Kinetical analysis of the heat treatment procedure in SmCo$_5$ and other rare-earth transition-metal sintered magnets

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Abstract

In the processing of all types of commercial sintered rare-earth transition-metal magnets (SmCo$_5$, Sm(CoCuFeZr)$_z$, NdFeB) a post-sintering heat treatment is included, which is responsible for large increase of the coercive field. During this post-sintering heat treatment, there are phase transformations with diffusion of the alloying elements, moving the system towards the thermodynamic equilibrium. Due to the larger size of the rare-earth atoms, the diffusion of the rare-earth atoms in the lattice of rare-earth transition-metal phases like SmCo$_5$, Sm$_2$(Co, Fe)$_{17}$ or Nd$_2$Fe$_{14}$B should be very slow, implying that the diffusion of the rare-earth atoms should be controlling the overall kinetics of the process. From the previous assumption, a parameter named "diffusion length of rare-earth atoms" is introduced as a tool to study the kinetics of the heat treatment in rare-earth magnets. Detailed microstructural characterization of SmCo$_5$ and NdFeB magnets did not indicate significant microstructural changes between sintering and heat treatment temperatures and it was suggested that the increase of coercivity can be related to decrease of the content of lattice defects. The sintering temperature is high, close to melting temperature, and in this condition there are large amount of defects in the lattice, possibly rare-earth solute atoms. Phase diagram analysis has suggested that a possible process for the coercivity increase can be the elimination of excess rare-earth atoms, i.e. solute atoms from a supersatured matrix. The "diffusion length of rare-earth atoms" estimated from diffusion kinetics is compatible with the diffusion length determined from microstructure. For the case of SmCo$_5$, it was found that the time of heat treatment necessary is around 20 times lower if an isothermal treatment at 850 °C is substituted by a slow cooling from sintering temperature 1150 to 850 °C. These results give support for the thesis that the coercivity increase is related to elimination of lattice defects. Although this example is for SmCo$_5$ magnets, this analysis can be used for the optimization of the heat treatment procedure in other cases, and it is also discussed how this method could be applied for Sm(CoCuFeZr)$_z$ and NdFeB sintered magnets.
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1. Introduction

The sintered rare-earth transition-metal magnets are often submitted to a heat treatment after the sintering, which is responsible for significant increase of the coercive field. This effect is observed for all main types of rare-earth transition-metal magnets like SmCo$_5$ [1–8], Sm(CoCuFeZr)$_z$ [8–12] and NdFeB [13–15], but the reason of the coercivity increase remains not plentifully clarified [3,4,11].

The concept of diffusion length will be introduced as an useful tool to help the elucidation of the coercivity increase of the magnets. The diffusion length can be compared with microstructural changes and used to evaluate possible phase transformations during the heat treatment.

The diffusion of the rare-earth atoms in the structure is believed be controlling the diffusion process. This is because rare-earth atoms are very large if compared with the transition-metal atoms.

The sintering temperature is high, close to melting temperature, and in this condition the lattice has large content of defects—as for example, vacancies or possibly rare-earth solute atoms. The equilibrium concentration of defects in the lattice of a stable phase, for example vacancies, interstitials or substitutionals, decreases exponentially with temperature. Thus, it is possible that the coercivity increase is directly related to the elimination of point-like defects.

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1.1. Lattice defects and coercivity

It has been noted, since the early stages of the development of SmCo$_5$ magnets [16–18] that lattice defects are responsible for reduction of coercivity. This was observed as consequence of the effect of intense milling, which damages the crystalline structure, reducing the coercivity [16–19]. A further annealing eliminates the lattice defects and restores coercivity [19]. It was also observed that variations of chemical composition in the SmCo$_5$ phase could affect the anisotropy field [16,20], thus influencing coercivity.

The degradation of magnetic properties after exposition under radiation [21,22] can also be ascribed as deleterious consequence of lattice defects for the coercivity. It has been suggested that the removal of lattice defects can be the responsible for the large increase of coercivity between sintering and heat treatment temperatures [2,3]. Even with a detailed verification of microstructure, before and after the post-sintering heat treatment in SmCo$_5$ [3,4,23] and Nd-FeB [4] magnets, no significant difference was found in microstructure, supporting the idea that the elimination of defects in atomic level can be the reason of the beneficial effect of heat treatment.

The objective of this study is to evaluate if the kinetics of the coercivity increase due to the post-sintering heat treatment could be related to the kinetics of punctual defects removal due to diffusion. Previous microstructural studies [3,4,23] indicated that a possible microstructural change—between sintering and heat-treatment temperatures—is the elimination of rare-earth atoms from a supersatured matrix. The calculation presented in this study will take into account the experimentally measured diffusion coefficients of Sm into SmCo$_5$ phase [24–26] and the Sm–Co phase diagram [27]. One of the aims of the present study is achieving a clear and succinct description of the kinetics of heat treatment, with mathematics as simple as possible.

