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Modeling of alloy composition and TMT on magnetic properties of Fe–28Cr–15Co–1Si alloy

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Abstract
In this work, the effects of the alloy composition in a Fe–28Cr–15Co–1Si permanent alloy on the magnetic properties of the prepared alloys were evaluated. The study not only paid particular attention to the concentration and type of additive (Mo and Ti) but also investigated the effect of thermomagnetic treatment temperature. A user-defined design related to response surface methodology was applied to model the effect of the mentioned parameters and optimize the magnetic performance. Two models fitted with experimental data obtained from Br and Hc measurement. The optimum conditions were determined at $T = 645 \ ^\circ\text{C}$ with 3% Mo. According to the derived models, this formulation would give a Magnetic alloy with a magnetic parameters of, $H_c = 18.15 \ \text{kAm}^{-1}$ and $B_r = 0.87 \ \text{T}$ during TMT treatment. The magnetic properties of sample in optimum condition after step aging obtained as $B_r = 0.98 \ \text{T}$ and $H_c = 67.66 \ \text{kAm}^{-1}$.

1. Introduction

Fe–Cr–Co permanent magnets have recently attracted again more attention in application such as magnetic sensors, telephone receivers, hysteresis motors, rotor for high-speed motors, aircraft magnetos etc, because of a combination of excellent ductility and good magnetic properties [1–5]. They are also appropriate for use in high working temperatures because of their high Curie temperature of $\sim 650 \ ^\circ\text{C}$ [6]. According to the previous research the excellent magnetic performance of Fe–Cr–Co alloys caused by the spinodal decomposition $\alpha$ phase at high temperature [6–10].

There is a miscibility gap in the Fe–Cr–Co ternary phase diagram. A spinodal decomposition of $\alpha$–solid solution into two Fe-Co rich ferromagnetic ($\alpha_1$) and Cr rich weakly-magnetic or paramagnetic ($\alpha_2$) phases, produces magnetic properties in the Fe–Cr–Co alloys [11–15]. The size, aspect ratio, orientation, interconnection and volume fraction of spinodal phases are all critical factors affecting the magnetic properties [16]. Literature review revealed that modification of the composition of alloy and the optimization of processing parameters are two approaches for improvement of Fe–Cr–Co based magnets. Addition of ferromagnetic forming elements such as Mo, V, Nb and Ti to Fe–Cr–Co alloys improve the hysteresis properties [16–20]. Optimization of the heat treatment conditions is also very effective in improving spinodal decomposition and thus increasing $H_y$ and $B_r$ of the magnets [21, 22].

The Fe–Cr–Co alloys during recent years have been studied constantly, but to the best of our knowledge the effect of Mo and Ti content effects during different heat treatment conditions did not evaluated. In the present work, a hard Fe–28Cr–15Co–1Si magnet has been developed through casting technique and effect of Ti and Mo additions and TMT parameters on hysteresis properties have been investigated. By using a response surface methodology (RSM), the Modeling and optimizing of the responses to achieve maximum magnetic performance have been conducted.

2. Experimental procedure

2.1. Materials and methods

Alloy ingots of Fe–28Cr–15Co–1Si–xM (wt%), M = Ti and Mo, x = 1, 2, 3 were prepared from 99.9% pure raw materials by melting the components together in a vacuum induction furnace (VIM), and casting in an alumina
tube (~26 mm diameter). Chemical composition of ingots were characterized by a wet chemical method and the results are shown in table 1. For chemical analyses, samples of each alloy were digested in hydrochloric and nitric acid mixture and then subjected to inductively coupled plasma spectrometer (ICP) using an ICP model Thermo Icap6300.

Magnetic samples with 9.6 mm diameter and 4.6 mm height were prepared by cutting the cast ingots using a wire cutting technique and subjecting the specimens to sequences of heat treatments. The heat treatment procedure is divided into three stages: (1) solution annealing for 2 h at 1250 °C followed by a rapid quenching in water in order to obtain a single phase with a BCC structure, (2) applying a thermomagnetic treatment (TMT) at a temperature range of 620 °C–680 °C in a magnetic field of ~240 kA m⁻¹, and (3) step-aging at 600 and 580 °C for 2 and 4 h respectively, in an attempt to develop permanent magnetic properties in the samples. The schematic of heat treatment cycle is shown in figure 1. Microstructural examinations were carried out using a NIKON optical microscope and a VEGA TESCAN scanning electron microscope (SEM). The magnetic properties were examined at room temperature using a MAGNET PHISIK - C-300 type permeameter. The density of all sample was the same and it was found around 7.80 ± 0.02 g cm⁻³.

