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Improved preparation of novel Magneto Caloric Materials

Currently the most promising magnetocaloric materials for near room-temperature heat-pump applications are quinary compounds base on Mn-Fe-P-Si-B. The combination of transition metal, metalloid and non-metal bears some complication for melt synthesis. Most refractory metals react at elevated temperatures with such a melt. Because there is no literature on the interaction of this type of multicomponent melts with solid surfaces, this project aimed at resolving this issue by extensive experimental tests. In collaboration with BASF various materials have been tested that may be suited to contain these melts at about 1500°C.

We have tested various materials that may be used as container for melts of magnetocaloric materials under realistic conditions that may be met in e.g. a melt-spinning setup or an atomizer. These types of setups are suited to prepare rapidly solidified materials that show a more homogeneous microstructure. Another advantage of these passes of synthesis is that impurity phases get separated from the melt and remain as slack in the crucible.

It turns out, for small batches and short melting periods quarts SiO_2 crucibles are sufficiently stable. SiO_2 is anyway the dominant impurity in the materials and the main problem is the softening of quarts which leads to deformation of the crucible and consequent failure of the container.

More stable performance has been observed for dense alumina Al_2O_3 crucibles. These containers however react with the B in the melt and therefore the composition of the melt varies with time. Another disadvantage is that the crucible can only be used once.

Crucibles made from zirconia ZrO_2 and yttrium stabilized zirconia appear to be able to contain melts both with and without boron for longer periods without significant changes in stoichiometry or shape of the crucible. These crucibles appear thus to be the best choice, but come at a rather high price.

A cheaper alternative are graphite crucibles. A small amount of carbon dissolves in the melt and alters the properties of the magnetocaloric alloy. However as soon as the melt is saturated the properties, in particular the critical temperature of the magnetocaloric material, does not change anymore. It is quite easy to remove the residual slack from the crucibles made from graphite and they can be reused several times. Another advantage of graphite crucibles is their coupling to radio frequency (RF) fields. Even very small amount of sample can be heated to high temperatures as the crucible material itself heats in the RF.

In summary, zirconia crucibles are the best solution with respect to preparation of high purity materials and graphite is a reasonable alternative as only a small amount of carbon is dissolved in the melt and stable magnetocaloric properties are retained. The metallic crucible materials appear to be less suited.

Personnel involved in the project:

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Materials budget; 17k€