2. Theory—kinetical analysis of the heat treatment

2.1. The diffusion length: estimation for isothermal and non-isothermal kinetics

One can compare the result or the effect of an isothermal annealing treatment with that of a continuous cooling one by means of their respective diffusion lengths.

The diffusion length, λ_I, of an isothermal heat treatment carried out at a temperature T_I for a time equal to τ_I is given by [28,29]:

$$\lambda_I = \sqrt{6D(T_I)\tau_I} \tag{1}$$

Alternatively, the time necessary to achieve a certain result, i.e., a certain diffusion length, in an isothermal heat treatment is:

$$\tau_I = \frac{\lambda_I^2}{6D(T_I)} \tag{2}$$

A simple kinetic formulation: the additivity principle [30] can be used to determine the diffusion length of a continuous cooling treatment in which the specimen was cooled from an initial temperature T_0 down to T_I in a cooling time equal to τ_C. The diffusion length of such a continuous cooling treatment is going to be equal to the diffusion length of an isothermal treatment carried out at a temperature T_I for a time equal to τ_I if:

$$\int_{t=0}^{t=\tau_C} \frac{\mathrm{d}t}{\tau_I(T)} = 1 \tag{3}$$

In the above equation $t = 0$ corresponds to $T = T_0$ and $t = \tau_C$ corresponds to $T = T_I$. Inserting Eq. (2) into Eq. (3) and assuming that the cooling rate is constant:

$$\int_{T=T_0}^{T=T_I} D(T)\,\mathrm{d}T = \frac{\lambda_I^2}{6}\left(\frac{T_0 - T_I}{\tau_C}\right) \tag{4}$$

The effect of the isothermal and continuous cooling treatments will be the same for a ratio of the isothermal time to the cooling time equal to:

$$\frac{\tau_I}{\tau_C} = \frac{\int_{T=T_0}^{T=T_I} D(T)\,\mathrm{d}T}{D(T_I)\,(T_0 - T_I)} \tag{5}$$

If, instead of continuous cooling a step-cooling heat treatment is used a similar expression is obtained:

$$\frac{\tau_I}{\tau_C} = \frac{\sum_{i=1}^{i=n} D(T_i)}{nD(T_I)} \tag{6}$$

where $T_1 = T_0$ and $T_n = T_I$. Eq. (6) is valid if the specimen is cooled in n isothermal steps and remains at each temperature for the same time.

Another possibility is to use a combination of continuous cooling followed by an isothermal heat treatment. Supposing that the cooling time is Δt_C and the isothermal time is Δt_I, the total heat treating time, τ_{CI}, can be written as:

$$\tau_{CI} = \Delta t_C + \Delta t_I \tag{7}$$

The additivity principle gives:

$$\int_{t=0}^{t=\Delta t_C} \frac{\mathrm{d}t}{\tau_I(T)} + \frac{\Delta t_I}{\tau_I(T_I)} = 1$$

The ratio of the combined heat treating time to the isothermal treatment is:

$$\frac{\tau_I}{\tau_{CI}} = \frac{1}{D(T_I)\,(T_0 - T_I)}\left(\frac{\Delta t_C}{\tau_{CI}}\right)\int_{T=T_0}^{T=T_I} D(T)\,\mathrm{d}T + \frac{\Delta t_I}{\tau_{CI}} \tag{8}$$

The diffusion length in this case is given by:

$$\lambda_I = \sqrt{6}\sqrt{\left(\frac{\Delta t_C}{T_0 - T_I}\right)\int_{T=T_0}^{T=T_I} D(T)\,\mathrm{d}T + D(T_I)\,\Delta t_I} \tag{9}$$

3. Discussion

3.1. Test of theory: Microstructure of a SmCo5 magnet

The theory will be tested taking into account the diffusion coefficient of Sm in $SmCo_5$ determined by Kimura et al. [26], that is similar to that measured by other authors [24,25]:

$$D(T) \, (m^2/s) = 6.9 \times 10^{-5} \exp\left(-\frac{220000 \, (J/mol)}{RT}\right) \quad (10)$$

For this case: $T_0 = 1150\,°C$, $T_I = 850\,°C$, $\Delta t_C = (1150–850)/2 = 150\,min$, $\Delta t_I = 150\,min$, so that Eq. (9) gives $\lambda_I = 86.2\,\mu m$.

