U.P.B. Sci. Bull., Series B, Vol. 73, Iss. 4, 2011 ISSN 1454-2331

# LOW CURIE TEMPERATURE IN Fe-Cr-Ni-Mn ALLOYS

Alexandru IORGA[1], Mirela M. CODESCU[2], Rami ŞABAN[3], Eros A. PĂTROI[4]

*Studiile şi cercetările experimentale se axează pe realizarea unor aliaje cu temperatură Curie scăzută care să fie utilizate în aplicaţii industriale. Cercetările au avut la baza studii asupra structurii şi proprietăţilor magnetice ale sistemului de aliaje Fe-Ni-Cr şi influenţa Mn asupra temperaturii Curie în aceste aliaje.*

*The study and experimental researches focus on the development of alloys with low Curie temperature that can be use in industry applications. Researches were based on studies of the structure and magnetic properties of Fe-Ni-Cr system alloys and the influence of Mn to Curie temperature in these alloys.*

**Keywords**: low Curie temperature, Fe-Ni-Cr alloys

## 1. Introduction

In this paper, the study and experimental research was focused on the behavior of several Fe-Ni-Cr alloys regarding the influence of Mn on the Curie temperature (Tc). Furthermore, it is important to measure the Curie temperature that determines the transition from the ferromagnetic to the paramagnetic state. The Curie temperature is one of the most important parameters for understanding the magnetic proprieties and the structure of ferromagnetic metallic glasses. We wanted to obtain an alloy with low Curie temperature, that latter will be transfer in practical use. One and the most important practical used until now, is manufacturing an overhead conductor with self protection to the deposit of ice / frost using a material with low Curie temperature [1, 2].

Modern technology allows adjustment of elementary composition to obtain preset values of Curie temperature. Currently, in practice are used mainly Fe-Ni alloys and not so much Ni-Cu or Fe-Ni-Cr. There are also other alloying elements that adversely affect the value of Curie temperatures in this area, the alloying with Ni, as would be Si, Al, Mn. Fe (1043K) and Ni (627K) have higher Curie temperature than Fe-Ni alloy. Around 40wt% of Ni, the Fe-Ni alloy shows a minimum Curie temperature, approximately 573K. Also have been conventionally

[1] PhD student, Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania, e-mail: iorga_alexandru@yahoo.com
[2] PhD Eng., National Institute for R&D in Electrical Engineering ICPE - CA, Bucharest, Romania
[3] Prof., Faculty of Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania
[4] PhD Phys., National Institute for R&D in Electrical Engineering ICPE - CA, Bucharest, Romania

used Fe-Ni alloyed with Cr in England and other countries as a magnetic material with low Curie temperature [1, 3, 4].

Structural and magnetic properties of alloys and compounds were investigated by optical microscopy, SEM, XRD, magnetization measurements, losses and Curie temperature was determined for each alloy separately.

## 2. Experimental

Melting alloying was carried out in controlled atmosphere (Argon) Heraeus furnace with induction heating at 10 kHz, starting from pure elements namely: Cr and Ni electrolytic (bulk resulting from electrolysis), Mn of 99.9% purity and Fe of 99.7% purity. After casting, the alloys were annealed for 3 hours at 1100$^{o}$C, cooling with furnace. Treatment was carried out in controlled atmosphere (Argon) at atmospheric pressure. In the composition Si was added as an alloying element to provide a deoxidation effect of melting and in achieving the crystalline grain by the tenths of percentage remaining in cast developed. The composition of the alloys is presented in table 1.

*Table 1*

**Chemical composition of the investigated alloys**

| Sample index | Chemical composition, wt % |
|---|---|
| MA | $Cr_4\ Ni_{32}\ Fe_{62}\ Mn_{1,5}\ Si_{0,5}$ |
| MB | $Cr_4\ Ni_{33}\ Fe_{62,5}\ Si_{0,5}$ |
| MC | $Cr_{10}\ Ni_{33}\ Fe_{53,5}\ Mn_3\ Si_{0,5}$ |
| MD | $Cr_{11}\ Ni_{35}\ Fe_{53.5}\ Si_{0,5}$ |

For metallographic and SEM investigations of the alloys, the samples were prepared by polishing the surface (sandpaper roughness successively 30, 15, 7, 3, 1 and 0.5 mm), bringing to "mirror" face. After this, the polish surfaced was chemically etched with Mable ($CuSO_4$ + HCl + $H_2O$) [5]. Optical Metallographic investigations of the three alloys were performed with Zeiss microscope and SEM investigations were performed on scanning electron microscope Carl Zeiss Auriga.

