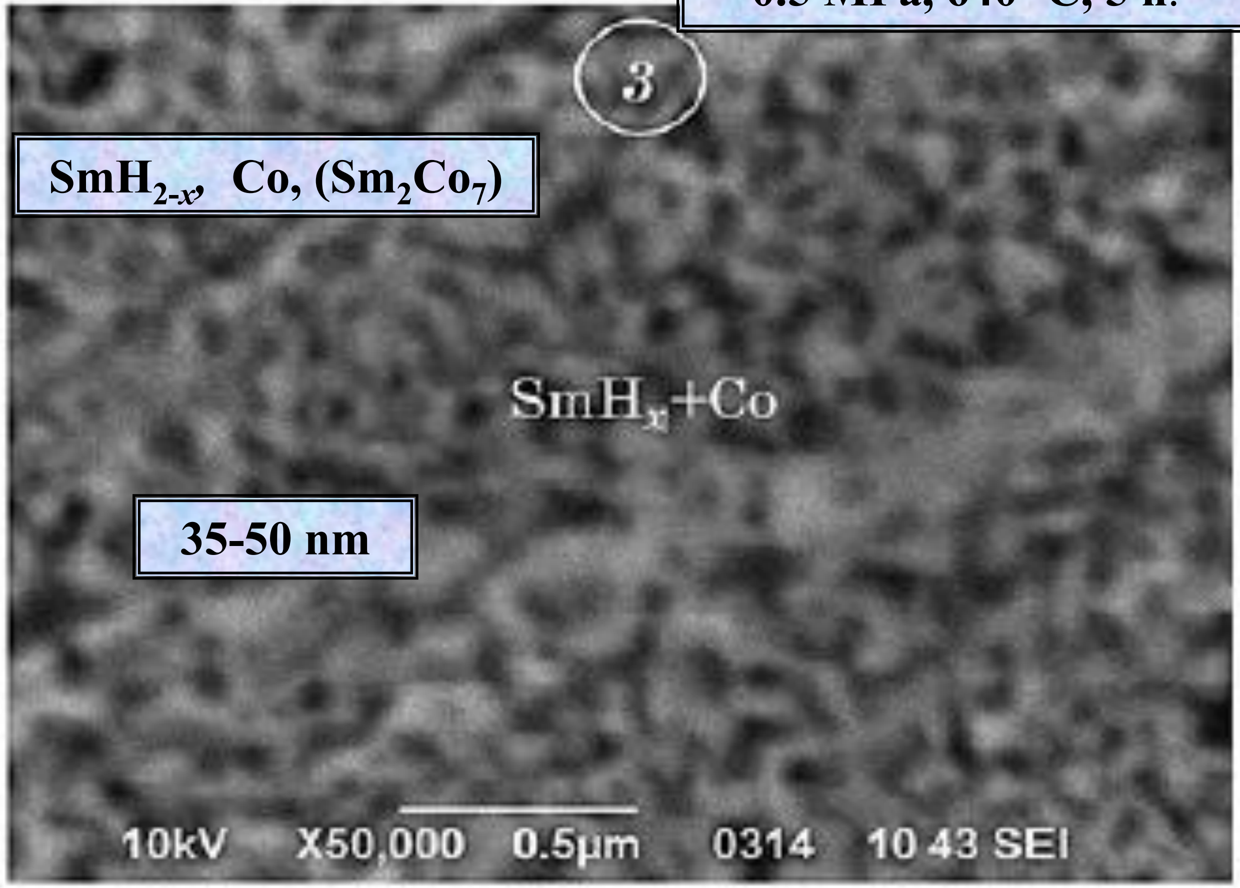
I.I. Bulyk, et all Metallofiz. Noveishie Tekhnol. 2015. #2. p. 169-184. http://mfint.imp.kiev.ua/ua/abstract/v37/i02/0169.html.

FEATURES OF THE MICROSTRUCTURE OF THE $SmCo_5$ ALLOY DURING HDDR

$SmCo_5$ ALLOY AFTER solid HD partially disproportionated

solid-HD:
0.5 MPa, 640 °C, 5 h.

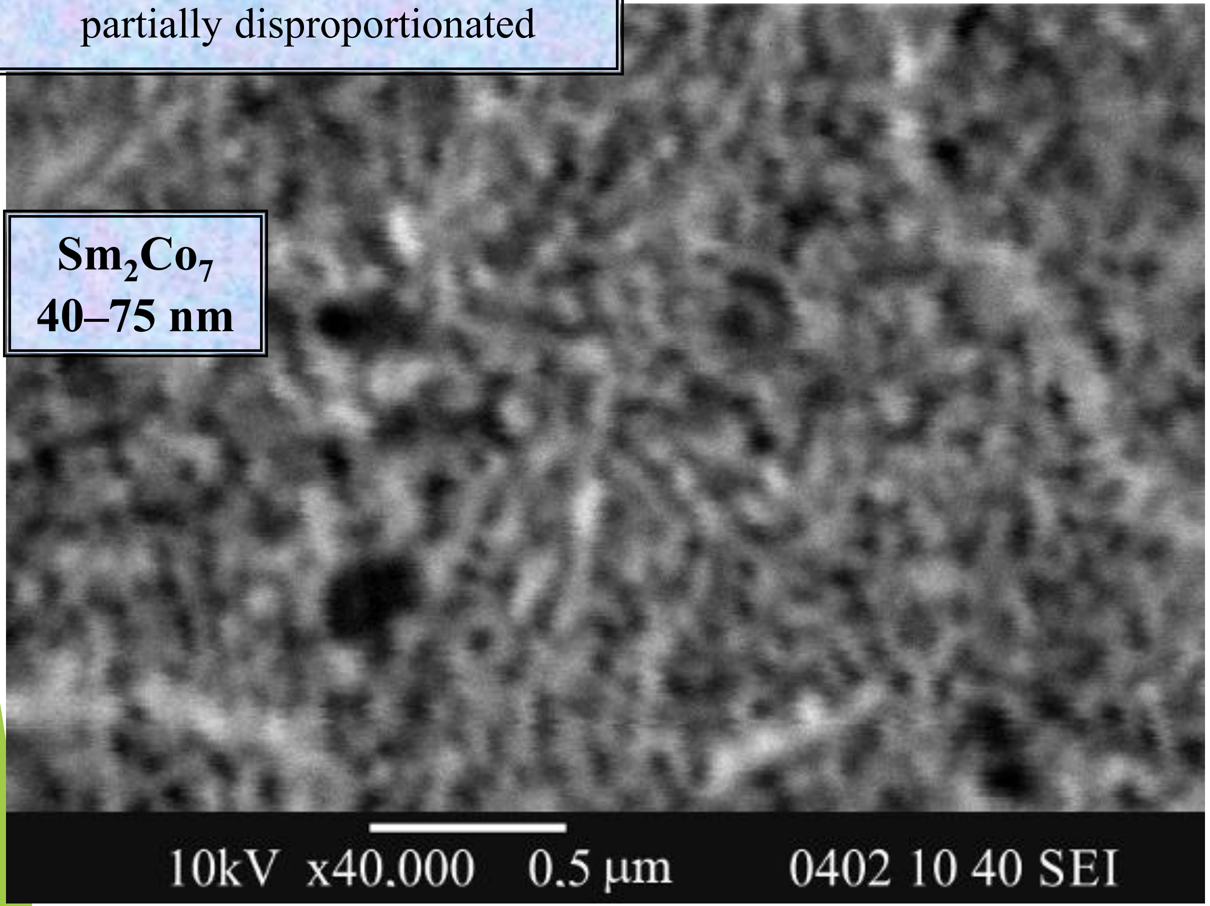




I.I. Bulyk, et all, Metallofiz. Noveishie Tekhnol. 2015. #2. p. 169-184. http://mfint.imp.kiev.ua/ua/abstract/v37/i02/0169.html.

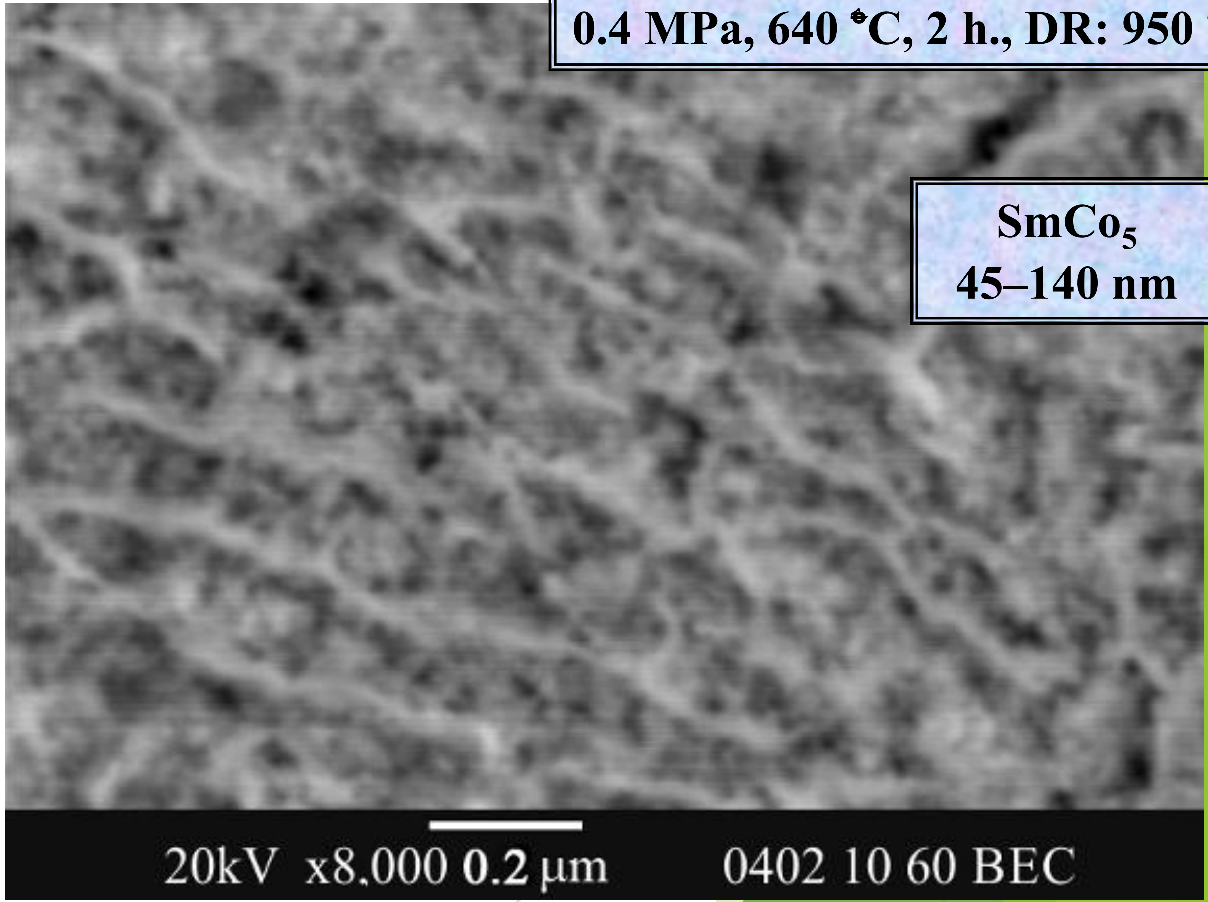
FEATURES OF THE MICROSTRUCTURE OF THE $SmCo_5$ ALLOY DURING HDDR

