ALTERNATIVE ROUTES TO OBTAIN MAGNETOCALORIC $La(Fe,Si)_{13}H_y$ COMPOUNDS

UNIVERSIDADE FEDERAL DE SANTA CATARINA

TEIXEIRA, C. S.[1]; BEZ, H. N.[1]; CARVALHO, M. A.[1]; LOZANO, J. A.[2]; WENDHAUSEN, P. A. P.[1]

[1] Magnetic Materials Laboratory (MAGMA), Department of Mechanical Engineering, UFSC, Florianópolis, Brazil

[2] POLO Research Laboratory, Department of Mechanical Engineering, UFSC, Florianópolis, Brazil

INTRODUCTION

$NaZn_{13}$-type $La(Fe,Si)_{13}$-based alloys are considered one of the most favourable working materials for magnetic refrigeration due to T_C and also a coexistent IEM transition exhibited at about 200 K [1 – 4];

However this T_C can be raised up to room temperature, and even higher, by interstitial modification with small atoms such as H, C, or substituting Si by various elements such as Co [5];

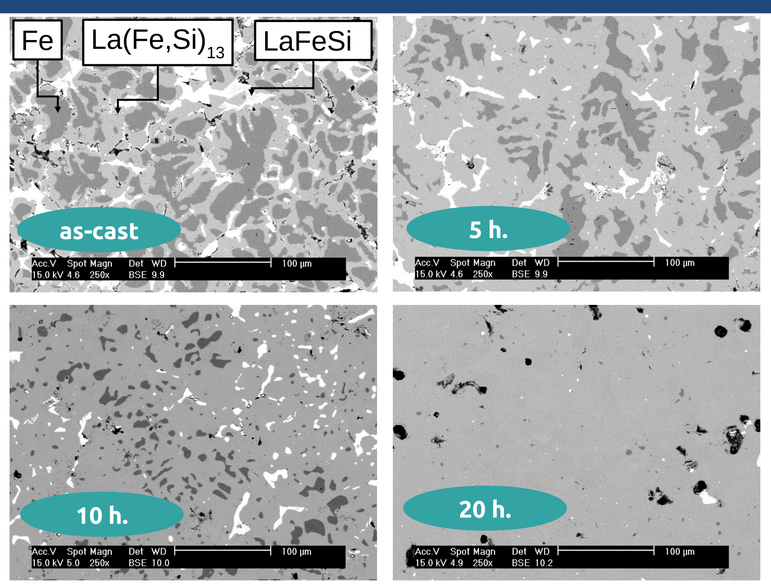
These compounds are typically synthesized via conventional arc or induction melting process followed by a prolonged heat treatment (about 7 days) to obtain nearly single 1:13 phase material [6];

To circumvent this long time annealing process, melt-spinning technique is proven to lead to the same results or better as for the conventional annealing process, in drastically shortened annealing time [1, 7];

A recent work has shown that high temperature annealing (1573 K) exceeding the typical annealing temperatures (1373 K) can reduce drastically the annealing process time from days to hours [8];

In this context, we are proposing two alternative routes to obtain these compounds. The first uses the high temperature annealing of bulk samples, with lower temperatures than that one proposed by literature and the second route makes use of the powder metallurgy principle, the so-called metallothermic reduction diffusion.

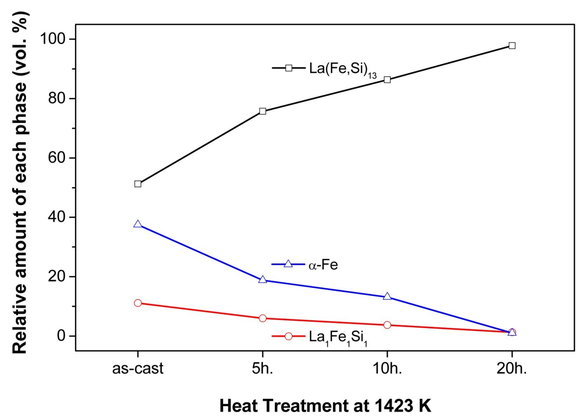
HIGH-TEMPERATURE ANNEALING



The samples were cut via electro erosion from commercially induction melted ingots with the nominal composition of $La_{17.23}Fe_{77.00}Si_{5.77}$;

The heat treatment was carried out in a furnace filled with argon at 1423 K, with 1 atm furnace pressure.