The structure investigations were performed also by X ray diffractions (XRD). The XRD were made on Bruker AXS D8 Advance using Mo K$\alpha_1$ radiation, the $\alpha_2$ component being eliminated by the use of a focusing Zr monochromator. This technique removes a major source of uncertainly in this interpretation of the diffraction patterns, namely that due to the extensive overlapping of the main lines and sidebands which results when both $\alpha_1$ and $\alpha_2$ components of K radiation contribute to the formation of the pattern. Also the background is very low and flat in the patterns made with monochromator, and this is of a great importance in obtaining accurate measurements [6].

Intrinsic magnetic properties, those characterized in terms of level size parameters of a magnetic material, are dependent on the elementary chemical composition (primary) thereof, especially its structural condition, defined by structural composition and the infrastructure elements. The fact that the component elements of the Fe-Ni-Cr alloy have close values for atomic weights and ionic radii, and also have cubic cell crystal system, provides a wide range of compositions as single phase, solid solution with atoms of alloying elements in substitution positions [7].

The magnetic measurements performed in this study include determination of the value of coercive field by first magnetization curves, magnetization and loss measurements, especially for measuring the Curie temperature. Curie temperature, were measured on two sample geometries, namely:

- Spherical samples, weighing between 6-8 mg, M = f (t);
- Toroidal samples Ø30 x Ø25 x 5mm, Js = f (T) both cast and annealed.

Curie point measurements made on toroidal samples were performed in closed magnetic circuit Brockhaus device, using a wattmeter and a climate chamber. Samples were wound with an equal number of turns, 70 turns for primary to 30 turns for secondary.

Measurements on spherical samples were performed using MPMS (Magnetically Properties Measurement System) SQUID facility, in 100 Öe magnetic field. For both types of measurements, the temperature range at which the measurements were made was 233K to 410K.

### 3. Results and Discussion

Alloys analyzed by optical microscopy and SEM revealed similar morphological and structural features. In Fig. 1 and 2 are given representative images for features of the structure observed by optical microscopy for the MB and MC alloys. The polished surface of each sample was etched with Marble for 10 seconds before taking this image.

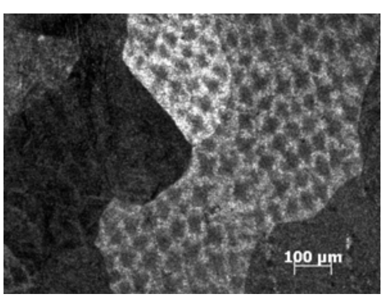

Fig. 1. MB alloy, Marble etching 10 sec.

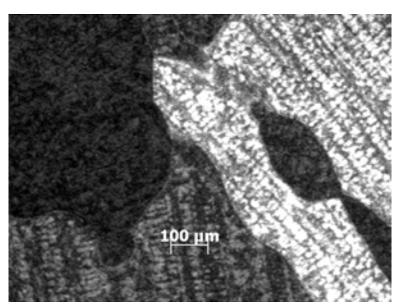

Fig. 2. MC alloy, Marble etching 10 sec.

SEM investigation indicates an homogenization phenomenon resulting from annealing. Thus the development of diffusion processes in solid state, metallic material structure with inter-dendritic segregation will become more homogeneous, typical dendritic appearance decreasing significantly. The most relevant aspect of homogenization is MC alloy microstructure (Fig. 3), the composition which contains the highest amount of Mn (3%).

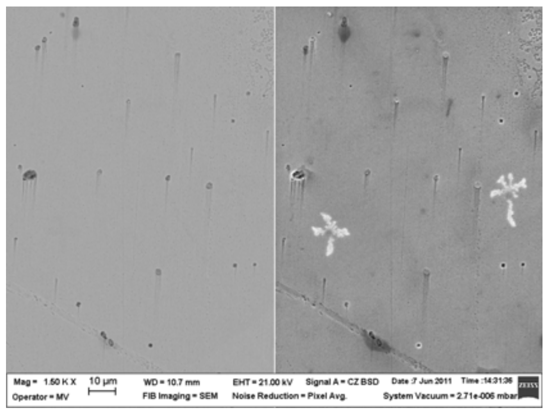


Fig. 3. SEM image of HC sample, non-etched – left, attacked – right (Marble, 10 sec.)

