acta phys. slov. 40 (1990), No. 5

# RADIATION-INDUCED CHANGES OF THE CURIE TEMPERATURE OF Fe—Ni—Cr—Mo—Si—B GLASSY METALS[1])

MIHALIK, M.,[2]) ZENTKO, A.,[2]) Košice, MACKO, Ľ.,[3]) Liptovský Mikuláš

This paper deals with the influence of neutron irradiation on the Curie temperature and coercivity of $Fe_{30}Ni_{48-x}Mo_2Si_5B_{15}$ glassy metals. It is pointed out that the decrease of the Curie temperature and coercivity is the outcome of the neutron irradiation. These results are briefly discussed in terms of the possible effects of structural and chemical changes in irradiated metallic glasses.

## I. INTRODUCTION

The Curie temperature $T_c$ of Fe—B glassy metals varies with the alloying of some metals. Cr, Mo, V, Mn and Nb cause marked decrease in $T_c$, on the other hand Co, Ni, Pt and Au cause a marked increase in $T_c$ [1, 2, 3]. The results may be interpreted on the basis that the additions have an effect on the chemical short range order (CSRO) of the glassy metals.

Besides, it was recognized that the Curie temperature of ferromagnetic metallic glasses is sensitive to heat treatment. $T_c$ increases with the temperature of heat treatment for the Fe—Ni based glassy metals [4] and decreases for the Fe—Cr ones [5]. Although this change is different, it represents basically the same behaviour, a temperature dependent equilibrium $T_c$. This behaviour can be explained in terms of the changes in CSRO. In Fe—Ni amorphous alloys, a close contact of iron and nickel atoms will raise $T_c$ [6], while in Fe—Cr that of iron and chromium will lower $T_c$ [5]. Recently we have shown that isothermal annealing of $Fe_{40}Ni_{36}Cr_{12}Mo_2Si_5B_{15}$ increases $T_c$ to saturation (about 523 K) [7].

The neutron irradiation procedure can lead to a decrease of the value of spontaneous magnetic polarization and the exchange constant [8] of some glassy metals. The Curie temperature of the Fe—Ni—B amorphous alloys increases

[1]) Contribution presented at the 8th Conference on Magnetism, KOŠICE 29. 8.—2. 9. 1988

[2]) Institute of Experimental Physics, Slovak Academy of Sciences, Solovjevova 47, 043 53 KOŠICE, CSFR.

[3]) Military Technical University of Czechoslovak-Soviet Friendship, LIPTOVSKÝ MIKULÁŠ, CSFR.

with neutron irradiation [10, 11]. Most papers dealing with the irradiation induced changes of the physical properties of metallic glasses refer to two processes from which the irradiation damage of the investigated sample result: displacements caused by high energy $\alpha$ — and Li particles resulting from the capture of thermal neutrons by $^{10}B$ and displacements caused by fast neutrons scattering [11, 12]. But there are more possibilities of the interaction between the neutrons and the irradiated material. These interactions can lead to radiactive gamma-emitter production, which fact offers the possibility of gamma-ray spectrometric investigations.

## II. METHODS AND RESULTS

The glassy metals $Fe_{30}Ni_{48-x}Cr_xMo_2Si_5B_{15}$ ($x = 0, 2, 4, 6, 8, 10, 12$) were prepared in the form of thin ribbons (about 30 μm thick and 6 mm wide) from the melt by a single-roller quenching technique. The as-quenched ribbons (about 7 cm long) were sealed in Al tubes and irradiated in a WWR-S-10 nuclear reactor at Řež. During the incore reactor irradiation these Al tubes were surrounded by water at ~50 °C, therefore the irradiation temperature of specimens did not exceed 100 °C. The samples were not shielded against any part of the neutron spectrum and were exposed to neutron irradiation with the total fluences $5 \times 10^{17}$, $5 \times 10^{18}$ and $1 \times 10^{19}$ neutrons/cm². The intensity ratio of fast to thermal neutrons was 0.9 : 1. For some specimens irradiated to the $5 \times 10^{18}$ n/cm² fluence control specimens were subjected to a corresponding heat-treatment in air at 100 °C and 150 °C without neutron irradiation (see Table 2). X-ray diffractions results showed that all investigated samples were in an amorphous state.

