

The synthesis of a magneto-caloric $Gd_5(GeSi)_4$ alloy using arc melting procedure

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Abstract: In this paper we report on the synthesis of a gadolinium-based magneto-caloric alloy using the technique of arc melting. This alloy belongs to the group of metallic materials that exhibit a considerable magneto-caloric effect, and which have the potential to be used for a range of refrigeration applications.

A series of five alloys weighing from 1 g to 5 g with the nominal composition $Gd_5Ge_2Si_2$ were prepared and examined using optical (LOM) and electron microscopy (SEM with EDS) and XRD in the as-cast and heat-treated conditions. The alloys in the as-cast state contain more than one phase, and only after the heat treatment at elevated temperature were we able to obtain a predominantly single-phase alloy with the required stoichiometry of $Gd_5Ge_2Si_2$.

Izvilleček: V delu je predstavljena sinteza magnetokalorične zlitine na osnovi gadolinija z uporabo taljenja pod oblokom. Ta zlitina spada med tiste kovinske materiale, ki izkazujejo izrazit magnetokaloričen učinek in bi bila lahko primerna za različne načine hlajenja. Izdelanih je bilo skupaj pet zlitin z nominalno sestavo $Gd_5Ge_2Si_2$ in maso od 1 g do 5 g, ki so bile pregledane v izhodnem in toplotno obdelanem stanju z uporabo svetlobne in elektronske mikroskopije ter rentgenske fazne analize. Zlitine v izhodnem stanju vsebujejo več kot le eno fazo, kar smo dosegli šele s toplotno obdelavo pri povišanih temperaturah, kjer smo dobili pretežno enofazne zlitine z želeno stehiometrijo $Gd_5Ge_2Si_2$.

Keywords: magneto-caloric effect, gadolinium alloys, arc melting

Ključne besede: magnetokalorični učinek, zlitine na osnovi gadolinija, taljenje pod oblokom

INTRODUCTION

Contemporary cooling systems for domestic applications are usually based on compression techniques. Such systems, although cheap, are not particularly efficient, and as such alternative refrigeration techniques are always of interest to manufacturers of cooling devices. Additionally, conventional cooling techniques involve gases and coolants that are ecologically problematic. In the late 1990s Gschneider and Pecharsky discovered alloys that exhibit the so-called giant magneto-caloric effect^[1] (GMCE). Such alloys tend to warm up when subjected to a magnetic field and cool down when the magnetic field is being removed. The same principle is used in conventional compressor refrigeration and thus this can be used for a practical cool-

ing system. Today there are several alloys known to exhibit this giant magnetocaloric effect, e.g., Fe-Zr-Y^[2], Co-Al-Ni^[3], Mn-Fe-P-Ge^[4], and La-Si-Fe^[5], but most of the research work has been focused on the Gd₅(GeSi)₄^[6,7] alloys, as the group of alloys with the great magneto-caloric potential (GMCE). These alloys, like many others, suffer from difficulties associated with their synthesis. This can result in a smaller magneto-caloric effect, which is related to the excessive heterogeneity and the presence of unwanted phases with low magneto-caloric effect. A heat treatment of the synthesised alloys based on gadolinium is usually required to achieve the desired or the best possible magneto-caloric effect. But first let us take a look at the basics of the cooling that results from the magneto-caloric effect.