2.2. Experiments design
Designing experiment and creating mathematical relationships through statistical analyzing can be obtained by response surface methodology (RSM). Recently this method have been used by many researchers to optimize and modeling of many engineering field [23–25]. The User-Defined design was employed as experiments design technique with 40 run experiments. The additive types were considered as categorical factor and TMT temperature and additive content input as the numeric factors. The obtained Hc and Br were the output responses. The levels, actual and coded values of parameters are presented in table 2. Also table 3 listed the experiments and obtained results.

Table 1. Chemical composition of cast alloys (wt%) determined by an ICP.

| Alloy designation | Cr   | Co   | Si   | Mo   | Ti   | Fe   |
|-------------------|------|------|------|------|------|------|
| A                 | 27.95| 15.02| 0.98 | —    | —    | Rem  |
| M1                | 28.1 | 14.90| 1.02 | 1.05 | —    | Rem  |
| M2                | 27.93| 15.15| 1.08 | 2.07 | —    | Rem  |
| M3                | 27.90| 15.12| 0.99 | 3.04 | —    | Rem  |
| T1                | 28.08| 14.95| 1.06 | —    | 0.98 | Rem  |
| T2                | 28.12| 14.97| 0.95 | —    | 2.09 | Rem  |
| T3                | 27.89| 15.10| 0.97 | —    | 3.06 | Rem  |
3. Result and discussion

3.1. Constructed model equation
Using multiple regression analysis, the experimental results (table 3) were fitted to a full quadratic model for Hc and Br value. The regression coefficients for the selected terms in the model were determined and found to be
This analysis enabled a model equation for $H_c$ and $B_r$ to be determined which included expressions for TMT temperature ($A$), additive percentage ($B$) for each additive as shown below:

For Ti additive:

$$H_c = -2089.63 + A(6.51) - (2.56)B + (7.61)^{-3}AB - (5.05)^{-3}A^2 - 0.18B^2$$

$$B_r = -77.29 + 0.24A - 0.11B + 3.32^{-4}AB - 1.89^{-4}A^2 - 0.01B^2$$

For Mo additive:

$$H_c = -2107.99 + A(6.54) - (2.09)B + (7.62)^{-3}AB - (5.05)^{-3}A^2 - 0.18B^2$$

$$B_r = -76.59 + 0.24A - 0.07B + 3.32^{-4}AB - 1.88^{-4}A^2 - 0.01B^2$$

### 3.2. Optimization studies and effect of evaluated parameters

The significance of the adopted model demonstrates by normal probability plot of residuals for responses as shown in figure 2. It demonstrates that the distribution of the residuals was normal type, and it nearly track a direct line. Figure 3 shows that the predicted responses compatible with the measured values. The 1:1 line has a slope about 1 and results are distributed uniformly and made a 45° angle with the x axis.

To compare the effect of parameters at a specific point in the design space, the perturbation plots can be used. According to figure 4, by increasing TMT temperature until the center point, the $H_c$ and $B_r$ values increase up to a maximum amount and then decreases for Mo additive the responses values increase up to maximum amount.
Hereafter, to illustrate significantly the influence of temperature and additive effects on Hc and Br, contour and 3D plots were provided in figures 5 and 6, for Ti and Mo respectively. Here, the full range of two parameters at the same time can be demonstrated and the figures were drawn for responses in terms of additive contents and TMT temperature. As it shown the magnetic performance parameters (Hc and Br) increased with increasing additive contents and TMT temperature. But this trend for TMT temperature continue to center point of temperature change. Additionally this trend is the same for Ti content but for Mo increased in 3% Mo. That shows that Mo significantly shows better influence for Magnetic performance. In the Fe-Cr-Co based alloys the optimal TMT temperature depends on the shape of the miscibility gap and the Curie temperature of the alloys. It is reported that in the alloys with 21–30 wt% Cr, the optimal TMT temperature is close to their Curie temperatures [26]. Both Hc and Br values increase by increasing the temperature up to 640 °C and then decrease with further increasing the temperature. It is reported that the increase of TMT temperature (decrease of undercooling) leads to an increase in the spinodal wavelength, which is related to the particle size of α1 phase [22]. The increase in length and aspect ratio of α1 phase reaches to their maximum values when TMT temperature is ~640 °C. Reduction in magnetic properties at higher TMT temperatures, might be related to tendency to spheroidization of the α1 particles due to reduction in surface energy.