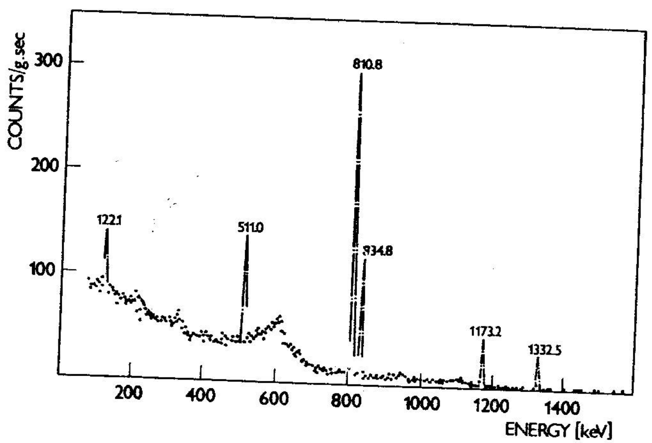


Fig. 1. The gamma spectrum of the specimen with $x = 12$ irradiated with the total fluence of $5 \times 10^{17}$ n/cm².

The gamma-spectra of the irradiated samples have been obtained using a Ge(Li) detector supplied with a multichannel amplitude analyser. Only specimens irradiated with the total fluence $5 \times 10^{17}$ n/cm² have been measured in $2\pi$ geometry (see Fig. 1). Measuring time was 600 s. The total absorption peak efficiency of the detector has been evaluated experimentally. All peaks in the spectrum have been identified by comparison with available published data [14] and quantitatively evaluated.

The Curie temperature was estimated by the transformer method [15]. A current of constant amplitude flowed in the primary coil and the secondary voltage, which is proportional to the initial permeability, was recorded as a function of temperature. We determined the Curie temperature from the point of the intersection of the two broken lines extrapolated as can be seen in Fig. 2. The coercivity was estimated from the quasi-static hysteresis loops (Fig. 4) which were measured at room temperature by means of a magnetization hysteresis loop tracer. The frequency of the magnetic reversal was 0.02 Hz and the maximum value of the magnetic fields was 200 A/m.

Fig. 1 shows the gama spectrum of the sample with $x = 12$ irradiated with the total fluence of $5 \times 10^{17}$ n/cm². The results of the gamma-spectrum analysis are summarized in Table 1. Four nuclear reactions caused by the neutron irradiation procedure have been identified. The most significant of them is the $^{58}Ni(n, p)^{58}Co$ reaction and a subsequent electron capture or an $e^+$-decay of the radioactive $^{58}Co$ isotope. These processes cause a decrease in a number of Ni

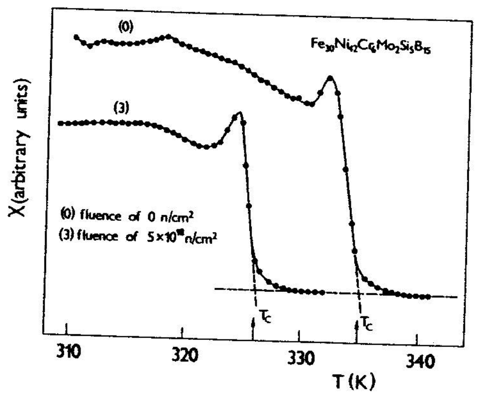


Fig. 2. The initial permeability vs temperature curves. We determined the Curie temperature from the point of intersection of the two broken lines.

