STUDY OF THE INLUENCE OF GRAIN SIZE ON THE MAGNETIC PROPERTIES OF THE GD5.09GE2.03SI1.88 MAGNETOCALORIC ALLOY USING THE ACOUSTIC DETECTION TECHNIQUE

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Abstract. *The magnetic refrigeration is an innovative technology due to its high efficiency, low energy consumption and environmental friendliness. However, the manufacturing process of magnetocaloric materials is an obstacle to their effective application in refrigeration systems, since they have to be in convenient shapes to be used as magnetic regenerators. In this work we present the magnetic characterization of the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ alloy, analyzing as-cast bulk and powder samples. The objective is to determinate the best grain size of this material to process it by powder metallurgy. The magnetic behaviour of the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ alloy is studied in function of the grain size of the pulverized samples using magnetoacoustic measurements, which is an alternative way to characterize the magnetocaloric effect of these materials. The results reveal that the samples present a first order magnetostructural transition (FOT) around 270 K and a second order magnetic transition (SOT) at 300 K. It´s also observed that the smaller the grain size, the higher is the intensity of the FOT and the entropy variation. The entropy variation for the as-cast sample is ΔS_T = -18/kg.K and for the sample with grain size < 25 μm is ΔS_T = -11/kg.K. On the other hand, it is verified that the FOT increases together with the magnetic field used to obtain the measurements while the SOT decreases.*

Keywords*: magnetocaloric effect, magnetoacoustic, GdGeSi*

1. INTRODUCTION

Recently Pecharsky and Gschneidner Jr. (1997a, 1997b), reported the giant magnetocaloric effect (GMCE) in the $Gd_5Ge_2Si_2$ compound and in other compounds of the family $Gd_5(Ge_xSi_{1-x})_4$. As shown by these researchers the $Gd_5Ge_2Si_2$ compound ins't the one that presents the greatest magnetocaloric effect (MCE), which is described by the quantity ΔS_{mag} (isothermal entropy variation), but it presents this effect around room temperature. This fact makes the compound $Gd_5Ge_2Si_2$ a potential candidate to be used as a refrigerant material in a magnetic refrigerator which is expected to substitute the conventional refrigerators and air-conditioning devices.

According to Pecharsky *et al.* (2002), the as-cast $Gd_5Ge_2Si_2$ compound presents two magnetic transitions, one of first-order nature around 277 K, due to a majority phase, and another of second-order nature around 300 K, due to a minority phase. Repeating their preparation procedures, but using commercial (low purity) gadolinium, we didn't obtain the same results. Our as-prepared $Gd_5Ge_2Si_2$ compound presented only the second-order transition at 300 K. To obtain the first-order transition, which is the one that occurs at the lowest temperature, it was necessary to carry out heat treatments (Alves *et al.*, 2004).

When we performed metallographic and WDS (Wavelenght Dispersive Spectroscopy) analyses, Gama *et al.* (2004) verified that our $Gd_5Ge_2Si_2$ compound presented two crystallographic phases: the majority phase, with stoichiometry $Gd_{5.09}Ge_{2.03}Si_{1.88}$, and the minority one, with stoichiometry $Gd_{4.59}Ge_{1.74}Si_{2.67}$. Then, we decided to prepare an alloy with the stoichiometry of the majority phase of $Gd_5Ge_2Si_2$, i. e., $Gd_{5.09}Ge_{2.03}Si_{1.88}$. As happens with the $Gd_5Ge_2Si_2$ stoichiometry, this new alloy didn't present a single phase. Nevertheless, the most important experimental observation was that, even in the as-cast condition, the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ alloy presents the two magnetic transitions, first and second-order ones, as in Pecharsky and Gschneidner's $Gd_5Ge_2Si_2$ compound. More important, the first-order transition is much stronger than the second-order one.