The microstructure of a $SmCo_5$ magnet is shown in Fig. 1. This diffusion length can be compared with the mean intercept length of the matrix phase that can be found with the following expression [31]:

$$\lambda_{matrix} = 4\left(\frac{1 - V_V}{S_V}\right) \quad (11)$$

where V_V is the volume fraction and S_V the surface density, i.e., the phase–interface area. V_V and S_V of the second phase can be determined by standard quantitative metalography techniques [31]. A typical micrograph of a $SmCo_5$ magnet [3,4,23] is shown in Fig. 1. The value for λ_{matrix} measured in the sample shown in Fig. 1 is $45\,\mu m$, that is compatible with the value of $86.2\,\mu m$ calculated for the diffusion length (from Eqs. (9) and (10)). This value should be also compared with the average grain size for these magnets, $\sim 10\,\mu m$. The higher value for the calculated diffusion length can be interpreted as follows: the time of heat treatment is more than the necessary time for completing the diffusion process and, thus, attaining high coercivities.

A very important conclusion that arises from this kind of comparison is that the "diffusion length of rare-earth" can be used, in principle, as a parameter to be compared with coercivity.

3.2. Comparison with literature data: why the "non-isothermal" heat treatment is the most efficient?

Now, it is interesting to compare the time necessary to achieve a certain result, reported by Martin et al. [1]: a "step-cooling" from 1100 to 850 °C, just 3 h for $SmCo_5$ allows intrinsic coercivity $\mu_{0i}H_c \sim 2.0\,T$, while isothermal 50 h at 850 °C would lead to a coercivity $\mu_{0i}H_c$ of only $\sim 1.5\,T$ [1]. Other authors [5,8] also indicate that a slow cooling is a better procedure to get high coercivities in $SmCo_5$ magnets. So, why is the "non-isothermal" heat treatment the most efficient?

For $T_0 = 1373\,K$ and $T_I = 1123\,K$ assuming continuous cooling gives (Eq. (5)):

$$\frac{\tau_I}{\tau_C} = 18.7$$

If the specimen is cooled in six isothermal steps: 1373, 1323, 1273, 1223, 1173 and 1123 and remains the same length of time, 30 min (1800 s) at each step (i.e. the procedure employed by Martin et al. [1]) (Eq. (6)):

$$\frac{\tau_I}{\tau_C} = 22.5$$

Therefore, the isothermal annealing time at $T_I = 1123\,K$ has to be roughly 20 times the continuous cooling time for $T_0 = 1373\,K$ for both treatments to produce the same result. This is in excellent agreement with Martin et al. [1] who found a similar ratio of $50/3 \cong 17$.
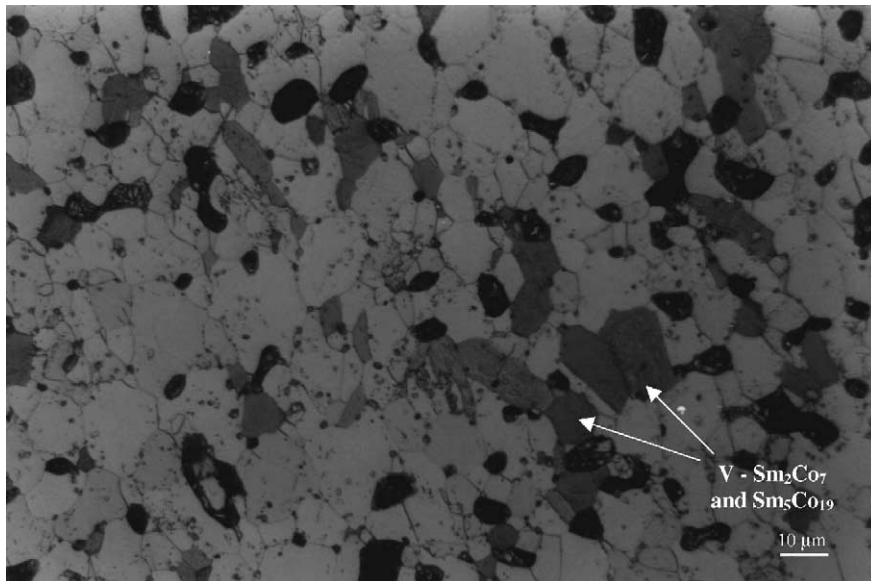

Fig. 1. Microstructure of a $SmCo_5$ magnet, with coercivity $\mu_{0i}H_c$ equal to 3.55 T. The volume fraction of the phase **V** (Sm_2Co_7 and Sm_5Co_{19}) [3,4] is around 12%. The heat treatment comprises cooling 1150–850 °C, at 2 °C/min + 2 h and 30 min at 850 °C.