Table 1

The results of the gamma-spectrum analysis.

| ENERGY (keV) | NUCLEAR REACTION | RADIOACTIVE DECAY AND PRODUCT | HALF-LIFE | BETA PARTICLE MAXIMUM ENERGY (keV) | NUMBER OF TRANSMUTED NUCLEI ($g^{-1}$) | SAMPLE ACTIVITY (Bq) MEASURED/ /INITIAL |
|---|---|---|---|---|---|---|
| 122.1 | $^{58}Ni(n, d)^{57}Co$ | E : $^{57}Fe$ | 272 d | — | $2 \times 10^{10}$ | 3/9 |
| 511.0 | — | $e^{+} e^{-}$ annih. | — | — | — | 100/8600 |
| 810.8 | $^{58}Ni(n, p)^{58}Co$ | E, $e^{+}$ : $^{58}Fe$ | 70.8 d | 480 | $3.5 \times 10^{13}$ | 710/61600 |
| 634.8 | $^{54}Fe(n, p)^{54}Mn$ | E : $^{54}Cr$ | 312 d | — | $2 \times 10^{12}$ | 280/780 |
| 1173.2<br>1332.5 | $^{60}Ni(n, p)^{60}Co$ | $e^{-}$ : $^{60}Ni$ | 5.27 y | 320 | $4 \times 10^{12}$ | 220/260 |

atoms about 0.01 ppm and a gradual increase in a number of Fe atoms of the same amount. The positrons are emitted with a maximum energy of 480 keV and thermalized by electron collisions. About 50 % of them annihilate in the sample volume.

As can be seen in Fig. 3 (see also Table 2) the Curie temperature decreases with a increase of the chromium content. The neutron irradiation procedure leads to a decrease of the Curie temperature. The higher flux of irradiation was used, the deeper decrease of the Curie temperature was estimated. The Curie temperature is more affected by neutron irradiation in the case of ribbons with a higher chromium content. Neutron irradiation causes no changes of the Curie temperature of the investigated glassy metals with chromium content less than or aqual to 4 %. The annealing procedure (Table 2) leads to the increase of $T_c$.

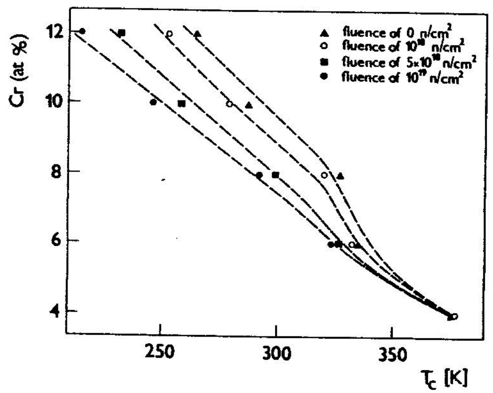


Fig. 3. The neutron irradiation leads to a decrease of the Curie temperature. On the other hand this procedure does not lead to large changes of the Curie temperature of the investigated glassy metals with a chromium content less than or equal to 4 %.

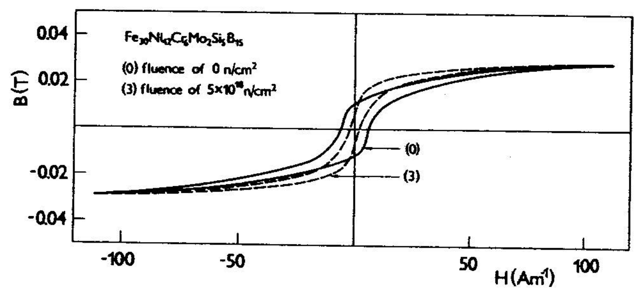


Fig. 4. The hystereses loops for unirradiated and irradiated ribbons. The neutron irradiation procedure leads to a decrease of coercivity.