It is important to remark that the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ alloy, as well as other magnetocaloric materials reported in the literature, certainly will not be used in their un-manufactured as-cast condition in future magnetic refrigeration applications. To use these materials as magnetic active regenerators it will be necessary to process them into forms dictated by the design of the machine, as wires, thin plates, spheres or other convenient shape. As this particular compound is very hard and brittle, we considered the use of powder metallurgy technique in order to prepare simple shapes with the material. One of the stages of this technique consists in pulverizing the alloy and then sieving it into convenient powder grain size. The objective was determinate the best grain size to produce tablets from the alloy. We

established a research program in which the magnetic properties of the material in several grain sizes were measured and compared with the properties of the bulk as-cast material. The ΔT measurements, used to characterize the magnetocaloric effect of the samples, were carried out in a thermoacoustic apparatus built by our research group. The obtained results suggested that X-rays diffraction measurements should be realized to follow the eventual changes that the material was undergoing on the samples with different grain sizes. This work reports our main results obtained for powders of the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ compound.

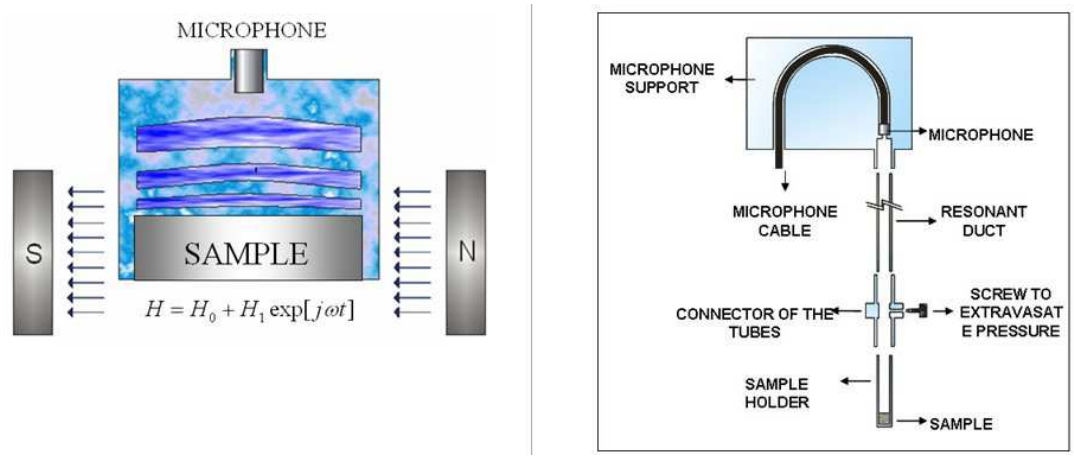
2. EXPERIMENTAL

The $Gd_{5,09}Ge_{2,03}Si_{1,88}$ sample was prepared from 99.95 wt.% Gd and with electronic grade Ge and Si by arc-melting three times to guarantee homogeneity. The mass of the sample was 5 g. The sample was then manually crushed and put into powder form. The resulting powder was sieved using sieves with apertures of 25 μm, 38 μm, 45 μm, 63 μm, 90 μm e 106 μm.

The powders and the bulk sample were separately characterized by either magnetic and thermoacoustic analyses.

Magnetic measurements were carried out using a commercial SQUID magnetometer (Quantum Design, model MPMS XL). Magnetization versus temperature data, which were always obtained in a zero-field cooling – field warming process, i. e., the sample is cooled from room temperature with no applied magnetic field and, when in the ferromagnetic regime, the magnetic field is applied and we perform the magnetization measurements increasing and then decreasing the temperature.

The MCE measurements were carried out using the acoustic detection technique with an apparatus built by the Grupo de Estudos de Fenômenos Fototérmicos (GEFF) of the Universidade Estadual de Maringá (Fig. 1). Our setup measures pressure variation in tight chamber as a consequence of MCE effect in the sample that releases heat into the gas under modulated magnetic field, following the principle of the photoacoustic effect.



(a) (b)

Figure 1. (a) Alternate Magnetic field produces acoustic wave in gas chamber in a sample due to modulated MCE effect, the detection uses high sensitivity microphone coupled to the cell; (b) designed Magnetoacoustic Cell based on photoacoustic principle

The magnetic field applied on the sample is composed by two components, a constant field (H_0) and a modulated one (H_1 *exp[jwt]*). The modulated magnetic field is produced under a frequency of 50 Hz, which presents a triangle wave with 0,02 Tesla of amplitude.