$SmCo_5$ AFTER solid HDDR
partially disproportionated



Sm_2Co_7
40–75 nm

solid-HD.
0.4 MPa, 640 °C, 2 h., DR: 950 °C



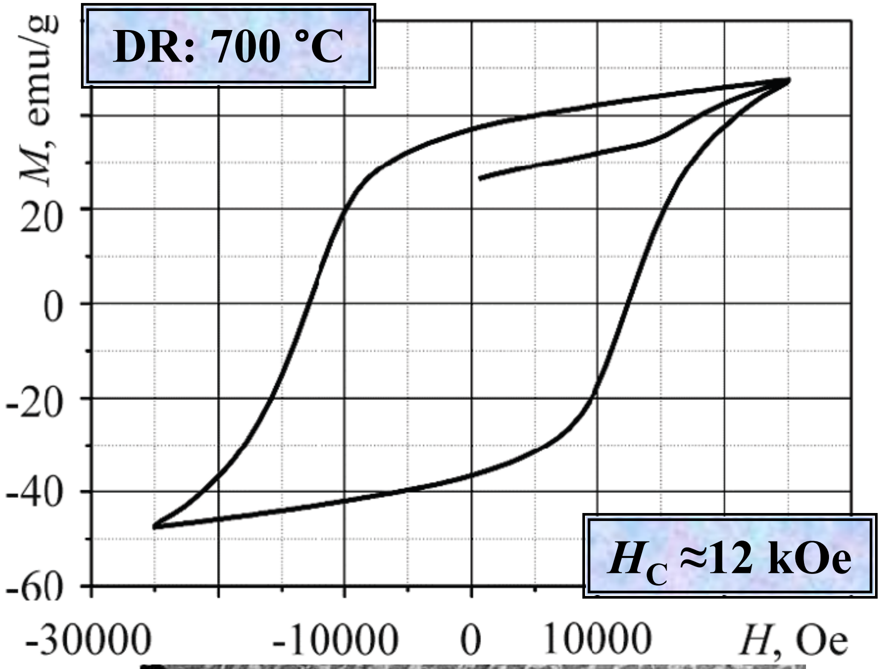
$SmCo_5$
45–140 nm

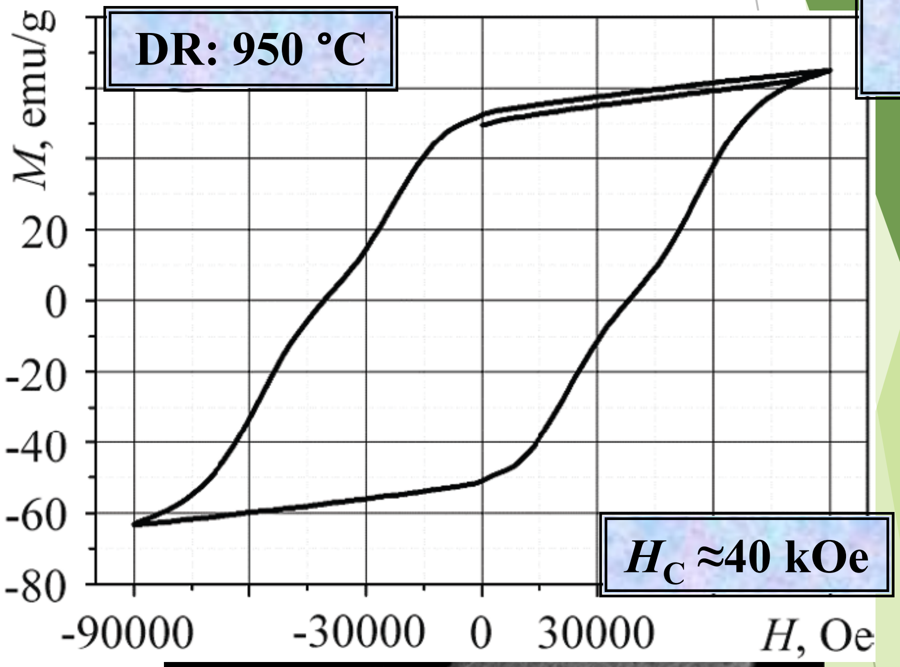
I. I. Bulyk , V. V. Burkhovetskyy. Powder Metall. Met. Ceram. 54 (2016) 614-623. http://link.springer.com/article/10.1007/s11106-016-9755-6.

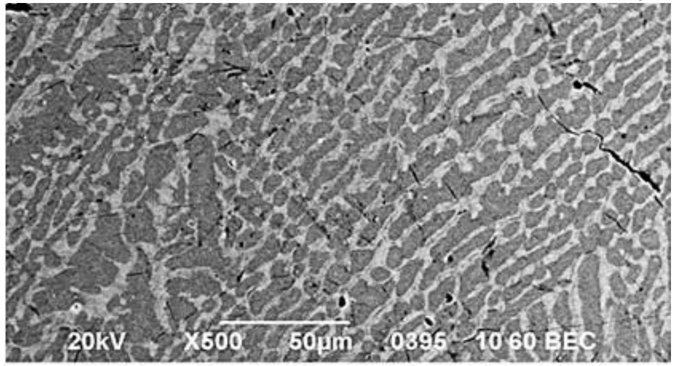
Preliminary Results of Sintering $SmCo_5$ *Magnetic Materials Using the HDDR Process*

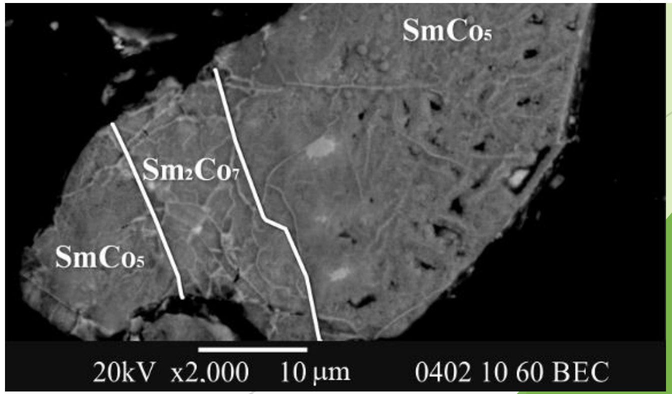
Magnetic properties of the $SmCo_5$ alloy powder after solid HDDR

solid-HD: 0.4 MPa, 640 °C, 2 h.