Table 2

The results of the Curie temperature and coercivity measurements.

| CHROMIUM CONTENT | AS QUENCHED $H_c$(A/m) | AS QUENCHED $T_c$(K) | 100 °C/50 hours $H_c$(A/m) | 100 °C/50 hours $T_c$(K) | 150 °C/50 hours $H_c$(A/m) | 150 °C/50 hours $T_c$(K) | $5 \times 10^{18}$ n/cm$^2$ $H_c$(A/m) | $5 \times 10^{18}$ n/cm$^2$ $T_c$(K) |
|---|---|---|---|---|---|---|---|---|
| 12 | — | 265 | — | 267 | — | 271 | — | 232 |
| 8 | 1.5 | 327 | — | — | — | — | 1.0 | 299 |
| 6 | 5.0 | 335 | 4.5 | 337 | 5.5 | 344 | 1.5 | 326 |
| 4 | 5.5 | 377 | 5.5 | 380 | 5.0 | 388 | 2.0 | 376 |
| 2 | 2.0 | 421 | — | — | — | — | 3.0 | 423 |
| 0 | 10.0 | 472 | — | — | 10.0 | — | 10.0 | 473 |

Fig. 4 shows hystereses loop for unirradiated and irradiated ($5 \times 10^{18}$ n/cm$^2$) ribbons of samples with $x = 6$. It seems that the coercivity increases with a decrease of the chromium content (see Table 2). The annealing procedure does not lead to changes in coercivity. The neutron irradiation procedure leads to a decrease of coercivity.

## III. DISCUSSION

As it was said in the introduction the Curie temperature of amorphous magnetic materials is controlled by several parameters which are related to local structure. It was considered [1] that Cr decreases CSRO by increasing the probability of having non-magnetic atoms as nereast neighbours which, in turn, causes the reduction of $T_c$. The important question is, whether neutron irradiation can lead to changes of the chemical composition. All identified nuclear reactions (see Table 1) lead to the production of new elements, but changes of chemical composition (about 0.01 ppm for $^{58}Ni(n,p)^{58}Co$ reaction) are probably negligible. The decrease in boron concentration (about 0.4 % [10]) obtained during irradiation should also infuence the value of $T_c$. However, Kudo [16] has shown that $T_c$ increases with the boron content decrease in the $Fe_{16}Ni_{59}(B_{1-y}Si_y)_{25}$ amorphous alloys. It therefore sems unlikely that nuclear $^{10}B(n,\alpha)^7Li$ reactions could lead to the observed large decrease of $T_c$ after neutron irradiation.

Changes in the Curie temperature were reported in several previous papers. The increase in $T_c$ about 10 K or 20 K was found in $Fe_{40}Ni_{40}B_{20}$ [10,11] and $Fe_{40}Ni_{40}P_{14}B_6$ [13] neutron irradiated ribbons and in $Fe_{80}B_{20}$, $Fe_{78}Mo_2B_{20}$ and $Fe_{83}B_{15}Si_2$ [9, 13] meltspun ribbons irradiated up to $1 \times 10^{19}$ n/cm$^2$. This increase of $T_c$ was thought to be due to a structural relaxation equivalent to that caused by thermal annealing [9, 13] or to irradiation enhanced clustering of $(FeNi)_3B$ [10, 11]. However, there was pointed out [11] that his clustering should not itself be sufficient to account for the increase of $T_c$ by 10 K. The decrease in $T_c$ of the last three above mentioned alloys was associated with an increase in free volume and disorder or with the transmutation of the $^{10}B$ in the $(n,\alpha)$ reaction [9, 13].

The above mentioned speculations and $T_c$ behaviour after annealing (see Table 2 and [7]) lead us to the following conclusions. The fluxes of neutron irradiation used in this work are sufficient to increase the free volume, to raise the density fluctuation and to decrease a close contact of iron and nickel in $Fe_{30}Ni_{48-x}Cr_xMo_2Si_5B_{15}$ ribbons with $x \leq 4$. The subsequent decrease of CSRO leads to a decrease of $T_c$. It seems that the lower the content of chromium in the ribbons is, the higher flux of neutron irradiation is necessary to the decrease of CSRO, which results in the corresponding decrease of $T_c$.

The hysteresis loop and coercivity of the amorphous alloys are mainly determined by elastic stresses due to defect structure and by distribution of local magnetic anisotropies [17]. For materials which are showing the Curie temperature $T_c$ significantly lower than the crystallization temperature $T_x$, simple non-field annealing at a temperature above the Curie point can relieve internal stresses and after annealing the materials can exhibit a very low coercivity. The decrease of coercivity in our irradiated specimens can hardly be explained only in this way, because our control specimens subjected to a corresponding heat-treatment did not exhibit a decrease of coercivity (see Table 2). On the other hand neutron irradiation can lead to internal stresses in the materials. One of the possible explanations could be a stress-induced anisotropy. But the verification of this possibility needs a more detailed study.