The magnetoacoustic curves presented in this work were obtained by the following this protocol: (1) increase the temperature of the sample up to 373 K; (2) apply the modulated magnetic field that is kept on during the whole measurement; (3) change the constant magnetic field and read the response utilizing a software (written by us) which registers the generated signals in Volts and calculates the average value of them for every single constant magnetic field applied (0, 2 and 8 Ampéres); (4) switch off the constant magnetic field and a set a new lower temperature; (5) when the temperature is kept stable by 20 seconds, restart the protocol in step 3.

3. RESULTS

The magnetization versus temperature (M vs. T) data for the powder of the as-cast $Gd_{5,09}Ge_{2,03}Si_{1,88}$ alloy in the bulk material is presented in Fig. 2. We noted that for the bulk material the first-order transition (FOT), around 267 K, is

relatively broad and there are traces of a second-order transition (SOT) at around 300 K as occurs for the optimally prepared $Gd_5Ge_2Si_2$ alloy of Pecharsky *et al.* (2003).

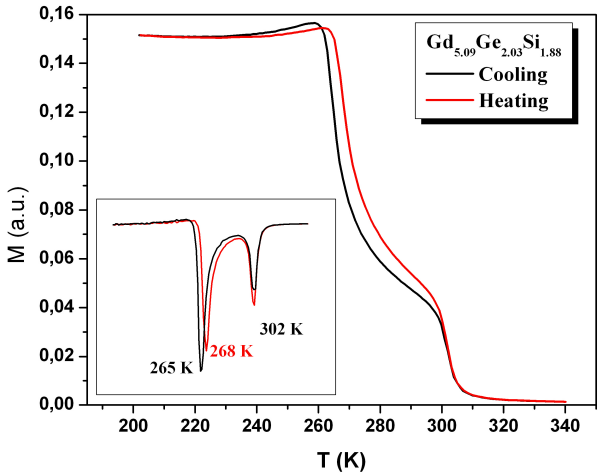


Figure 2. Magnetization as a function of temperature for the bulk alloy measured by SQUID (H = 16 kA/m)

It was not possible to obtain the same data using the thermoacoustic technique which detects only the second order transition. At this time we can not find an explanation for this.

Table 1 shows all the ranges of grain sizes we have used to get the results that are presented in this work and the masses of each one. That is important, because the magnetic and the thermoacoustic measurements are sensitive to the mass of the sample, so we have used around 95 mg of sample for all measurements.

Table 1. Mass of each sample as a function of the medium grain size

Grain size range (μm)	x < 25	25 < x < 38	38 < x < 45	45 < x < 63	63 < x < 90	90 < x < 106
Mass (mg)	95.5	95.1	95.0	95.6	95.0	95.0

Figure 3 shows the thermoacoustic heating curves for the pulverized samples.

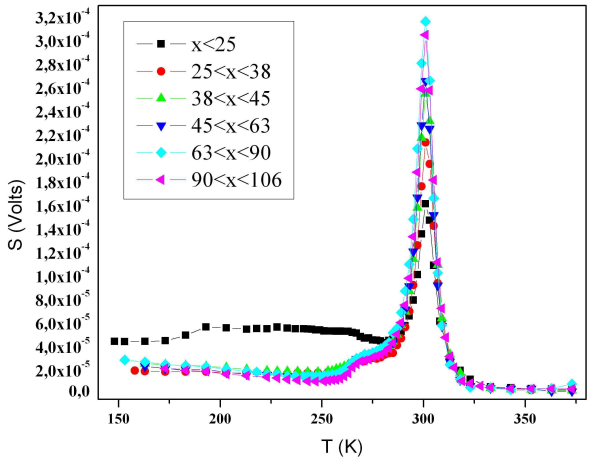
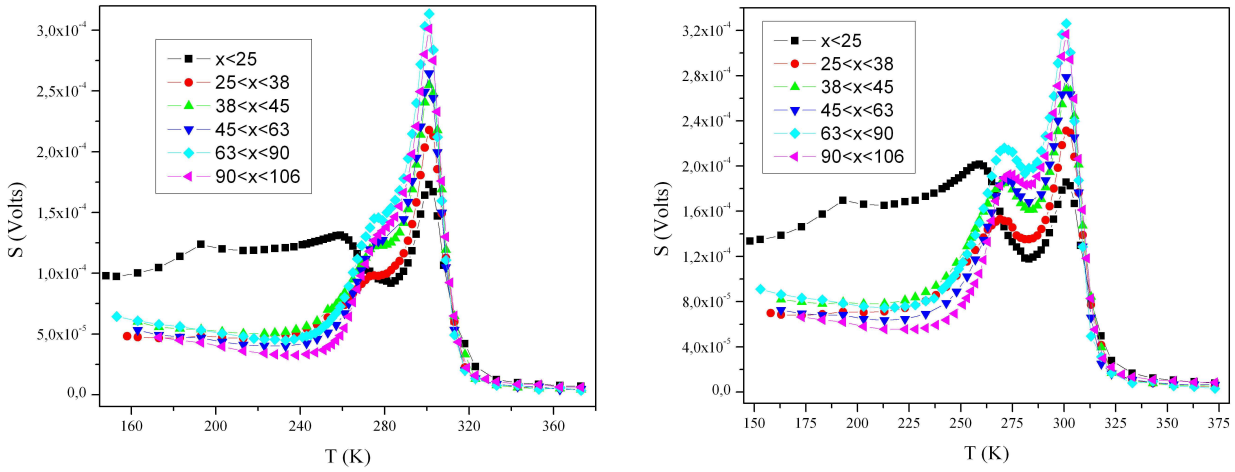