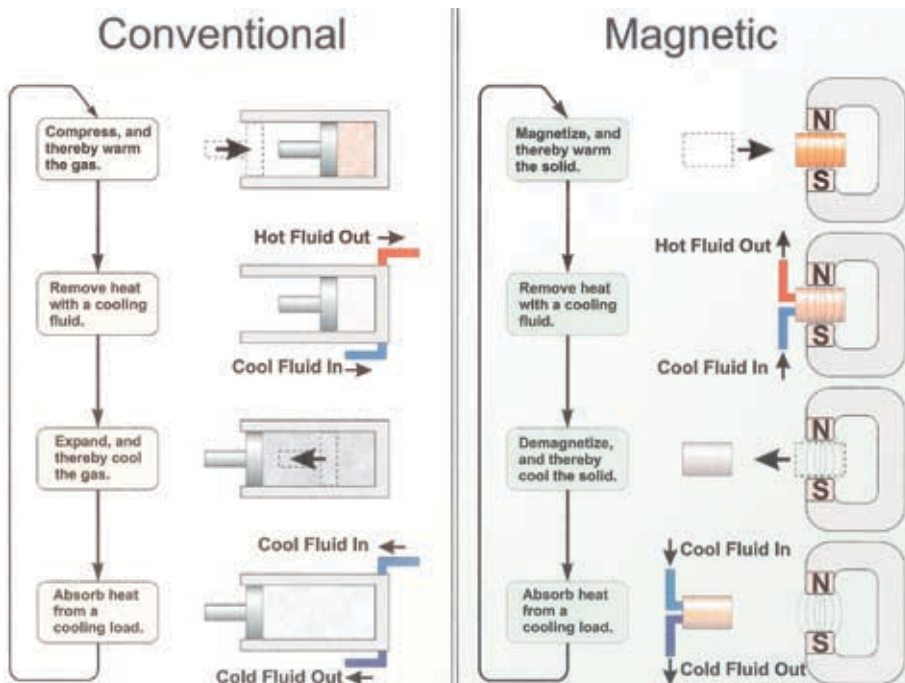


Figure 1. Schematic presentation of the principles of conventional and magnetic cooling

PRINCIPLES OF A “MAGNETIC” REFRIGERATOR

The following scheme (Figure 1) shows a comparison between the basics of conventional cooling using standard gas compression and expansion, and the magnetic cooling, which is based on the magneto-caloric effect. As the cooling gas is compressed in a piston it heats up.

The coolant (e.g. water) then removes the excess heat generated due to the compression and cools down the cooling gas, which is then further cooled by the rapid expansion. The cycle can be repeated over and over again. In the case of the magneto-caloric effect the metallic magneto-caloric material is magnetized using magnets, which leads to the heating of the material in the magnetic field. The excess heat, that is, the heat generated because of the magnetization can be removed by the liquid coolant (e.g. water) as in the case of conventional cooling. The magneto-caloric material is then demagnetized right after the cooling with the liquid coolant and thus cooled down. So this cycle can be utilised for the everyday cooling of stored food in pretty much the same way as with conventional refrigerators. The major drawback to the mass production of magneto-caloric refrigerators is the cost and the sheer size of the device that contains the magnets and the magneto-caloric material and the cooling system containing the liquid coolant. Namely, conventional refrigerators have the whole cooling system in the size of a typical shoebox, whilst the magnetic refrigerator would have a cooling unit the size of a conventional refrigerator itself.

SYNTHESIS OF MAGNETO-CALORIC ALLOYS

Among the different magneto-caloric alloys each alloy requires a specific synthesis route. In our research we focused ourselves on the synthesis of the most promising magneto-caloric alloy, containing gadolinium (Gd), germanium (Ge) and silicon (Si), so as to achieve a stoichiometry of $Gd_5(Ge_2Si)_4$. In order to get the so-called giant magneto-caloric effect (GMCE) the alloy must have a stoichiometry of $Gd_5(Si_xGe_{1-x})_4$ where $0.24 \leq x \leq 0.5$, and the monoclinically distorted derivative of the orthorhombic Sm_5Ge_4 -type structure are present. This is by no means an easy task, because the gadolinium itself is a very reactive element, so that conventional synthesis by melting in a crucible is not an option. Therefore, we employed arc melting in an inert atmosphere of argon using a pure copper hearth as the mould. This method proved to be very effective in terms of negligible mass losses of the charge material, but problematic due to the excessive heterogeneity in the microstructure of the synthesised alloys.