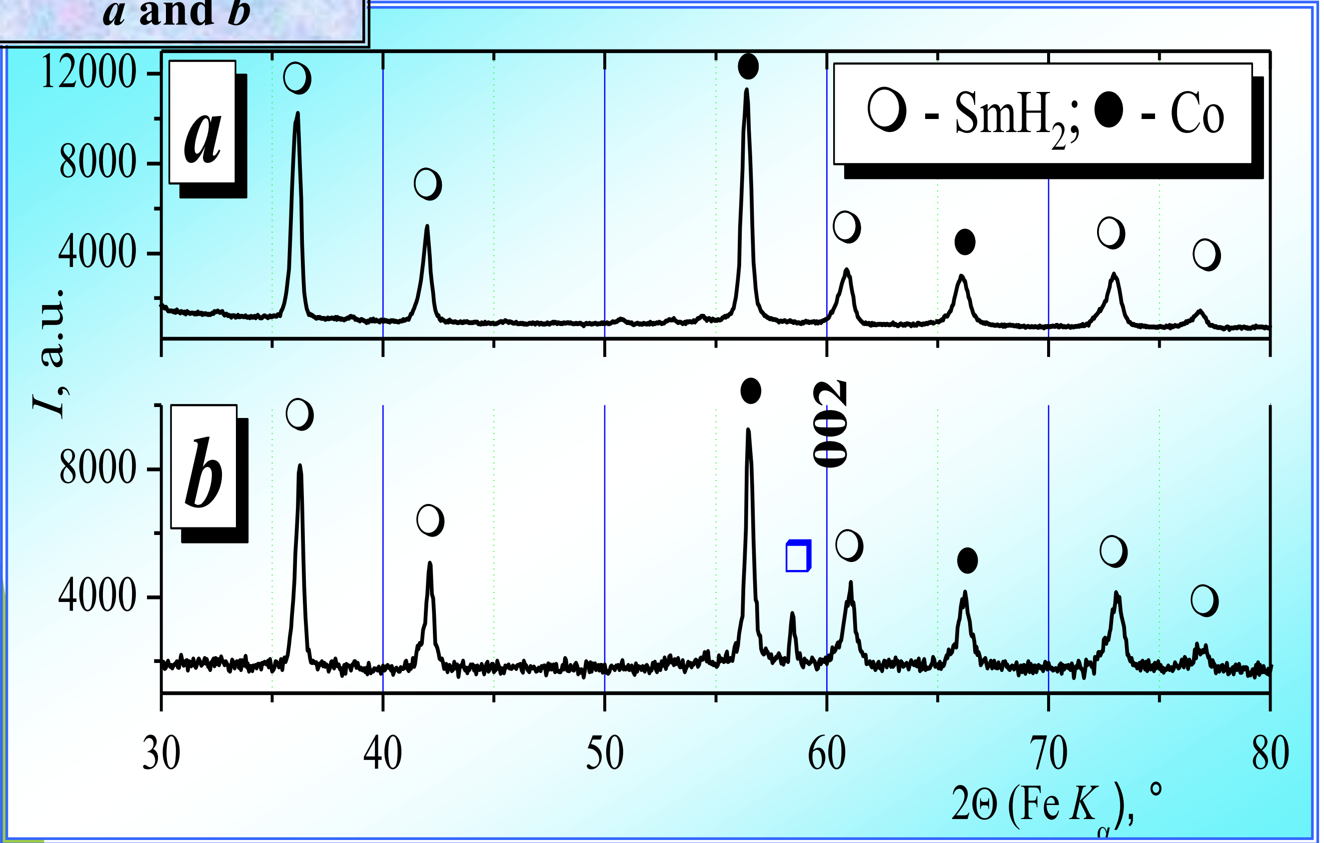




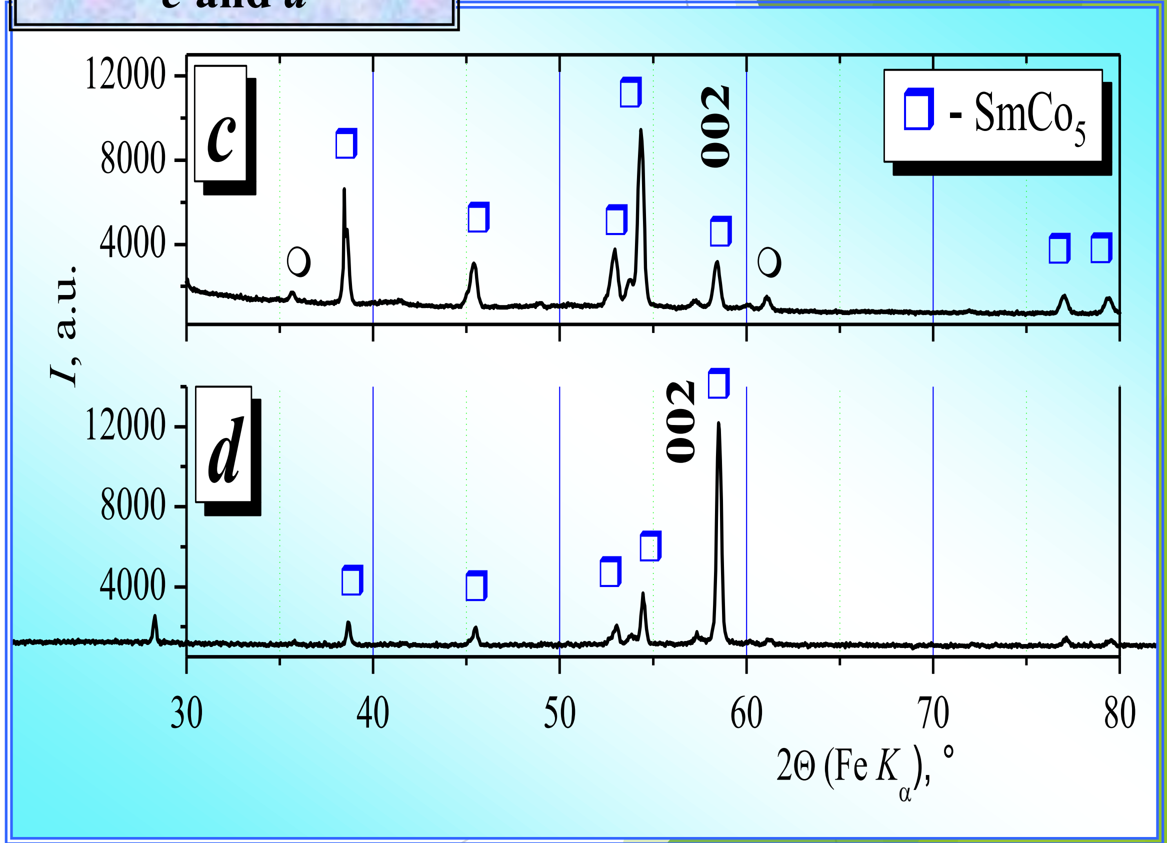
Bulyk I.I., Panasyuk V.V., Materials Science. 48 (2012) 1-11. http://rd.springer.com/journal/11003/48/1.

TEXTURE MEMORY MECHANISM IN Sm-Co MATERIALS AFTER HDDR

$SmCo_5$ after HD: *a* and *b*



$SmCo_5$ after HDDR: *c* and *d*



XRD patterns measured for:
***a* and *c* – random powders; *b* and *d* – powders oriented in magnetic field.**

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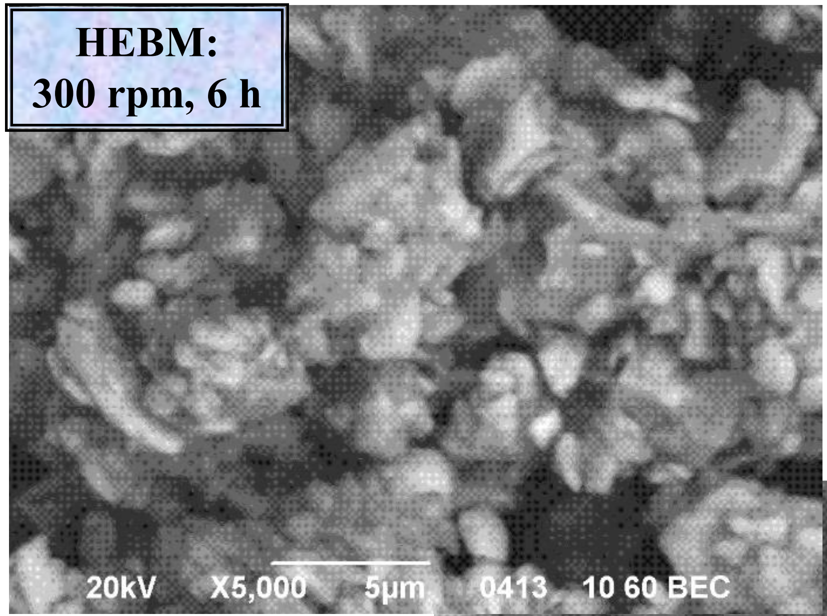
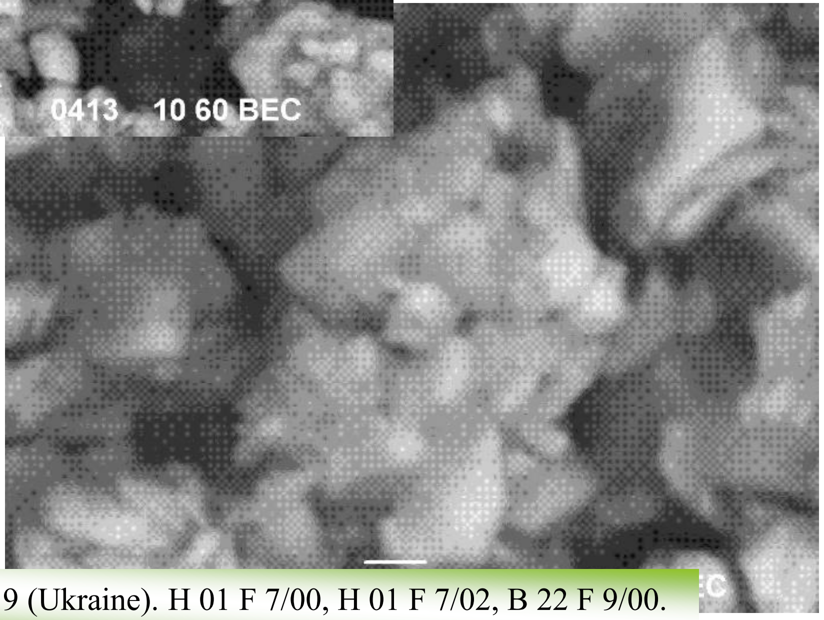
*Preliminary Results of Sintering **$SmCo_5$** Magnetic Materials Using the HDDR Process*