Figure 3. Signal (S) as a function of temperature (T) for the pulverized samples measured by thermoacoustic detection at zero Ampére (H = 0.085 Tesla).

In comparison to the bulk sample, even when a low constant field is applied, it is observed that all samples present a very strong SOT signal at around 300 K (Figs. 3, 4 and 5). On the other hand, for this same constant field (H = 0.085 T), the FOT appears very broad and with low intensity (Fig. 3).

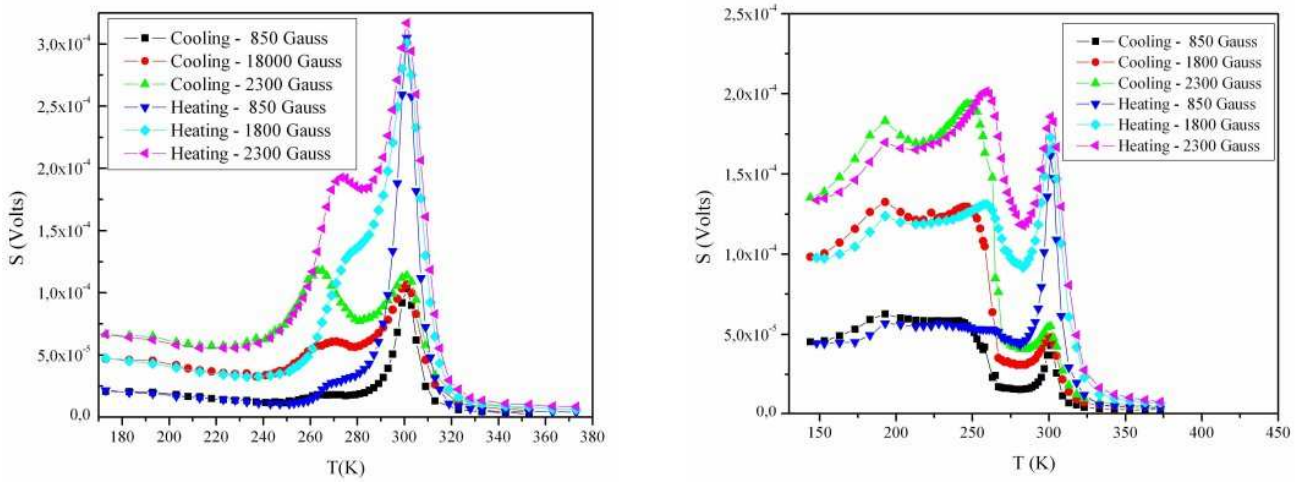
At the same time, it's noted another signal around 180 K, which appears for the sample with the grain size smaller than 25 μm (Figs. 4(a), 4 (b) and 5(b)). Similar behavior was reported by Alves *et al.*(2004) and Magnus *et al.*(2007) in hydrogenated samples of GdGeSi. This behavior possibly happens because when the material is pulverized it acquires induced residual tensions in it, which are more intense for smaller granulometries (x < 25 μm). These residual tensions can induce the formation of a new magnetic phase or a new magnetic transition, in this case at low temperatures.