## ACKNOWLEDGEMENT

We would like to thank Dr. P. Duhaj (Institute of Physics, Slovak Academy of Sciences, Bratislava) for the preparation of the amorphous samples. The gamma-ray spectrometric measurements have been performed at the Department of Nuclear Physics of the Comenius University in Bratislava. The authors wish to thank Dr. I. Szarka for his help with these measurements.

## REFERENCES

[1] Walter, J. L., Berkowitz, A. E.: in *Rapidly Quenched Metals*, Eds. S. Steeb, H. Warlimont, Würzburg, 1985, Vol. 2, p. 1303.

[2] Soumura, T., Takeda, K., Terasawa, K., Maeda, T.: J. Magn. Magn. Mat. *58* (1986), 202.

[3] Kedves, F. T., Hordós, M., Potocký, L., Kisdi-Koszó, É., Kováč, J.: phys. stat. sol. (a) *103* (1987), 273.

[4] Liebermann, H. H., Graham, C. D. (jun.), Flanders, P. J.: IEEE Trans. Magn. MAG-*13* (1977), 1541.

[5] Kudo, T., Egami, T., Liebermann, H. H.: in *Rapidly Quenched Metals*, Eds. T. Masumoto, K. Suzuki, Sendai, 1982, p. 1187.
[6] Egami, T.: IEEE Trans. Magn., MAG-*17* (1981), 1600.
[7] Mihalik, M., Zentko, A., Panfilov, A. S., Svechkarev, I. V.: Czech. J. Phys. *B37* (1987), 16.
[8] Škorvánek, I., Zentko, A.: phys. stat. sol. (a) *99* (1987), 275.
[9] Grundy, P. J., Parker, S. F. H., Jones, G. A.: Nuclear Instruments and Methods *209—210* (1983), 421.
[10] Tolouni, B., Kursumovič, A., Cahn, R. W.: Scripta Met. *19* (1985), 947.
[11] Gerling, R., Wagner, R.: J. Nucl. Mater., *107* (1982), 311.
[12] Gerling, R., Schimansky, F. O., Wagner, R.: Scripta Met. *17* (1983), 203.
[13] Grundy, P. J., Jones, G. A., Parker, S. F. H.: IEEE Trans. Magn. MAG-*19* (1983), 1913.
[14] Mednik, I. V.: *Gamma-izlutchenije radionuklidov primeňjajenych v nejtronno-aktivacionom analyze.* Spravotchnik. ZINATNE, Riga, 1983.
[15] Leger, J. M., Loriers-Susse, C., Vodar, B.: Phys. Rev. *B6* (1972), 4250.
[16] Kudo, T.: J. Appl. Phys. *52* (1981), 1797.
[17] Fink-Finowicki, J., Lisowski, B.: in *Summer School on Amorphous Metals*, Eds. H. Matyja, P. G. Zieliński, Wilga, 1985, p. 263.

Received November 1st, 1988
Accepted for publication March 7th, 1989

## ИЗМЕНЕНИЕ ТЕМПЕРАТУРЫ КЮРИ МЕТАЛЛИЧЕСКИХ СТЁКЛ Fe—Ni—Cr—Mo—Si—B ОБУСЛОВЛЕННОЕ ОБЛУЧЕНИЕМ.

В работе изучается влияние нейтронного облучения на температуру Кюри и на коэрцитивность металлических стёкл $Fe_{30}Ni_{48-x}Cr_xMo_2Si_5B_{15}$. Показано что вследствие облучения нейтронами падает как температура Кюри $T_c$ так и коёрцитивность исследуемых образцов. Результаты обслуждаются с точки зрения возможных эффектов структурных и химических изменений в облученных металлических стёклах.