After structural characterization by optical microscopy, according to the SEM and XRD phase diagrams of ternary system Fe-Ni-Cr [8] shows the following aspects: they are all single phase high on large temperature range, from room temperature up to melting point (~ 1723 K). Metallographic constituent type is solid substitution solution. The structure is of type γ, f.c.c., for all alloys examined and the lattice parameter *a*, is synthesized in the range of values determined: a = 3,558 Å / MC alloy ÷ 3.586 Å / MB alloy. It is noted that here γ phase developed with the lattice f.c.c. of primary nickel which has network parameter a = 3.524 Å, and by alloying with Cr, Mn, Fe in solid solution substitution positions f.c.c. the lattice parameters in phase γ increased.

The first magnetization curve plotting (Fig. 4) revealed that no notable differences between the studied alloys and they are soft magnetic materials. Coercive field measured values are small; the results are presented in Table 2.

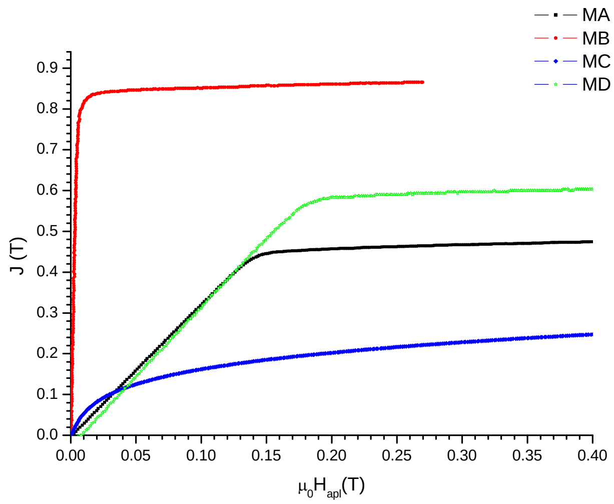


Fig. 4. Magnetization first curves of the studied alloys

*Table 2*

**Magnetic measurement results on spherical samples - coercive field**

| Sample index | Hc [Oe] | ρ [g/cm3] |
|---|---|---|
| MA | 14 | 7,845 |
| MB | 32 | 7,842 |
| MC | 24 | 7,821 |
| MD | 27 | 7,826 |

The Curie temperature Tc is the temperature below which there is a spontaneous magnetization M in the absence of an externally applied magnetic field, and above which the material is paramagnetic. In the disordered state above the Curie temperature, thermal energy overrides any interactions between the local magnetic moments of ions. Below the Curie temperature, these interactions are predominant and cause the local moments to align so that there is a net spontaneous magnetization.

For each alloy two distinctive curves have been plotted, one on spherical samples and the other one on toroidal samples. They have to have a smooth, continuous appearance. The tangents to each curve at the inflexion points will be drawn. Two values of the temperature will be obtained at their intersections with the abscise axis; their mean is the Curie temperature as Fig. 5 and 6 shows for the MC sample.

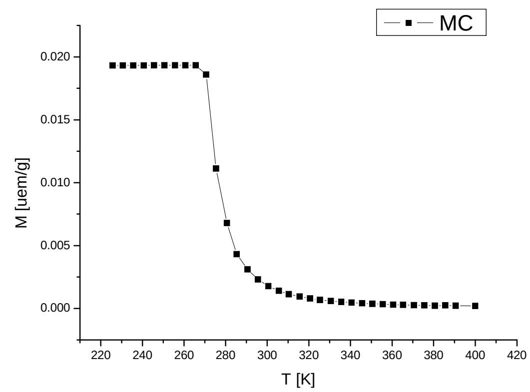


Fig. 5. Graphical representation of M = f (T) for spherical sample MC

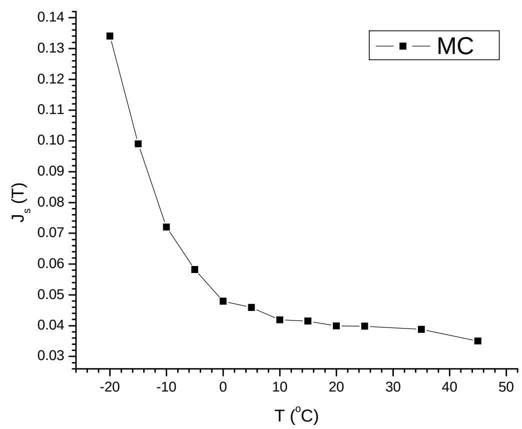


Fig. 6. Graphical representation Js = f (T) for toroidal sample MC

Using the data from the graphs, the obtained values are presented in Table 3.