Morphology of $Sm(Co,Zr)_5$ powders after HEBM

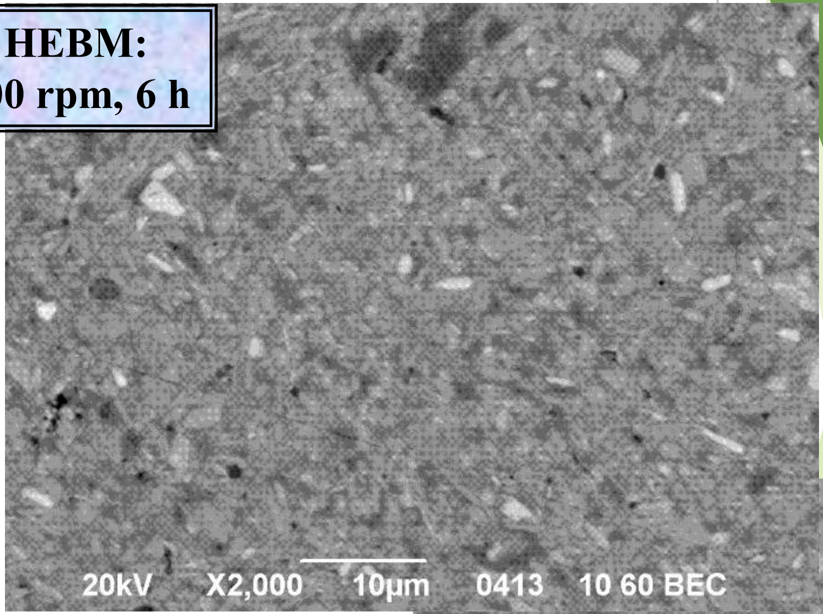
HEBM:
300 rpm, 6 h

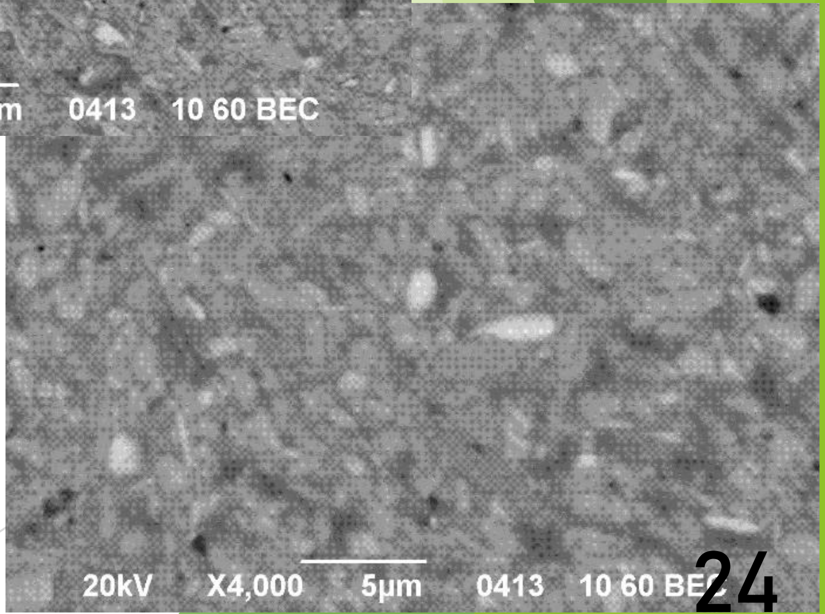




Microstructure of $Sm(Co,Zr)_5$ materials sintered by HDDR

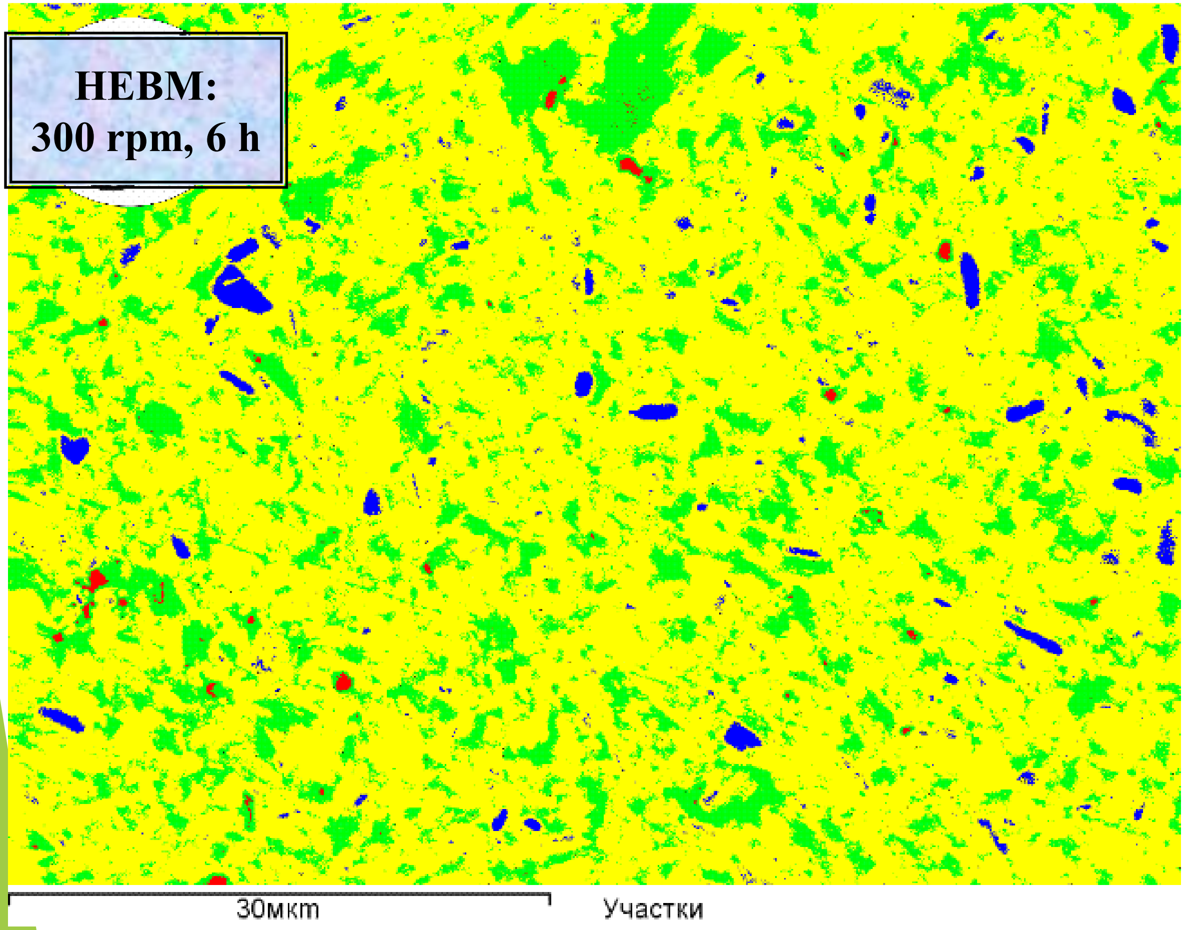
HEBM:
300 rpm, 6 h

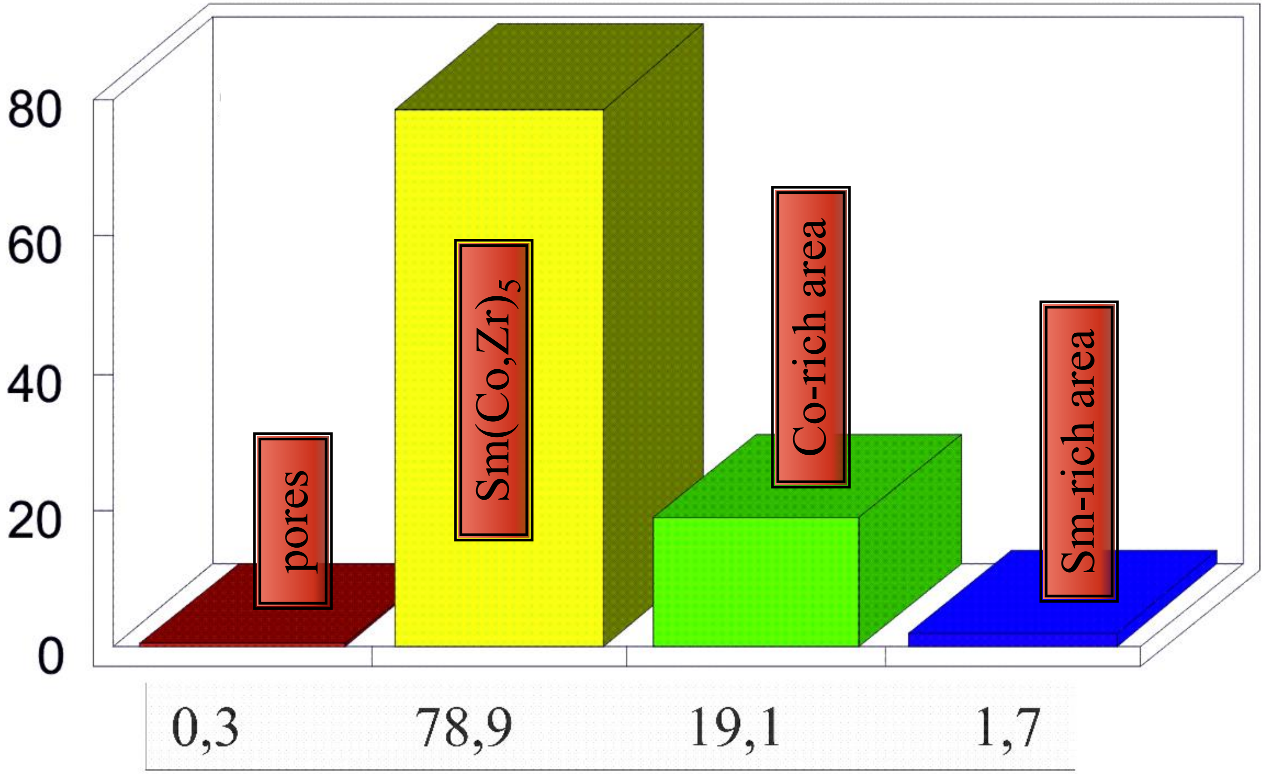




I.I. Bulyk, et al., Patent 117119 (Ukraine). H 01 F 7/00, H 01 F 7/02, B 22 F 9/00.

Morphology and Ratio of microstructure components of $Sm(Co,Zr)_5$ alloy sintered by HDDR

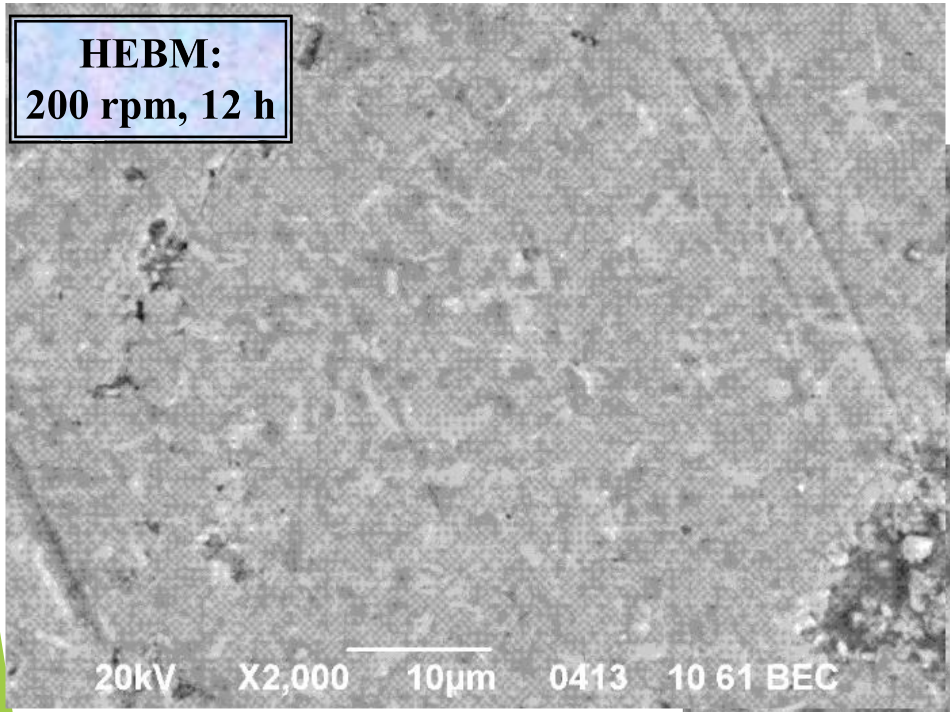


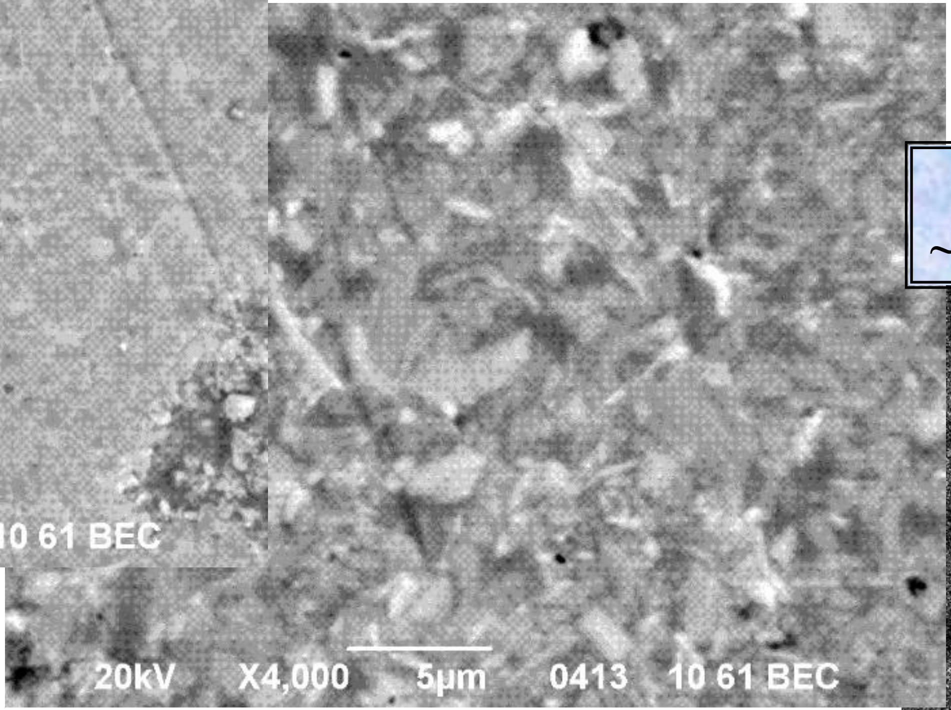


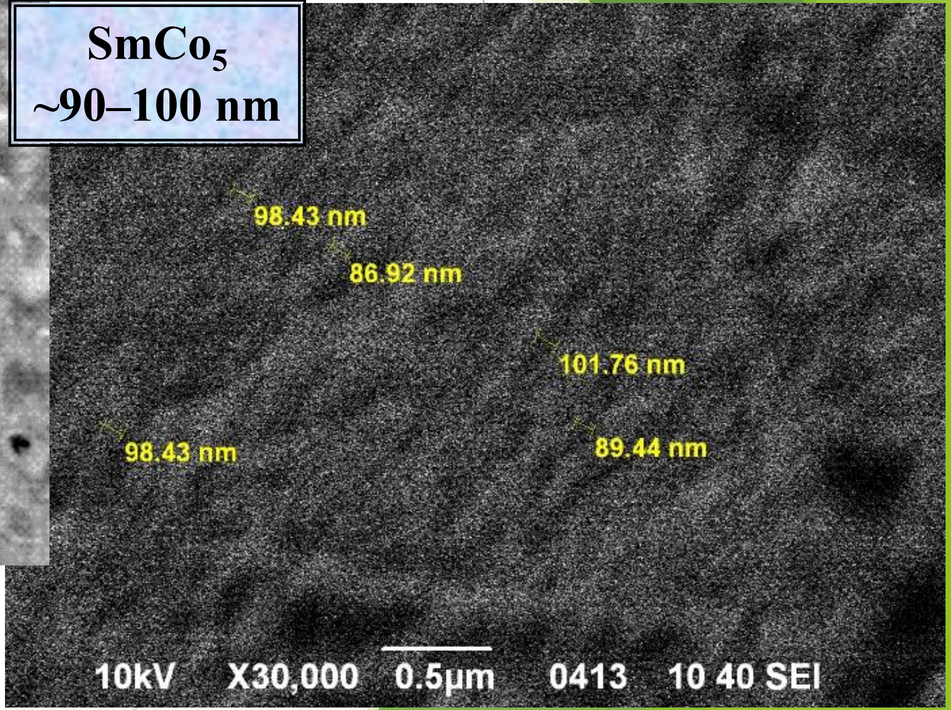
I.I. Bulyk, et al., Patent 117119 (Ukraine). H 01 F 7/00, H 01 F 7/02, B 22 F 9/00.