3.3. Would the coercive field be related to the diffusion length of rare-earth atoms?

Some authors have presented curves of coercive field as function of heat treatment temperature [6,7]. These curves show continuous increase of coercivity when temperature is decreased. Thus, it is possible, in an empirical way, obtaining curves of coercivity as function of time and temperature of heat treatment. However, it should be added that grain size is another variable with enormous effect on coercive field [32]. The effect of this variable needs be considered for case of comparison with experimental data.

Excluding the effect of the grain size, the same principle, the rare-earth diffusion length could be compared with the coercivity and, thus, be applied for describing, in a phenomenological way, $_iH_c(t, T)$ (where t is time and T the temperature).

In the case of $SmCo_5$, the lower limit temperature for heat treatment is $850\,°C$ (because the drastic decrease of coercivity under 750–$800\,°C$, effect attributed to the eutectoid decomposition of $SmCo_5$ phase [23,33–35]).

3.4. Application of this methodology for other cases (Sm_2Co_{17}-based magnets and NdFeB magnets)

The method of analysis described in this paper suggests, for a given thermal cycle—where temperature and time are processing variables—the comparison of the coercivity with the rare-earth diffusion length, which can also be related with possible phase transformations involved in this process.

But, another possibility could be, in a more direct way, trying to relate the amount of rare-earth atoms in a supersatured matrix with the coercivity. For instance, the same reasoning applied for $SmCo_5$ magnets could be, in principle, tested for NdFeB magnets, in this case supposing the expulsion of Nd atoms from a matrix ($Nd_2Fe_{14}B$) supersaturated in Nd [4]. This may also apply for $Sm(CoCuFeZr)_z$ magnets based on Sm_2Co_{17} phase, since it is a possible supposition that at least part of the increase of coercivity can be related to the expulsion of Sm atoms from a supersaturated in Sm $Sm_2(Co, Fe)_{17}$ matrix phase towards $Sm(Co, Cu)_5$ cell boundary phase. But, the case of $Sm(CoCuFeZr)_z$ is more difficult to study, because at same time there are diffusion of the other alloying elements: Cu, Fe, Zr, as it is discussed below.

3.4.1. Case of Sm(CoCuFeZr) magnets based on Sm_2Co_{17} phase

The two main microstructural constituents in $Sm(CoCuFeZr)_z$ magnets are 2:17 phase $Sm_2(Co, Fe)_{17}$ and 1:5 cell boundary phase $Sm(Co, Cu)_5$. It should be noted that it was already reported that $Sm(CoCuFeZr)_z$ magnets present some microstructural change between homogenization ($\sim800\,°C$) and final heat treatment ($\sim400\,°C$) temperatures: an increase of Cu content inside the $Sm(Co, Cu)_5$ phase [12]. Some intrinsic properties of $Sm(Co, Cu)_5$, like magnetization of saturation, constant of anisotropy K_1, and Curie temperature

are reduced when Cu increases and this, no doubt, has effect on the coercivity. In an extreme case, if the Cu content inside $Sm(Co, Cu)_5$ is sufficiently high, this phase become paramagnetic and an "insulating effect" is expected [36]. In this situation, there are islands of $Sm_2(Co, Cu)_{17}$ phase separated by a paramagnetic $Sm(Co, Cu)_5$. Then, these magnets would be better classified as nanocrystalline nucleation-controlled magnets [11,37].

It is fortuitous to add that the reasoning described further in this section only applies if the $Sm(CoCuFeZr)_z$ magnets are nucleation controlled magnets. Indeed, recent studies have provided evidence in favor of the nucleation controlled hypothesis [11,37].

Thus, let suppose that part of the overall effect of the heat treatment on the coercivity can be related to the expulsion of Sm from a supersatured matrix $Sm_2(Co, Fe)_{17}$. Taking the diffusion coefficient of Sm in Sm_2Co_{17} determined by Kimura et al. [26]:

$$D(T)\,(\text{m}^2/\text{s}) = 1.17 \times 10^{-3} \exp\left(-\frac{265000\,(\text{J/mol})}{RT}\right) \tag{12}$$

For a continuous cooling, from 800 down to $400\,°C$ during 6 h, the estimated rare-earth diffusion length is $1.17\,\mu m$, according to Eq. (9). This is compatible with the microstructure of the $Sm(CoCuFeZr)_z$ magnets, because the 2:17 grains are nanometric ~100–$200\,nm$ [11,12]. This small distance should favor attaining high coercivities after the continuous cooling heat treatment.