EXPERIMENTAL WORK

Pure gadolinium (99.99 %), silicon (99.9995 %) and germanium (99.9999 %) were used to produce fine pellets of Gd-Ge-Si alloys weighing from 1 g to 5 g. Each time the ratio between the alloy elements was kept at Gd5 : Ge2 : Si2 in atomic percent. An arc melting facility that allows the internal atmosphere to be removed and replaced by pure argon was used (see Figure 2).

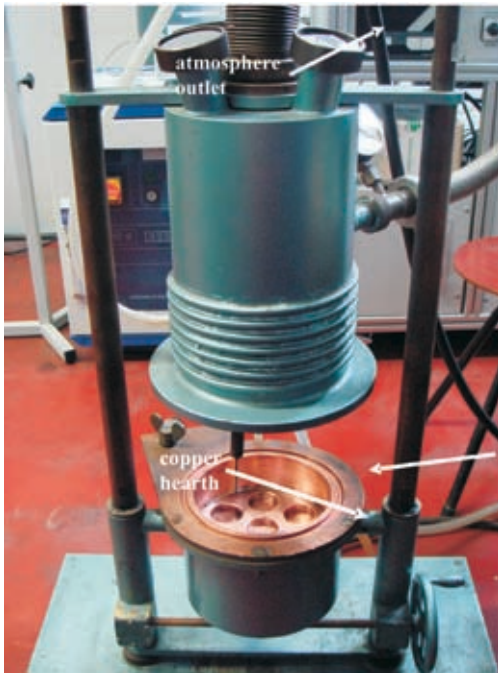


Figure 2. The melting facility with a water-cooled copper mould at the bottom and the tungsten tip used to produce the electric arc

Prior to introducing the argon into the arc-melter a small amount of pure titanium was ignited in order to remove any remaining oxygen. Each set of the charge material, weighing from 1 g to 5 g, consisted of small pieces of gadolinium, germanium and silicon, and was placed on the water-cooled copper hearth. Each set of the charge material was then remelted for four times where DC electric current of 90 A was used. After each melting time the buttons were turned upside down and remelted in order to increase the homogeneity of the synthesised alloys. Weighing the synthesised alloys revealed that the mass losses during the synthesis process were of $(0.4 \pm 0.2) \%$, which is more than acceptable. The synthesised

pellets were then cut in half and specimens were prepared for the optical (LOM; Reichert MeF2) and electron microscopy (SEM with EDS; JEOL JSM-5800). The remaining halves of the synthesised alloys were divided into two pieces, one of them being ground into a fine powder to be used for the XRD (Bruker AXS Endeavor D4) examination and the other one used for the heat treatment. The heat treatment of the synthesised alloys was carried out in an inert atmosphere of argon for 1 hour at 1300 °C. The reason for varying the amount of charge material from 1 g up to 5 g was to effectively influence the cooling rate in order to see what effect this had on the crystallization path and therefore on the microstructure of synthesised alloys.

RESULTS AND DISCUSSION

The synthesised alloys were first examined using scanning electron microscopy to reveal the effect of the cooling rate on both the surface structure (Figure 3) and the microstructure (Figure 4).

It is obvious from Figure 3 that the cooling rate, which is higher in the case of the 1 g sample, has a profound effect on the surface structure with the formation of a “sinew” effect on the upper surface of the button (Figure 3 a) e.g. the flat plateaus on the alloy button tend to break up. This feature is all but absent with the 5 g sample (Figure 3 b). The 5 g sample has a smoother surface consisting of fairly regular pentagons and hexagons (reminiscent of the Fullerene