(a) (b)

Figure 4. S vs. T for the pulverized samples measured by thermoacoustic detection at (a) 2 A (heating) and (b) 8 A (heating).

We have two parameters to discuss here, the medium grain size and the constant field used to carry on the measurements. On the influence of the grain size of the samples, it is observed that the temperature of the FOT displaces to lower values with decreasing the grain size, as shown in Fig. 4. This variation is remarkable to the sample with grain size < 25 μm. Also, it is observed that the signal intensity for the FOT is somewhat greater for the sample with x < 25 μm during heating process. If only the signal intensity for the FOT is considered, it is verified a decreasing tendency for this value with a decrease in the grain size. However, when the grain size is less than 25 μm, there is a complete change in behavior, as the FOT assumes a more intense signal than the second order (Fig. 4(b)).



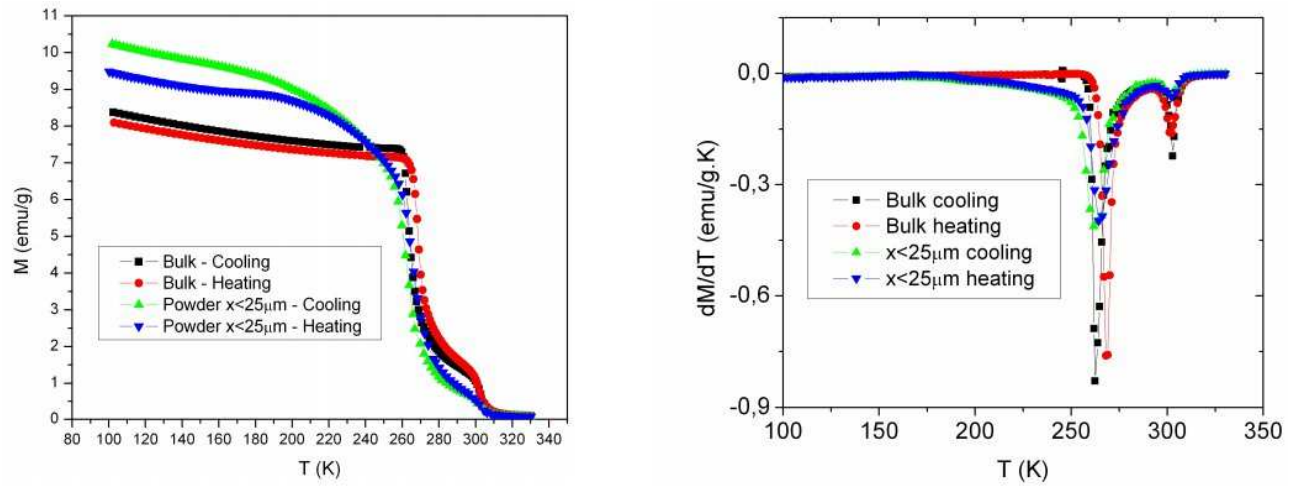
(a) (b)

Figure 5. S vs. T measured by thermoacoustic detection for the pulverized samples with (a) 90 μm < x < 106 μm and (b) x < 25 μm.

When we analyze the influence of the constant field on the magnetic transitions of the samples, the signals of the FOT and the SOT for the heating curves are always less intense than the same signals for the cooling curves, as we can see in Fig. 5. We believe this have some relation with the equipment we use to control the temperature of the system. The temperature controller is more efficient during the heating than cooling, once the measurement for each temperature is taken when the temperature is stable. If the time to this stabilization is too long, part of the sound waves generated by the sample during its magnetic transition can't be registered.

Still, the intensity of the signal for the FOT increases together with the constant field. Again, with x < 25 μm the effect of the constant field is noteworthy, especially when the sample is cooling. It can verified that the signal for FOT increases with the applied Field, in such a way that fields greater than 850 Gauss (0,085 T) the FOT signal becomes more intense than the SOT.

Otherwise, we note that the signal vs. temperature curves are relatively sharp and we observe negligible thermal hysteresis for the SOT and the temperatures of the FOT and the SOT, taken by thermoacoustic technique, are in accordance with the magnetization measurements (Fig. 6).