*Preliminary Results of Sintering **$SmCo_5$** Magnetic Materials Using the HDDR Process*

Microstructure of $Sm(Co,V)_5$ alloy sintered by HDDR







I.I. Bulyk, et al., Patent 117119 (Ukraine). H 01 F 7/00, H 01 F 7/02, B 22 F 9/00.

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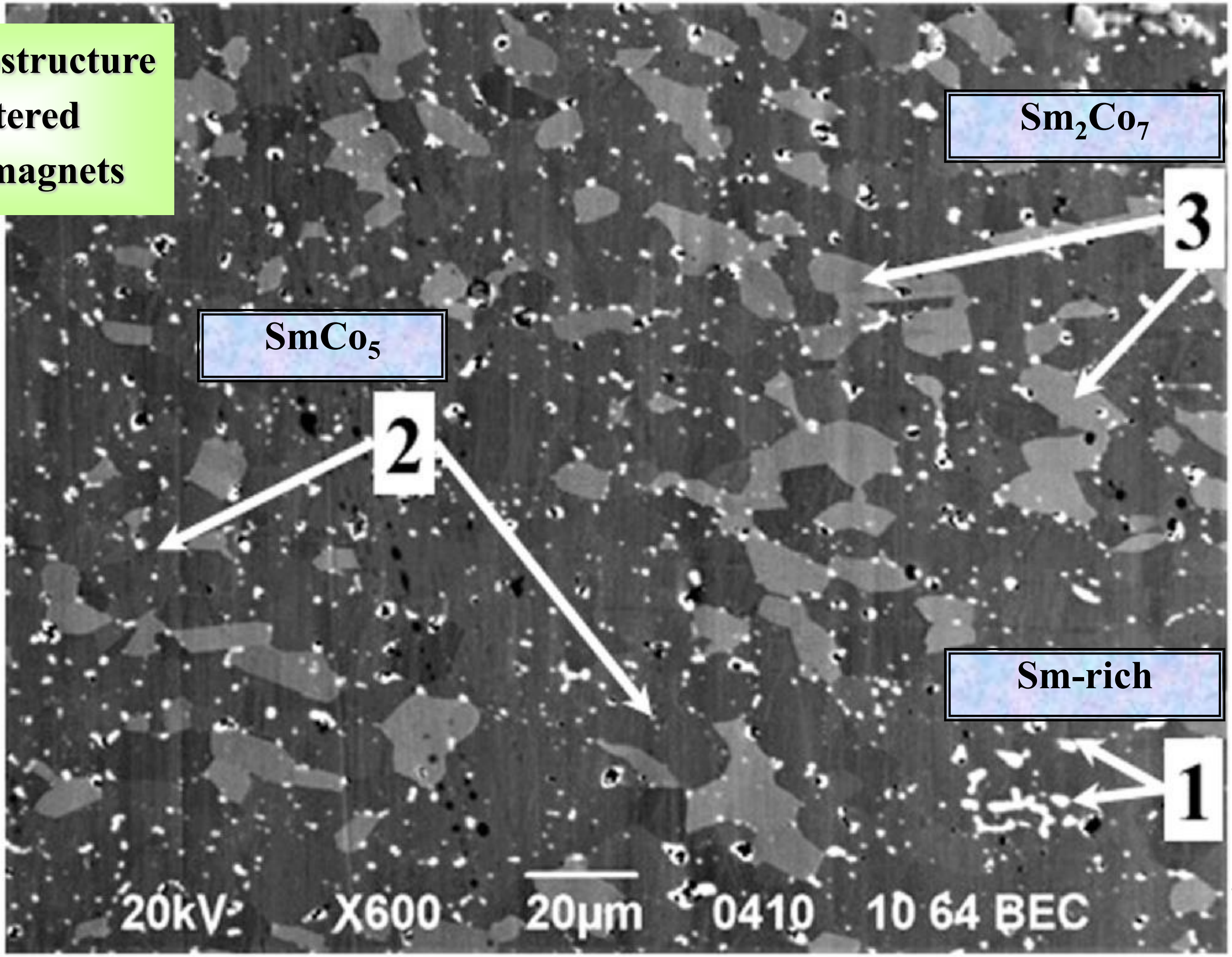
POST-SINTERING TREATMENT OF $SmCo_5$ ALLOY BY HDDR

REPM 2025 NIMS TSUKUBA

The microstructure of sintered $SmCo_5$ magnets



POST-SINTERING TREATMENT:

solid HD,
temperature of **650 °C**,
without holding at this temperature,
hydrogen pressure – up to **1.1 Mpa**;

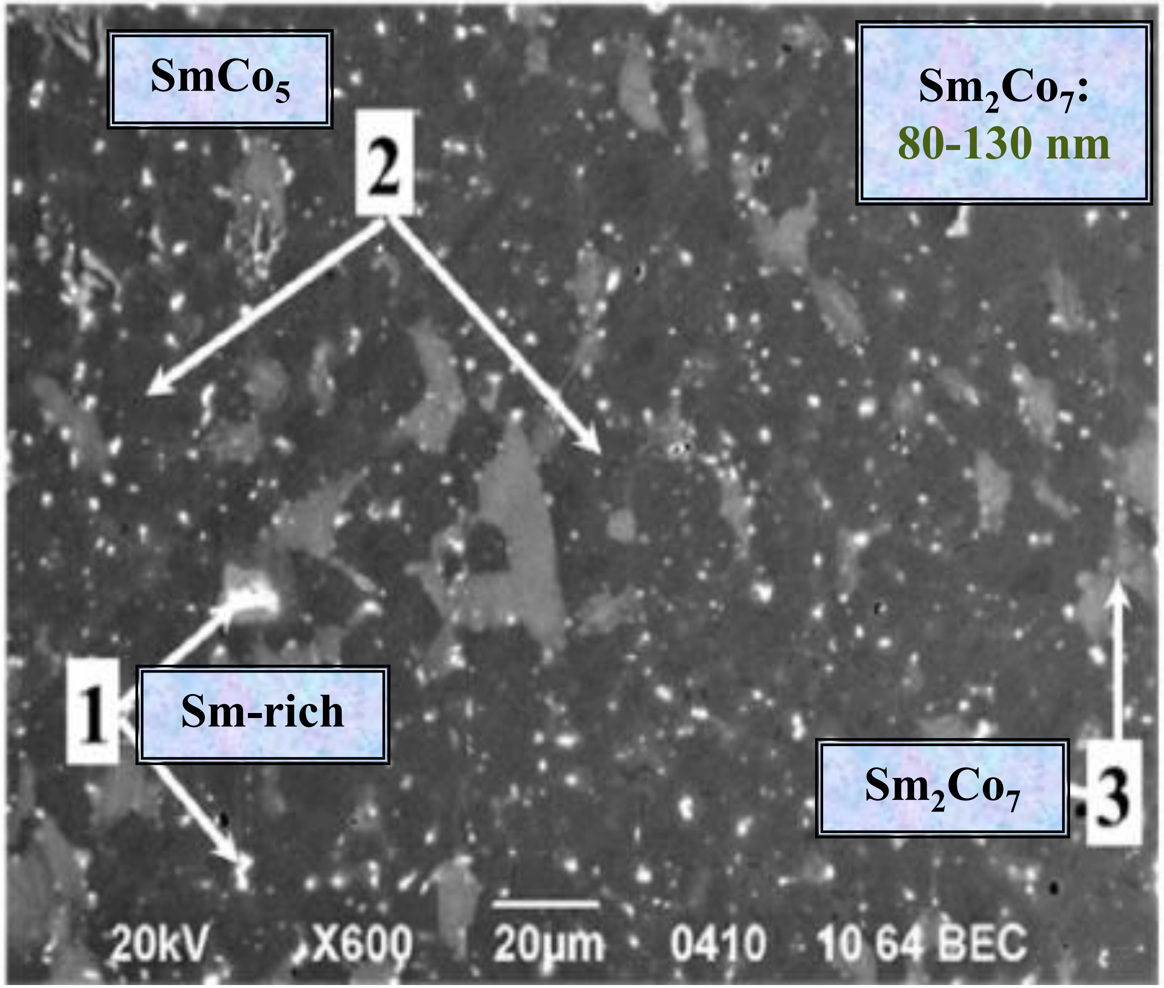
DR: vacuum
1 – 850 °C;
2 – 850 °C, 1 h;
3 – 950 °C

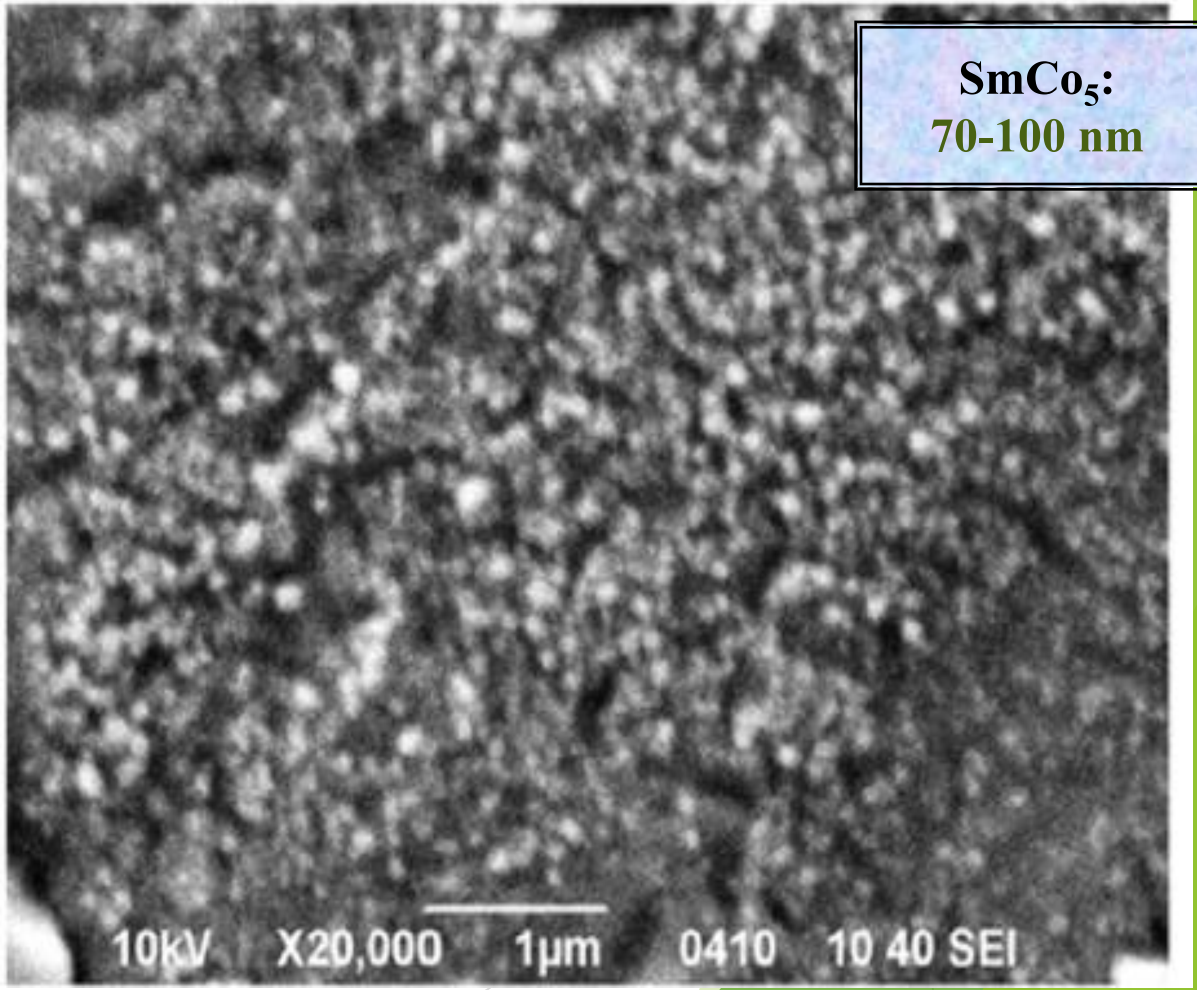
I.I. Bulyk, et al., J. Alloys Comp. 866 (2021) 158272. https://doi.org/10.1016/j.jallcom.2020.158272.