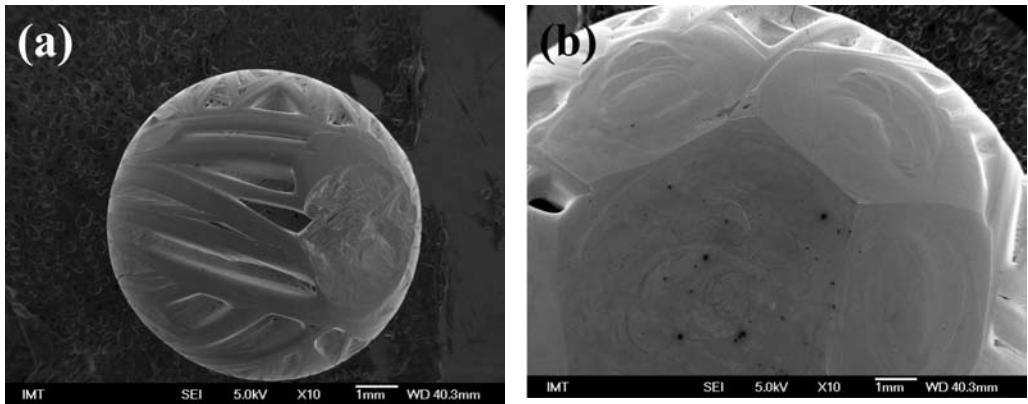


Figure 3. Surface structure of the $Gd_5Ge_2Si_2$ alloy button in the as-cast state: (a) 1 g of charge material and (b) 5 g of charge material

structure) that is typical for the crystallisation of semi-conducting elements, such as silicon and germanium (often also referred to as semi-metals) when moderate cooling rates are present. The metals, on the other hand, tend to form a curvaceous or uneven crystallisation front (on atomic scale) because of the small difference in the entropy of the solid and liquid state (melting entropy). This is not the case with silicon and germanium, both of which have large melting entropies (order of 30 J/(K mol), whilst order of 4–8 J/(K mol) for metals),

leading to the formation of facets during the process of crystallisation. The comparison of the microstructure of the sample with the highest cooling rate (Figure 4 a) and the sample with the lowest cooling rate (Figure 4 b) reveals that in both cases the as-cast state provides us with at least three phases, with the dendritic-columnar phase being the dominant one.

This phase also contains small needle-like precipitates that lie within the dendritic columns at an angle of 90° and approx.

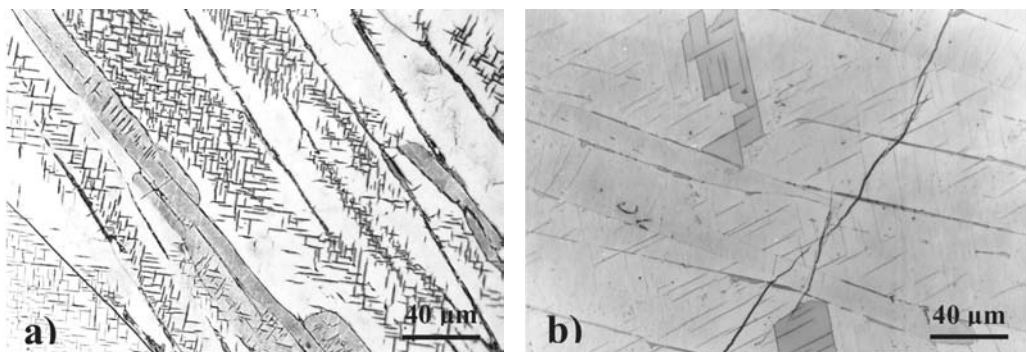


Figure 4. Optical micrographs of the microstructure of the $Gd_5Ge_2Si_2$ alloy in as-cast state: (a) 1 g of charge material and (b) 5 g of charge material