(a) (b)

Figure 6. M vs. T curves (a) and the derivative of these curves (b) for the samples in bulk and with x < 25 μm (H = 16 kA/m)

The MCE is proportional to the intensity of the magnetic entropy variation (ΔS) of the alloy, which is more intense around the FOT. Also, that value has direct relation with the relative amounts of the monoclinic phase (which is responsible for the FOT of the $Gd_{5.09}Ge_{2.03}Si_{1.88}$) and other present phases. Figure 7 presents the MCE curves to some of our samples and it shows that the samples with bigger grain size presents a MCE greater (ΔS = -16 J/kg.K) than the samples with lower one (ΔS = - 11 J/kg.K).

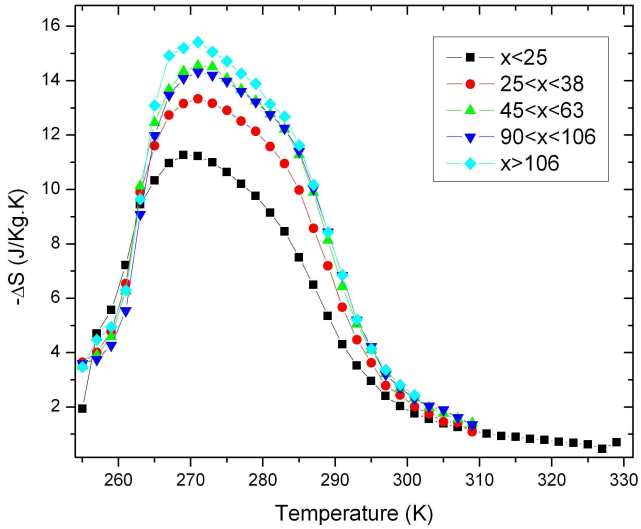


Figure 7. MCE as a function of the medium grain size (ΔH = 0 – 5T)

4. CONCLUSIONS

The magnetic curves for the $Gd_{5.09}Ge_{2.03}Si_{1.88}$ alloy at 16 kA/m presents two peaks: the lowest temperature peak (~ 267 K) is due to irreversible processes and the highest temperature peak (~ 302 K) is due to second order magnetic transition. Decreasing grain size, the lowest temperature peak displaces to lower temperatures, which is an indicative the grinding process stabilizes the orthorhombic structure instead the monoclinic one, which is responsible for the GMCE. The magnitude of the other peak tends to decrease until the grain size is around 25 μm. The induced structural defects stabilize the orthorhombic phase, and, possibly through the strong magnetoelastic effect observed for these materials, lower the Curie temperature of the compound in a way directly proportional to the mean size of the grains of the samples. When x < 25 μm, two different things occurs: the intensity of the FOT increases remarkably and appears a new magnetic transition at low temperature ((~ 175 K). This happens because when the powder is ground it acquires residual tensions that are more intense for smaller granulometries. This suggests that the temperature interval of

monoclinic phase formation has been altered, probably by the defects induced into the microstructure of the alloy during the grinding process. At the same time, it can occur a microdeformation into the microstructure of the alloy, which explains the appearing of that new magnetic transition at low temperature.

In all grain size range, we observe the FOT and the SOT increases with the applied field, but, again, the behavior for the sample with $x < 25$ μm is quite different of the other samples. Only for this sample the intensity of the FOT is bigger than the SOT for all fields applied. Probably it is the consequence of the microstructural changes the grinding caused to the sample. Anyway, the more intense FOT, more intense should be the MCE, but it didn't happen with the sample with $x < 25$ μm. In this case, the MCE of the samples decreases with the mean grain size of the sample and $\Delta S = 16$ J/kg.K for $x > 106$ μm and $\Delta S = 11$ J/kg.K for $x < 25$ μm. Again, this indicates the monoclinic structure is being destroyed by the grinding process and the orthorhombic structure is being stabilizing.

The results are an indication of a build up of structural defects due to the grinding process as the grain size decreases, and these defects can be of different types, as vacancies, dislocations, grain boundaries, etc.

A heat treatment should recover, even partially, the properties of the small grain size samples. On this way, the microstructure study of these heat treated alloys is indispensable and will be published soon.

3. ACKNOWLEDGEMENTS

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