POST-SINTERING TREATMENT OF $SmCo_5$ ALLOY BY HDDR

Microstructure sintered $SmCo_5$ magnets after HDDR

DR: 850 °C

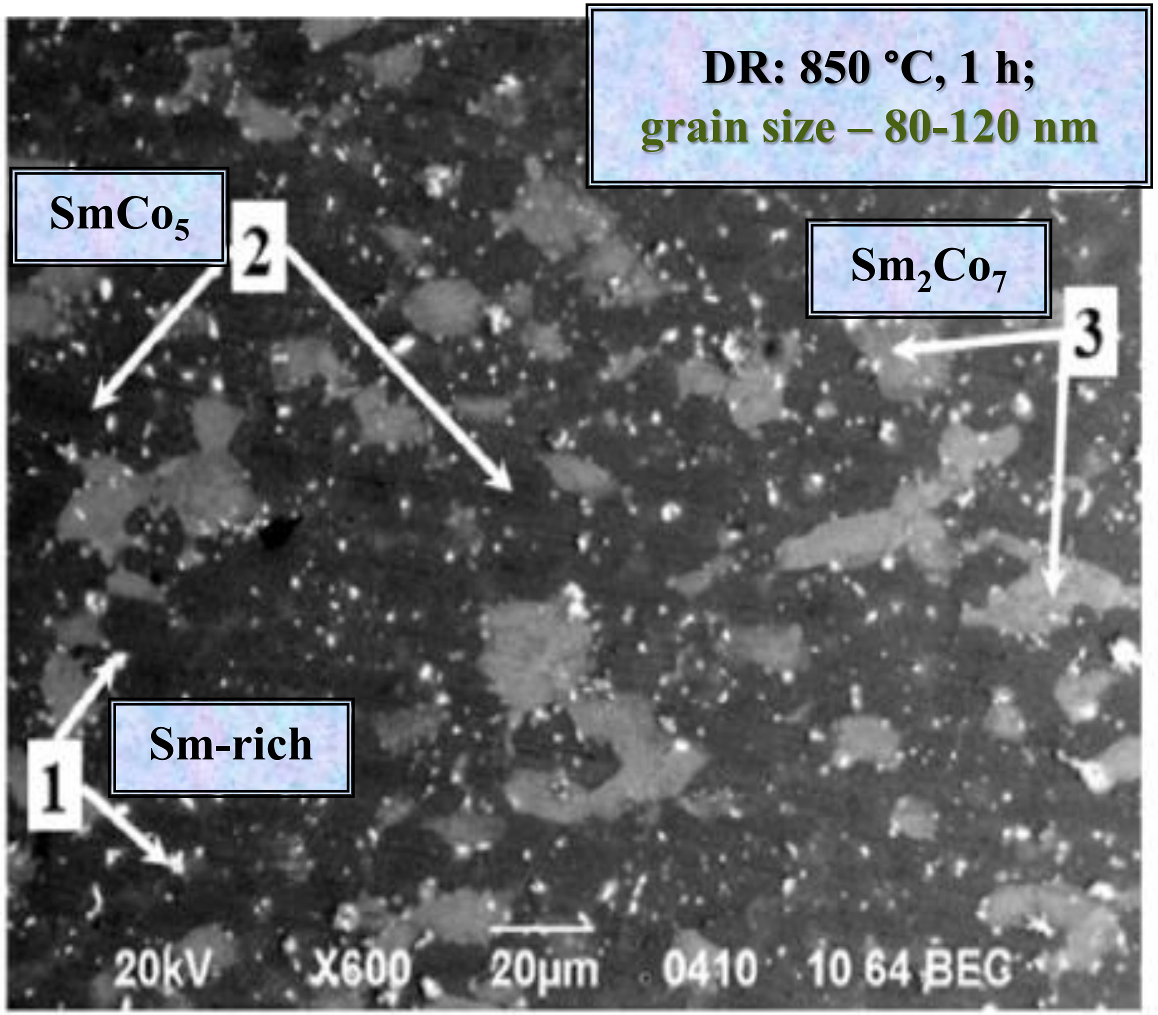


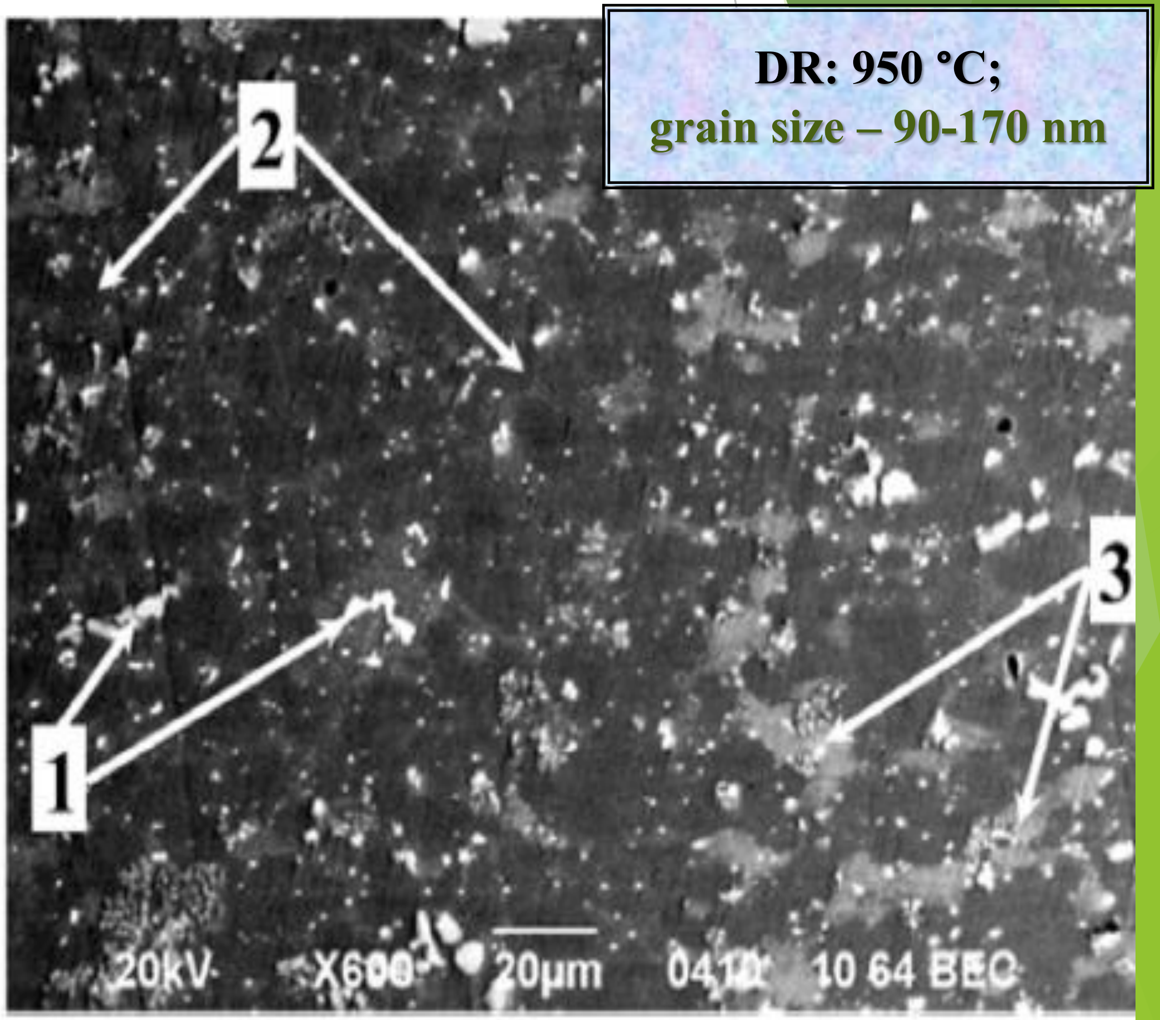


I.I. Bulyk, et al., J. Alloys Comp. 866 (2021) 158272. https://doi.org/10.1016/j.jallcom.2020.158272.

POST-SINTERING TREATMENT OF $SmCo_5$ ALLOY BY HDDR

Microstructure sintered $SmCo_5$ magnets after HDDR

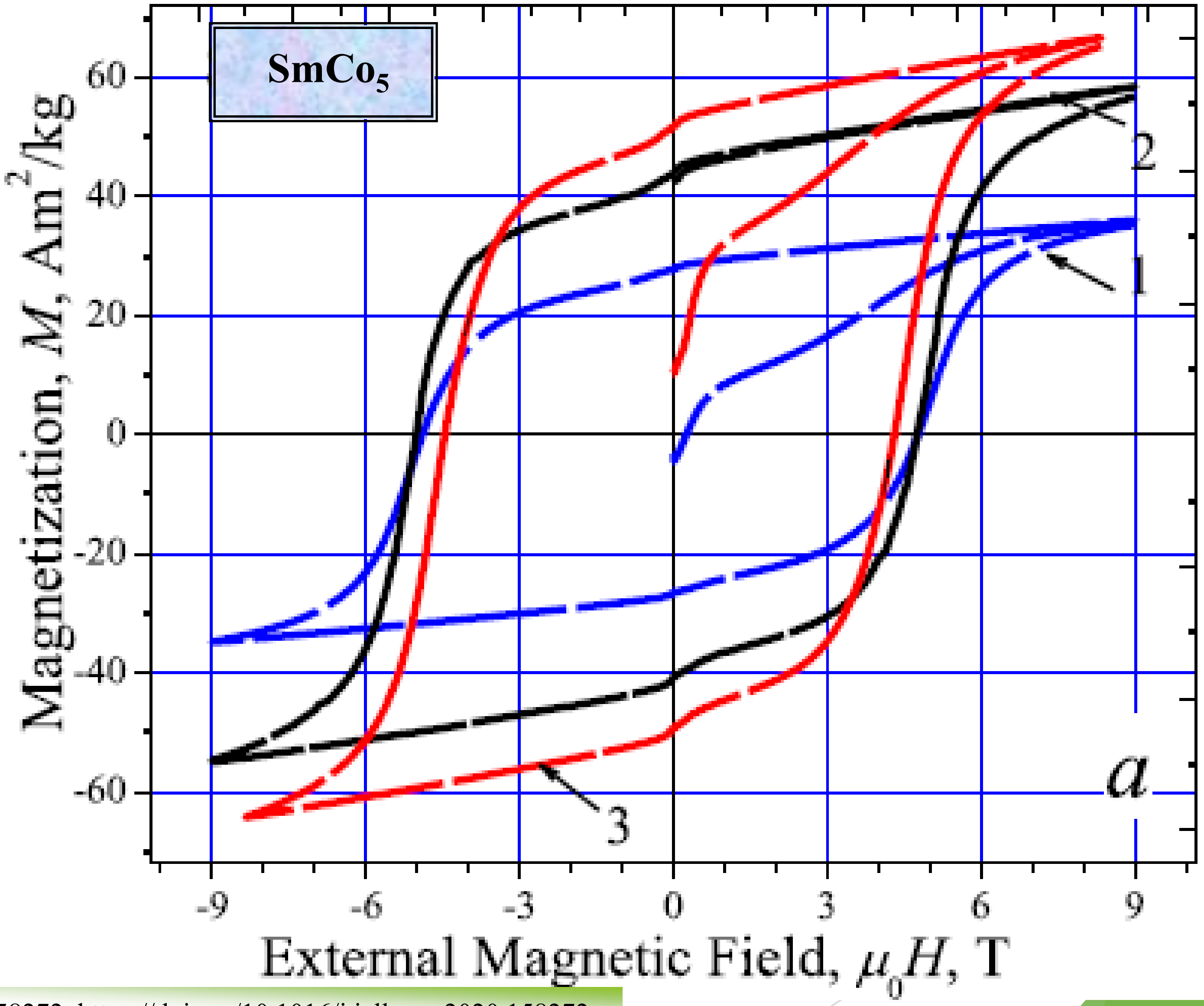




I.I. Bulyk, et al., J. Alloys Comp. 866 (2021) 158272. https://doi.org/10.1016/j.jallcom.2020.158272.