75° to each other. The intercolumnar space is filled with a third phase, which is rich in gadolinium and silicon. The columnar phase exhibits different shade effects because of the differences in the orientation of individual columns towards the sample surface, so that they produce the so-called orientation contrast. The number of phases revealed by the optical microscope is also confirmed by the SEM and EDS (Figure 5), which both show that the columnar phase has mole fractions of Si 22.9 %, Ge 21.0 % and Gd 56.1 %, the intercolumnar phase has mole fractions 31.6 % Si, 17.5 % Ge and 50.9 % Gd, and the precipitated phase has composition mole fractions of 17.3 % Si, 21.9 % Ge and 60.8 % Gd. The X-ray spectra of the as-cast samples weighing 1 g and 5 g are the same. Although there may be significant microstructural differences between the two samples the crystal structure of the main phase is the same for both samples. The X-ray diffraction pattern of the as-cast button weighing 5 g is shown in Figure 6a together with the calculated spectrum for the Gd_5Si_4 -structure. This Gd_5Si_4 -based solid solution allows

germanium to substitute for silicon in the range $0.5 \leq x \leq 1.0$. On the other hand, the Gd_5Ge_4 solid solution extends from $0 \leq x \leq 0.2$. If we compare the two spectra, the experimentally obtained spectra and the calculated spectra, it is clear that they exhibit a good fit, albeit with a slight shift to higher angles, which is increasingly obvious to the right-hand side of the graph. This shift is due to the substitution of approximately 50 % of the silicon atoms by germanium atoms, and is inline with the observations of Pecharsky and Gschneidner [1]. However, after heat-treating the material at 1300 °C for one hour a change in the crystal structure is observed (Figure 6b). Here we observe the monoclinically distorted derivative of the orthorhombic Sm_5Ge_4 -type phase, which we refer to in the figure as the $Gd_5Ge_2Si_2$ structure. It is believed that the heat treatment for 1 h at 1300 °C results in some phase purification and homogenisation of the arc-melted buttons, leading to a partial ordering of the crystal structure via a redistribution of silicon and germanium atoms among the various crystallographic sites. The annealing causes an enrichment

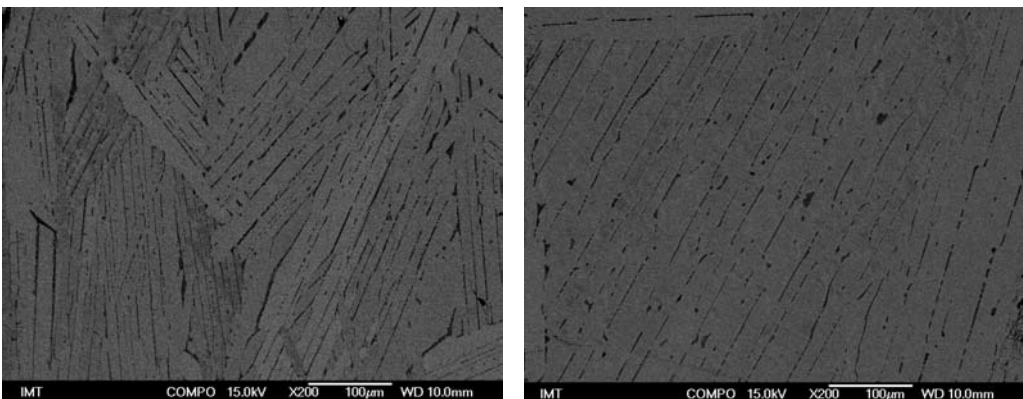


Figure 5. SEM micrographs of the microstructure of the $Gd_5Ge_2Si_2$ alloy in as synthesised state: (a) 1 g of charge material and (b) 5 g of charge material