In the case of the $Sm(CoCuFeZr)_z$ (with $z = 7$–8) magnets, the maximum coercivity is obtained near $400\,°C$ [9–12], after long time of continuous-cooling heat-treatment starting at ~800–$850\,°C$: 6 h [9] up to 20 h [10], depending on the reference. This long time suggests that mechanism similar to that presented to explain the coercivity increase in $SmCo_5$ is taking place.

Now, it is also important to note that the "rare-earth diffusion length" determined for $Sm(CoCuFeZr)_z$ magnets is much smaller than for $SmCo_5$ magnets. In fact, it is around 10^2 higher for $SmCo_5$ type magnets. This is compatible with the grain size of the matrix of these magnets, that is $\sim100\,nm$ for $Sm(CoCuFeZr)_z$ and $\sim10\,\mu m$ for $SmCo_5$ type magnets.

3.4.2. Case of NdFeB magnets based on $Nd_2Fe_{14}B$ phase

In the case of NdFeB, the maximum coercive field is also obtained at low temperatures, near $600\,°C$ [13–15]. Some authors [13–15] have shown that, at an intermediate temperature (~850–$900\,°C$), the $_iH_c$ is intermediate between those for $1080\,°C$ (sintering temperature) and $600\,°C$ (heat treatment temperature). Thus, the same reasoning applied for $SmCo_5$ could also be employed for this case.

In this case the relevant diffusion length for modeling the kinetics of heat treatment could be the kinetics of expulsion of Nd atoms from $Nd_2Fe_{14}B$, towards, probably, the Nd-rich phase [4].

It has been reported that $Nd_2Fe_{14}B$ phase has a very small homogeneity range [38], and thus, the Nd in the supersatured matrix at sintering temperature would be very small. This could cause some difficulties when applying for NdFeB the same reasoning proposed for $SmCo_5$.

The data in literature [38–41] is controversial about the extension of the homogeneity range of $Nd_2Fe_{14}B$ phase. The data of Buschow et al. indicates some variation of lattice parameters and Curie temperature T_c [38] in the $N_2Fe_{14}B$ phase. According to Chin and coworkers [39,40], the homogeneity range of $Nd_2Fe_{14}B$ is significant. Variations found in the Curie temperature of Nd–Fe–B and Pr–Fe–B alloys with different compositions [41] also indicate that the 2:14:1 compound is non-stoichiometric. It seems that more experimental studies are necessary to clarify this question.

The solubility of an element in a given phase maybe small, in such a way that does not exceed the width of a line in the phase diagram, but is not zero. Thus, all compound exhibits solubility. For a regular solid solution, the maximum concentration of a solute can be described with a function of type $C \exp(-Q/RT)$, where C is a constant (supposed almost independent of the temperature) related to entropy variation ΔS, Q is an enthalpy change and R a universal constant. Thus, it is expected that the solubility of an element in a given phase increases exponentially with the temperature. In analogous way, the vacancy equilibrium concentration also tends to increase exponentially with the temperature.

As the above reasoning, the hypothesis that the coercivity may be directly related to the expulsion of the rare-earth atoms from a supersatured matrix can be considered valid, even for a compound where the homogeneity range is believed to be small, like $Nd_2Fe_{14}B$.

But, even if the solubility of Nd into $Nd_2Fe_{14}B$ is very small and the matrix is not supersatured with Nd, the diffusion of the large rare-earth atom Nd should have important contribution about the kinetics of the elimination of the equilibrium lattice defects, that might exist at the sintering temperature.

4. Conclusions

A parameter named "diffusion length of rare-earth atoms" is introduced as a tool to study the kinetics of the heat treatment in rare-earth magnets.

The "diffusion length of rare-earth atom" determined from diffusion equations is compatible with the diffusion length found from microstructure. The "diffusion length of rare-earth atom" can be used as a parameter to be compared with coercivity.

The process of elimination of excess rare-earth atoms, i.e. solute atoms from a supersatured matrix, was modeled. The results indicate that the kinetics of elimination of solute atoms from a supersatured matrix (in this case, Sm from $SmCo_5$) is similar to the kinetics of the coercivity increase.

The results reported by Martin et al. [1] and others [5–8,19], about the dependence of coercivity on the temperature and time of heat treatment could be explained in terms of the presented "diffusion length of rare-earth atoms" model.

The obtained results also give support for the thesis that the coercivity increase due to heat treatment is related to elimination of the equilibrium lattice defects, after annealing at lower temperatures.

Similar kind of analysis can be used for the optimization of the heat treatment procedure for $Sm(CoCuFeZr)_z$ and NdFeB magnets.

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