The optimum conditions were established from the mathematical models. To get the maximum Hc and Br parameters as magnetic performance, the optimum condition was selected using Design-Expert 8 as shown in figure 7. It can be seen that the optimum condition was achieved at 645 °C TMT temperature and 3% Mo.

Figure 4. Perturbation plot showing the effect of the evaluated parameters on the Br and Hc.
additive content with 0.925 desirability. In the optimum condition, the amount of $H_c$ and $B_r$ were equal to 18.14 KA m$^{-1}$ and 0.87 T, respectively.

3.3. Materials characterization in optimum conditions

After conducting optimization, the sample in optimum conditions, have been prepared for more comprehensive study. As it mentioned before the TMT temperature and additive content and type have been optimized. So the sample named M3 with 3% Mo and in 645 °C TMT temperature (named M3) have been prepared. The Magnetic properties of the alloy M3 after different stages of heat treatment are listed in table 4. As it can be seen the magnetic properties of sample in optimum condition are better than predicted value and this is show the model validity.

As it can be seen the magnetic properties of this alloy are very low in as-cast and in solution annealed conditions but are significantly enhanced to $B_r = 0.93$ T, $H_c = 18.29$ kA m$^{-1}$ by applying TMT. After step aging, they are further increased to $B_r = 0.95$ T, $H_c = 54.13$ kA m$^{-1}$, and $B_r = 0.98$ T, $H_c = 67.66$ kA m$^{-1}$ after 1st and 2nd stage of aging heat treatments, respectively. Thus, TMT seems to be important sequence in development of the magnetic properties. At TMT, the spinodal decomposition takes place and the $\alpha_1$ phase is formed in the direction of applied magnetic field [27]. According to Stoner and Wohlfarth model [28], the critical field for magnetization reversal of an aligned set of strongly magnetic $\alpha_1$ particles in a weakly magnetic $\alpha_2$ matrix is given by the relation (5).

$$H_{c1} = P(1 - P)(Nb - Na)(J_{s1} - J_{s2})^2 / \mu_0 J_s$$

where $P$ is the volume fraction of $\alpha_1$ phase, $J_{s1}$ and $J_{s2}$ are the saturation magnetic polarizations of $\alpha_1$ and $\alpha_2$ phases, respectively, $N_a$ and $N_b$ are the demagnetizing factors of $\alpha_1$ particles along the a and b axes, respectively, and $J_s$ is the saturation polarization of the alloy [29].
The difference between $J_{\alpha_1}$ and $J_{\alpha_2}$, i.e. $(J_{\alpha_1} - J_{\alpha_2})$, is small after thermomagnetic treatment, thus the value of $H_c$ at this stage is low (19.29 kA m$^{-1}$). During the step aging treatment, the chemical compositions of the two phases ($\alpha_1$ and $\alpha_2$) are changed. Therefore, the increase in coercivity during step aging could be associated with a change in composition of $\alpha_1$ and $\alpha_2$ phases, which results in an increase in $J_{\alpha_1} - J_{\alpha_2}$ [30].
For demonstrating effect of Mo on microstructure, the alloy with 0% Mo (named Alloy A) have been choose as second alloy for microstructure study. Figure 8, shows the optical microstructure of alloy A in the as-cast and solution annealed states. In as-cast condition the alloy shows a dendritic structure. After solution annealing the microstructure consists of coarse grains of α phase with a small amount of unwanted non-magnetic γ phase at grain boundaries. The average grain size of α phase was measured to be ~470 μm. Furthermore some dark precipitates were observed inside the grains of α solid solution. Figures 9(a), (b) shows the SEM images of the precipitates. The energy dispersive spectroscopy (EDS) analysis of the precipitates (figure 9(c)) revealed them as Cr–rich particles which could be Cr$_{23}$C$_6$ and Cr$_2$N inclusions.
The microstructure of alloys A and M3 in the solution annealed state are presented in figures 10(a) and 10(b), respectively. The Mo addition, increases the kinetics and strain energy of decomposition and leads to the development of shape anisotropy in ferromagnetic rich $\alpha_1$ particles, which in turn improves the magnetic properties of the alloys. Carbon and nitrogen are $\gamma$-forming elements that can be introduced from the raw materials or atmosphere. The addition of Mo suppressed the formation of non-magnetic $\gamma$ phase (figure 10). The average grain size of $\alpha$ phase in A and M3 alloys was measured as around 470 and 515 $\mu$m respectively.