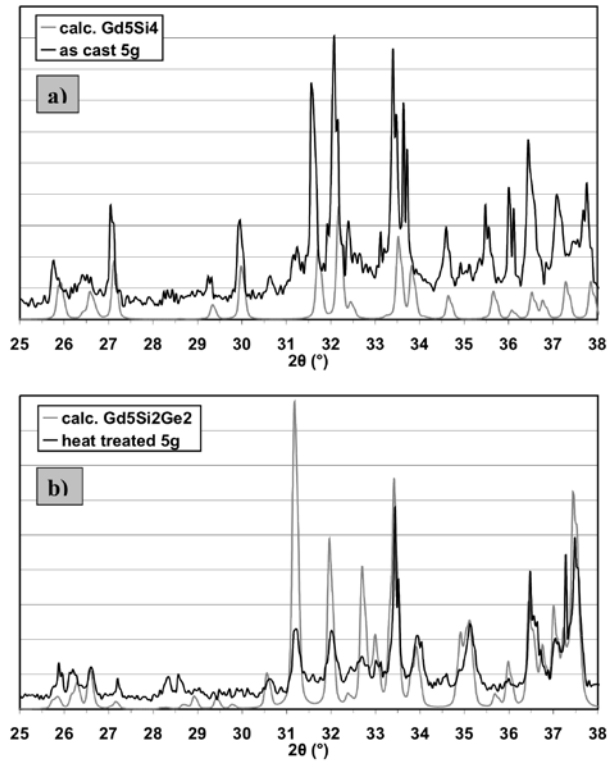


Figure 6. XRD analysis of the $Gd_5Ge_2Si_2$: (a) as-cast state and (b) heat treated state

of germanium for the sites responsible for a considerable enhancement of the giant magneto-caloric effect. the interslab bonding, thereby resulting in

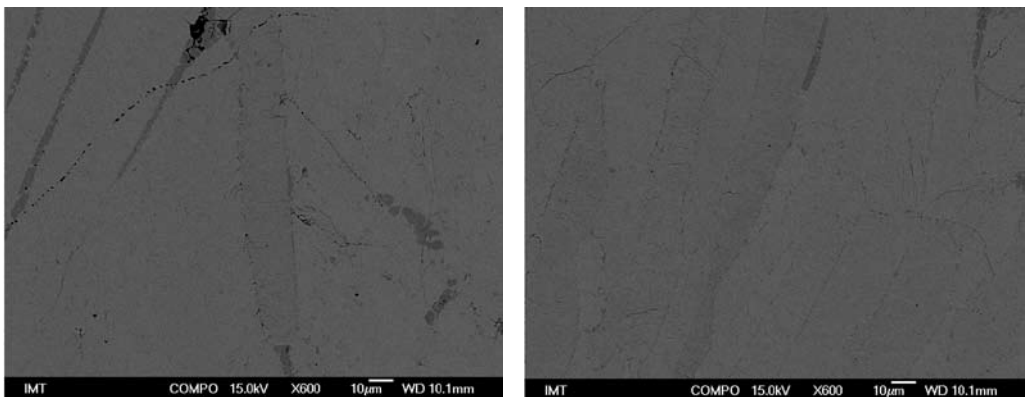


Figure 7. SEM micrograph of the microstructure of the $Gd_5Ge_2Si_2$ alloy in heat-treated state: (a) 1 g of charge material and (b) 5 g of charge material

From Figure 7 we can see that after the heat treatment at 1300 °C we get a largely single-phased alloy with the composition very close to that of $\text{Gd}_5\text{Si}_2\text{Ge}_2$. This combination of the right chemistry and the right crystal structure should give us a material with a large magneto-caloric effect (GMCE) with an entropy effect of about $-35 \text{ J}/(\text{kg K})$.

CONCLUSIONS

A series of five alloys with the composition close to $\text{Gd}_5\text{Ge}_2\text{Si}_2$ weighing from 1 g to 5 g were prepared by arc melting. This synthesis route provided alloys with a significant heterogeneity in their microstructures and at least three different phases.

However, a heat treatment at 1300 °C for an hour initiated the transformation of these phases into the desired $\text{Gd}_5\text{Ge}_2\text{Si}_2$ phase, which exhibits a pronounced magneto-caloric effect and could potentially be used for the cooling applications.

The variations in the mass of the initial charge of material effectively influenced the cooling rate, causing marked effects on the surface of the buttons, producing a sinew appearance at fast cooling rates, which disappears as the mass of buttons increases towards 5 g.

The crystal structures of the main phases in the buttons were found to be largely independent of mass, and therefore of cooling rate, and a heat treatment at 1300 °C for one hour was sufficient to produce a single-phased material with the desired crystal structure.

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