SEM pictures shown the evolution of the phases during the heat treatment at distinct times. Pointing that at 1423 K for 20 hours almost single 1:13 phase was obtained.

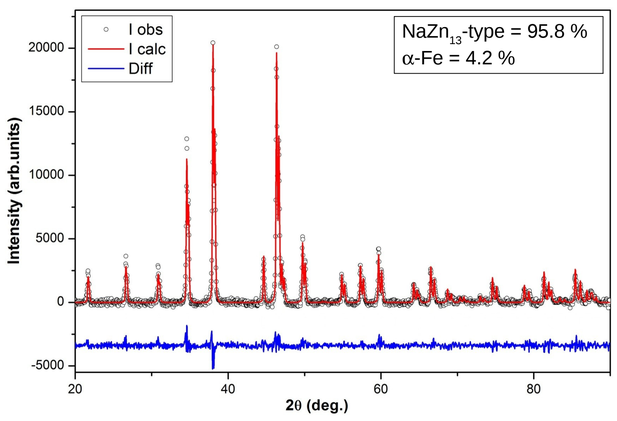


XRD patterns and *Rietveld* refinement method confirm the increasing of the $NaZn_{13}$-type structure amount with increasing the annealing time, which are in good agreement with SEM results.

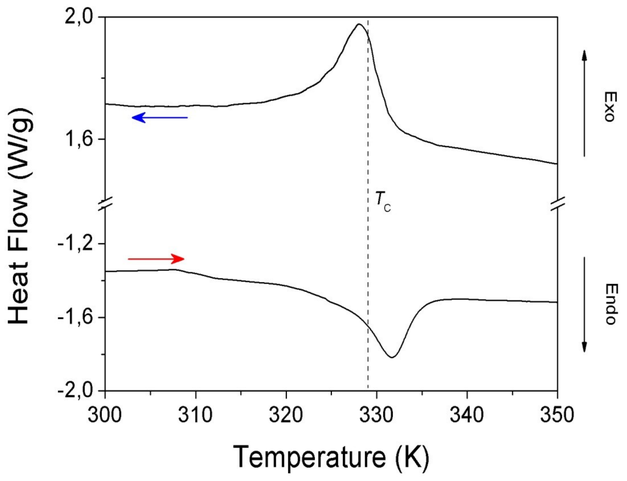
THE REDUCTION/DIFFUSION PROCESS

Commercially powder of raw materials were mixed and heat treated at 1423 K by 6 hours in order to promote the reduction of La_2O_3 by Ca and the diffusion of La, Fe and Si atoms.

The heat treatment was carried out in furnace filled with argon at 1 atm pressure.



The XRD and *Rietveld* refinement results show the presence of about 95 Wt.% of $NaZn_{13}$-type structure phase and about 5 Wt.% of α-Fe.



In order to remove the CaO of the samples, a lixiviation process was carried out with deionized water.

The DSC results confirm that the T_C of the final powder, after the washing process, is about 329 K, due to the interstitial presence of H from the water.

SUMMARY

High temperature annealing (1423 K) for 20 hours yields almost single 1:13 phase samples;

Heat treatment can be carried out in Ar atmosphere with ambient pressure, with no need of sealing samples in quartz ampoules;

The 1:13 phase is also obtained via the reduction/diffusion process, where almost single 1:13 phase is obtained after short heat treatments of about 6 hours;

In order to increase T_C to near room temperature, the hydrogenation process was carried out during the washing process to remove the CaO and Ca excess, which dissociate the water molecules to form $Ca(OH)_2$ and H.

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