POST-SINTERING TREATMENT OF $SmCo_5$ ALLOY BY HDDR

Hysteresis loops of sintered $SmCo_5$ magnets after HDDR



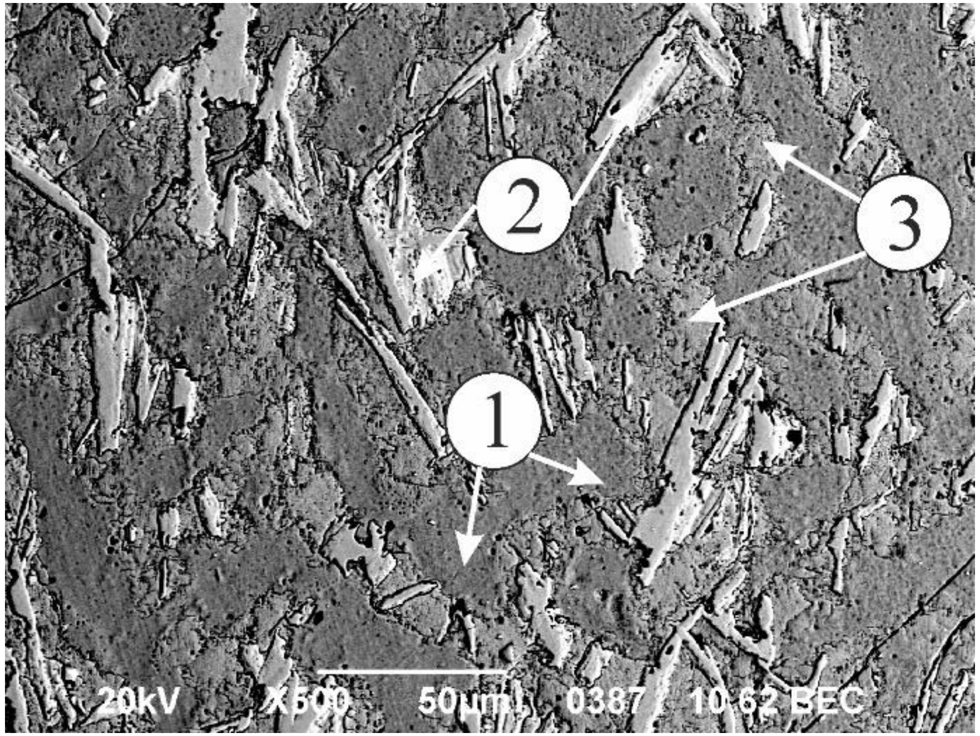
DR:
1 – 850 °C;
2 – 850 °C, 1 h;
3 – 950 °C

$\mu_o H_C \approx 5$ T

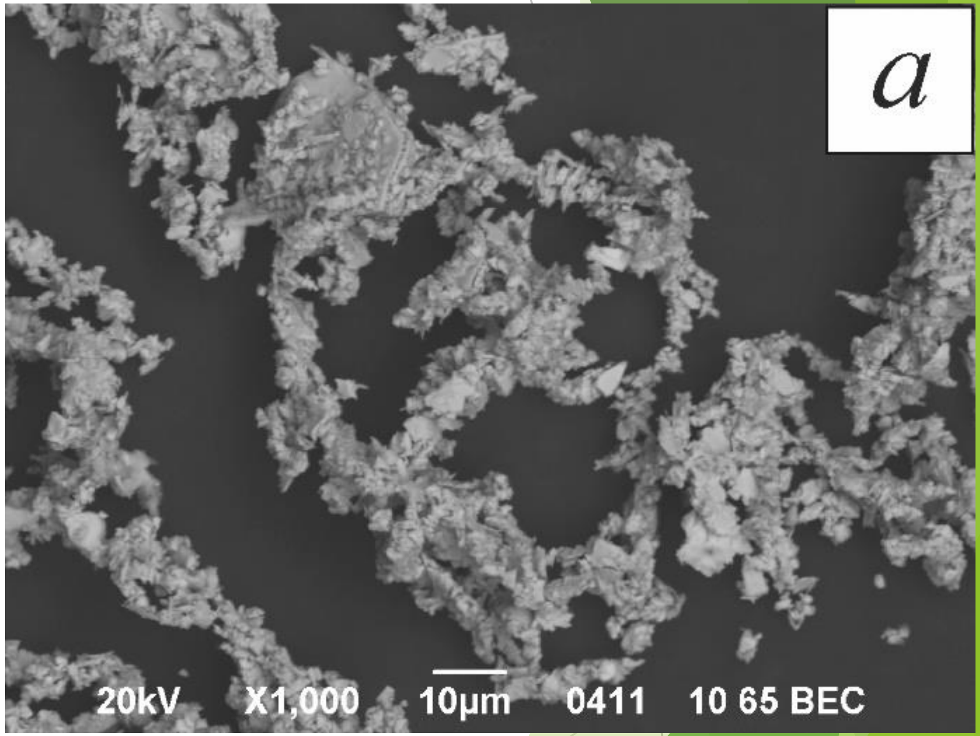
I.I. Bulyk, et al., J. Alloys Comp. 866 (2021) 158272. https://doi.org/10.1016/j.jallcom.2020.158272.

Preliminary Results of Sintering ***Sm_2Co_{17}*** *Magnetic Materials Using the HDDR Process*

Industrial Ferromagnetic $Sm_2(Co,Fe,Zr,Cu)_{17}$ Alloy



Microstructure of the starting alloy:
1) $Sm_2(Co,Fe,Zr,Cu)_{17}$ phase,
2) $Sm(Co,Fe,Zr,Cu)_5$ phase,
3) $Sm_2(Co,Fe,Zr,Cu)_7$ phase



Morphology of the $Sm_2(Co,Fe,Zr,Cu)_{17}$ powder

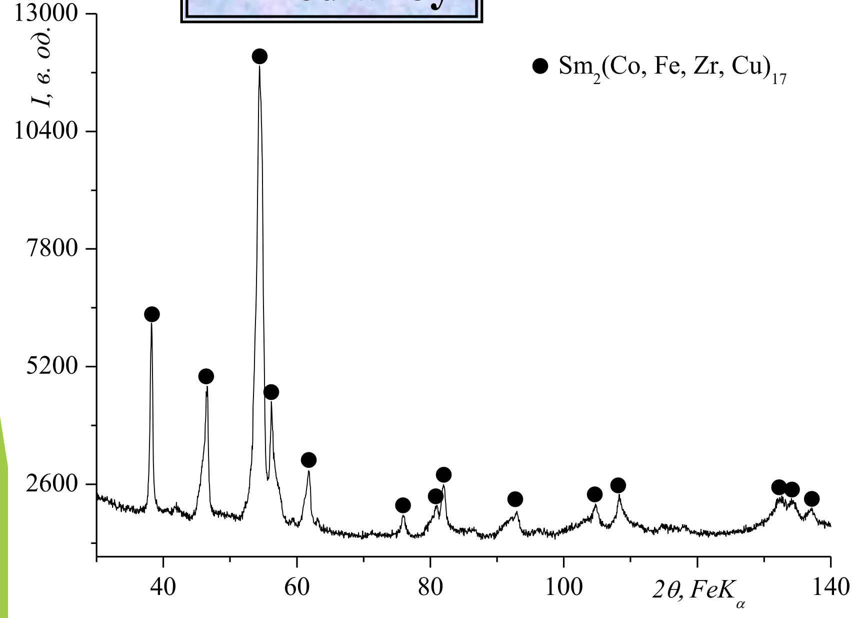
HEBM

Industrial Ferromagnetic $Sm_2(Co,Fe,Zr,Cu)_{17}$ Alloy

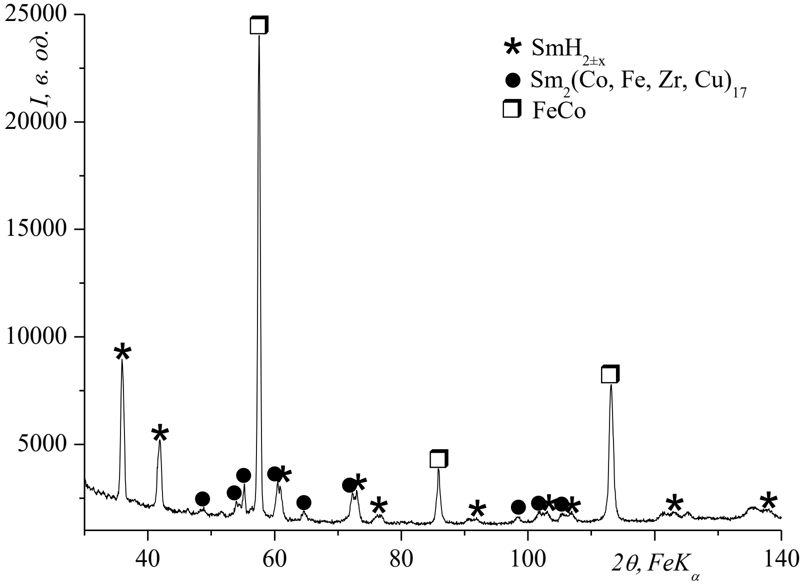
The HD stage proceeded at 700°C and DR at 950°C.
Hydrogen pressure of ≤1.5 MPa

XRD patterns measured for:

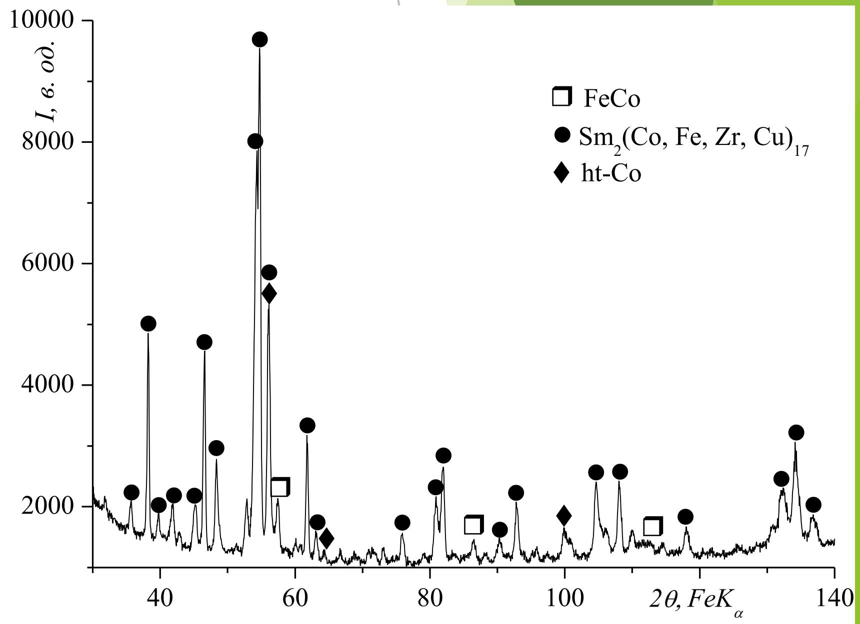
Milled alloy



After HD



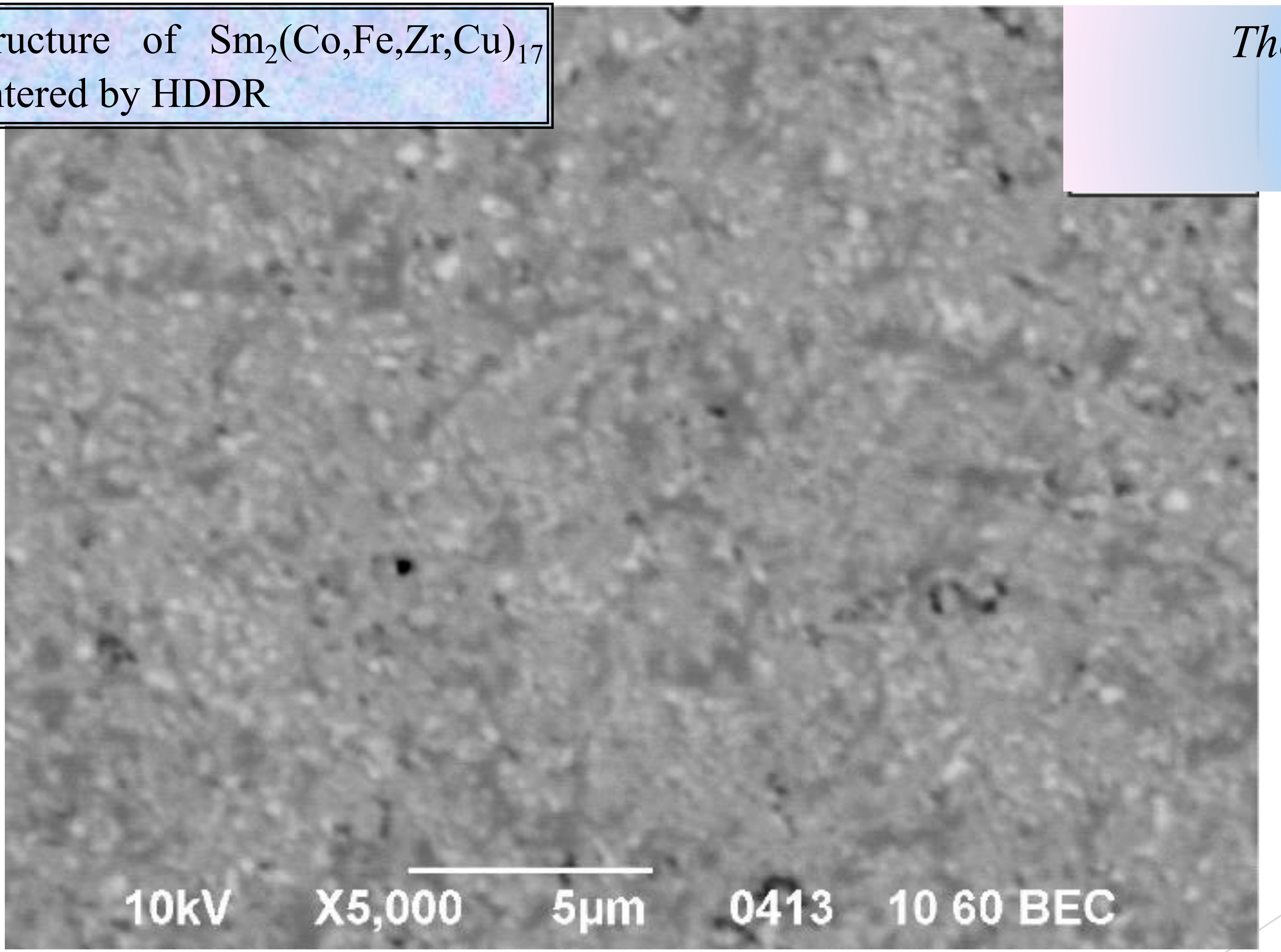
After HDDR



Preliminary Results of Sintering ***Sm_2Co_{17}*** *Magnetic Materials Using the HDDR Process*

Industrial Ferromagnetic $Sm_2(Co,Fe,Zr,Cu)_{17}$ Alloy

Microstructure of $Sm_2(Co,Fe,Zr,Cu)_{17}$ alloy sintered by HDDR



The HD stage: temperature of 700°C, hydrogen pressure of ≤1.5 MPa and DR at 950°C.

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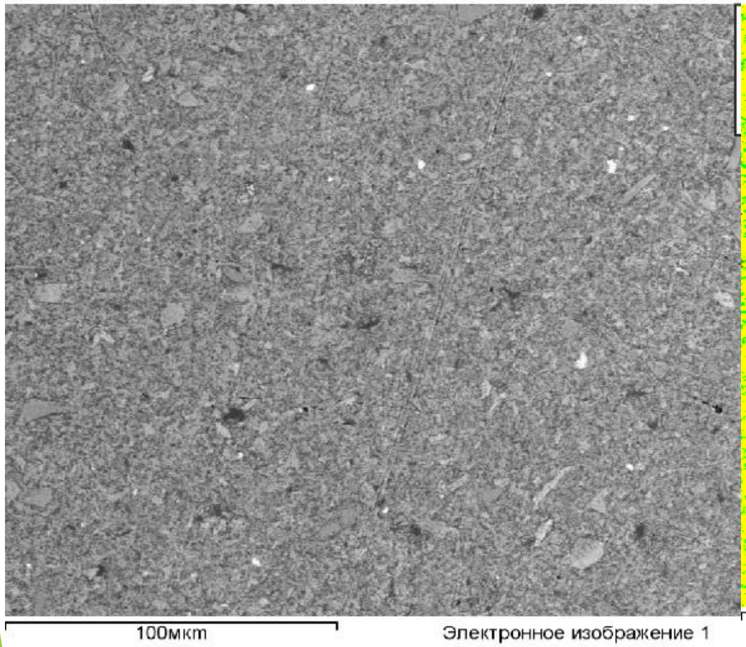
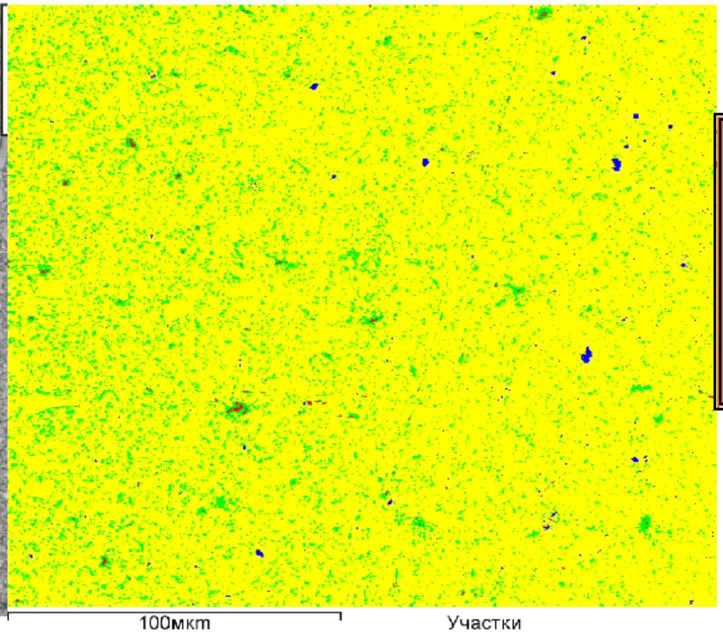
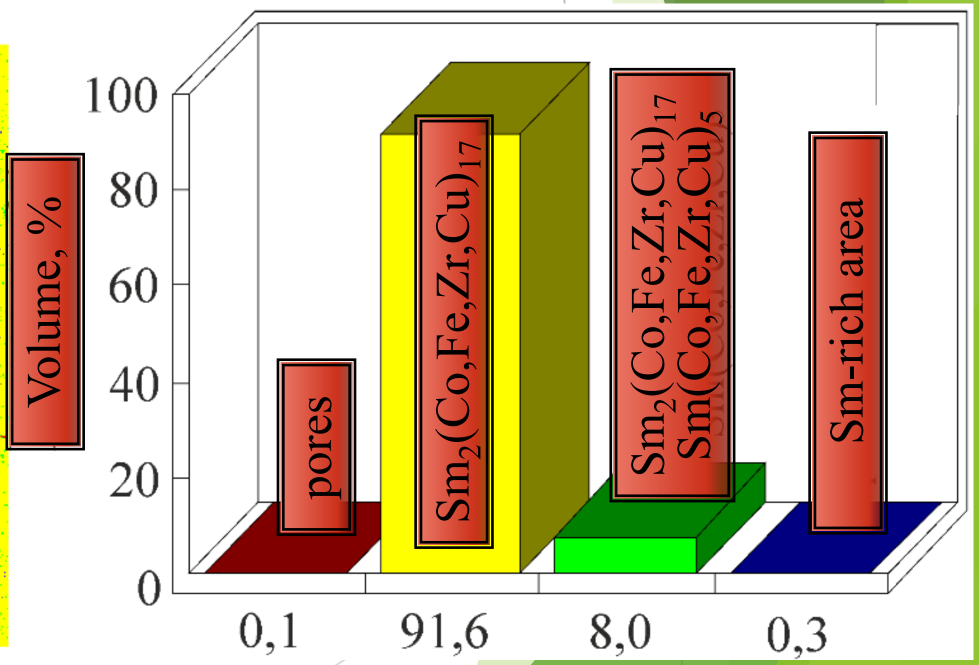
Industrial Ferromagnetic $Sm_2(Co,Fe,Zr,Cu)_{17}$ Alloy

The HD stage proceeded at 700°C and DR at 950°C.
Hydrogen pressure of ≤1.5 MPa

Quantitative analysis of microstructural components of the $Sm_2(Co,Fe,Zr,Cu)_{17}$ alloy







I.I. Bulyk, and M.V. Pylat. Patent 116891 (Ukraine).

Preliminary Results of Sintering $R_2Fe_{14}B$, $SmCo_5$-, and Sm_2Co_{17} Magnetic Materials Using the HDDR Process

Conclusions

It has been ascertained that $R_2Fe_{14}B$-, $SmCo_5$-, and Sm_2Co_{17}-based powders can be sintered in hydrogen at temperatures below 950°C.

The grain sizes of the ferromagnetic phases vary from a few dozens to 300 nm.

The porosity of the sintered materials diminishes with increasing compaction pressure and sintering temperature.

The parameters for producing nanostructured magnets sintered in hydrogen warrant further optimization.

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Thank you!