*Table 3*

**Curie temperature Tc obtained experimentally**

| Sample index | Chemical composition [wt. %] | TC spherical sample [K] | TC toroidal sample [K] |
|---|---|---|---|
| MA | $Cr_4$ $Ni_{32}$ $Fe_{62}$ $Mn_{1,5}$ $Si_{0,5}$ | 328 | 330 |
| MB | $Cr_4$ $Ni_{33}$ $Fe_{62,5}$ $Si_{0,5}$ | 393 | 398 |
| MC | $Cr_{10}$ $Ni_{33}$ $Fe_{53,5}$ $Mn_3$ $Si_{0,5}$ | 283 | 285 |
| MD | $Cr_{11}$ $Ni_{35}$ $Fe_{53,5}$ $Si_{0,5}$ | 339 | 340 |

The two methods for determining the Curie temperature showed similar values with small differences may be due to measurement errors and curves determination or errors of the device. These errors are below 2%, being acceptably low.

## 4. Conclusions

The alloy is single phase and the phase being a solid solution of substitution type γ / f.c.c., is most convenient for obtaining high values of magnetization M and saturation induction Js, obviously taking into account the nature of elements and types of atoms that make it up, in our case Cr, Ni, Fe and Mn.

We found that addition of Mn (+ 2-3%) clearly influence the desired lowering of Tc, with superior efficacy to the addition of Cr. In addition, it is an advantage, for a sum of percentages Cr + Mn ≈ 4 to 6% is more effective and economical alloying only with Cr alone (10-12%), which is ~ 4 times more expensive than Mn.

Curie temperature Tc value depends essentially on the chemical composition and practically does not depend on the material structure. Also, the correlation between composition and Tc, has no linear trend, even within a single phase material. The predictability of Tc parameter is complicated even more because the material has 3 and respectively 4 active magnetic components. This is due to the occurrence of unwanted phases. This led us the number of alloy composition tested, mainly by maintaining one or two elements constant.

Based on those experiments, we propose that by multi-modal modeling to generate solutions of tailoring desired magnetic proprieties. This is desirable especially in the application of magnetic material to reduce costs.

## Acknowledgement

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/6/1.5/S/16.

## R E F E R E N C E S

[1] *T. Kitamura*, Snow-melting Magnetic Material Wire, in Fujikura Technical Review (2003) p.23-25

[2] *T. Todaka, T. Kishino, M. Enokizono*, Low Curie temperature material for induction heating self-temperature controlling system, Journal of Magnetism and Magnetic Materials 320, 2008,p. 702–707

[3] *L. Palii, A. Iorga, M.Codescu, I. Racovitan, I. Ionescu*, Electrical overhead conductor with self-protection at the deposits of ice/frost (Conductor electric aerian de înatlă tensiune

autoprotector la depunerile de chiciura/gheata), Tehnologiile Energiei Magazine, **Vol. 12**, 2010, p.18 – 21

[4] *A. Iorga et al*., Thermo-sensitive magnetic properties in the alloy system Fe-Ni-Cr, Scientific Bulletin of Politehnica Iaşi, **Vol. LVII** (LXI) Fasc. 3, p.195-200

[5] Metallography and Microstructures, **Vol. 9**, ASM Handbook, ASM International, Materials Park, OH, 2005.

[6] *B.D. Cullity*, Elements of X-Ray Diffraction (2nd ed.). Reading, Massachusetts: Addison-Wesley Publishing Company. 1978.

[7] *R. Saban, C. Dumitrescu, M. Petrescu*, Treatise of Science and Engineering Metalic Materials, **Vol. III**, cap. 21 Materiale Magnetice, AGIR 2009

[8] *T.B. Massalski*, Binary alloy phase diagrams, 2$^{nd}$ ed. **Vol. 2**, ASM International, 1737, 1990