The XRD pattern obtained for the specimen of alloy A in the solution annealed state is shown in figure 11. A (110) peak broadening takes place by Mo addition. In the Fe–Cr–Co based alloys, due to little differences between the lattice parameters of $\alpha_1$ and $\alpha_2$ phases, the strain energy resulting from the spinodal decomposition is low. However, in the Mo containing alloys, Mo concentrates mainly in the $\alpha_2$ phase and increases the difference between the lattice parameters of the spinodal phases which increases the strain energy of decomposition and thus the peak broadening occurs. The peak profile of (110) reflection in the Ti containing alloy T2 is even higher than alloy M3. Furthermore, the presence of a sideband

![Figure 10. Microstructure of alloys (a) A and (b) M3 in the solution annealed condition.](image1)

![Figure 11. XRD pattern of alloy A in the solution annealed state.](image2)

| Heat treatment | $B_r$ (T) | $H_c$ (kA m$^{-1}$) |
|----------------|----------|---------------------|
| As-cast        | 0.07     | 1.27                |
| Solution treatment | 0.15   | 1.59                |
| TMT            | 0.93     | 18.29               |
| Aging- step1   | 0.95     | 54.13               |
| Aging- step2   | 0.98     | 67.66               |

The microstructure of alloys A and M3 in the solution annealed state are presented in figures 10(a) and (b), respectively. The Mo addition, increases the kinetics and strain energy of decomposition and leads to the development of shape anisotropy in ferromagnetic rich $\alpha_1$ particles, which in turn improves the magnetic properties of the alloys. Carbon and nitrogen are $\gamma$-forming elements that can be introduced from the raw materials or atmosphere. The addition of Mo suppressed the formation of non-magnetic $\gamma$ phase (figure 10). The average grain size of $\alpha$ phase in A and M3 alloys was measured as around 470 and 515 $\mu$m respectively.

The XRD pattern obtained for the specimen of alloy A in the solution annealed state is shown in figure 11. As expected, the microstructure of this alloy consists of a BCC $\alpha$ phase. Figure 12 shows the peak profile of (110) reflection in A, M3 and T2 alloys after TMT. A (110) peak broadening takes place by Mo addition. In the Fe–Cr–Co based alloys, due to little differences between the lattice parameters of $\alpha_1$ and $\alpha_2$ phases, the strain energy resulting from the spinodal decomposition is low. However, in the Mo containing alloys, Mo concentrates mainly in the $\alpha_2$ phase and increases the difference between the lattice parameters of the spinodal phases which increases the strain energy of decomposition and thus the peak broadening occurs. The peak profile of (110) reflection in the Ti containing alloy T2 is even higher than alloy M3. Furthermore, the presence of a sideband
alongside the (110) reflection peak is a general characteristic of the spinodal decomposition and is due to periodic fluctuations in composition induced by the spinodal decomposition [27].

4. Conclusion

The effect of additive concentration, types and TMT temperature on magnetic properties of an anisotropic Fe–28Cr–15Co–1 Si alloy were investigated. The obtained important results can be summarized as follow:

Optical microscopy figures revealed that microstructure of solution annealed specimens consists of coarse grains of a body centered cubic (BCC) $\alpha$ phase which was spinodally decomposed into two $\alpha_1$ and $\alpha_2$ phases during the thermomagnetic treatment.

The Mo addition to Fe–28Cr–15Co–1Si alloy increased the strain energy of decomposition by concentrating in the $\alpha_2$ phase and increasing the difference in lattice parameters between $\alpha_1$ and $\alpha_2$ phases, thus led to improvement of magnetic properties.

Temperature in TMT stage is important factors in obtaining the best magnetic properties.

The magnetic properties of sample in optimum condition are better than predicted value and this is show that the obtained models can be applied in generating virtual laboratory before actual application.

The optimum condition was achieved at 645 °C TMT temperature and 3% Mo additive content with 0.925 desirability. In the optimum condition, the amount of Hc and Br were equal to 18.14 KA m$^{-1}$ and 0.87 T, respectively.

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