Study of thermal ageing behaviour of Fe-Cr model alloys by magnetic hysteresis loop technique

J N Mohapatra¹, Y Kamada¹, H Kikuchi¹, S Kobayashi¹, J Echigoya¹, D G Park² and Y M Cheong²
¹NDE and Science Research Center, Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka, 020-8551, Japan
²Korea Atomic Energy Research Institute, Yusung, Taejon 305-600, South Korea
E-mail: jnmohapatra@gmail.com

Abstract. Fe-Cr alloys with different Cr content (5-20 wt. %) were prepared by arc melting technique. The alloys were solution annealed at 1050 °C/ 2h and air quenched and then tempered at 750 °C/ 1h followed by air cooling. Thermal ageing was carried at 475 °C for various lengths of time up to 1000 hours (hrs) to produce thermal embrittlement. The hardness and coercivity of Fe-20% Cr alloys were increased and the remanence was decreased, being due to the precipitation of Cr-rich $\alpha'$ phase and their subsequent growth. In Fe-15% Cr and Fe-10% Cr alloys, it was found that the coercivity decreased at the initial ageing period and then increased subsequently due to the competing effect of recovery of dislocations and precipitation of Cr rich phase. The change in magnetic properties in Fe-5% Cr alloy was different than other alloys since it was within the solubility limit of Cr in Fe. A linear relationship was found between the coercivity and hardness in Fe-20% Cr alloy, indicating that Magnetic Hysteresis Loop (MHL) technique would be a good tool for the Non-Destructive Evaluation (NDE) of embrittlement in Fe-Cr alloys.

1. Introduction
Fe-Cr base steels are widely used in nuclear industries due to superior mechanical properties and good resistance to radiation induced swelling [1]. Such alloys undergo embrittlement in temperature range 450-550 °C called as 475° embrittlement, produces hardening due to $\alpha$-$\alpha'$ phase separation [2]. Precipitation of Cr-rich isolated $\alpha'$-phase and their subsequent linkage to form a highly interconnected region largely affect mechanical properties particularly increase the hardness of the material and decrease the toughness [3-9]. Such behavior of phase separation is enhanced under irradiation and produced even at much lower temperature [10, 11]. A change in microstructure of materials alters both the mechanical as well as physical (electrical, magnetic, ultrasonic etc.) properties. Hence a good correlation of the physical properties with mechanical properties which alter due to microstructural modifications will be helpful for the evaluation of material properties in non-invasive way. An in-depth knowledge on mechanism of change in properties and their correlation are needed for the development of NDE based methodologies for the safe operation of the materials in industrial components. Magnetic NDE techniques have been used to evaluate the ageing creep and fatigue behaviour due to its better sensitivity to the microstructural modifications in steels [12-16]. In the
present study, thermal ageing have been carried out in various Fe-Cr alloys to produce the 475°C embrittlement, and magnetic properties and mechanical properties have been found to be correlated to use magnetic technique as a NDE tool for evaluation of embrittlement in nuclear components.

2. Experimental
Fe-Cr model alloys with different Cr (5, 10, 15, 20 wt. %) content were prepared by arc melting technique using Fe with 99.99 % and Cr 99.9 % purity in argon atmosphere. The alloys were solution annealed at 1050 °C/ 2 h followed by air quenching. EDM cutting was used for the sample preparation. Toroid (thick: 2 mm, ID: 10 mm, OD: 15 mm) samples were prepared for the magnetic measurement. All the samples were tempered at 750 °C/ 1h and air-cooled to remove the residual stress generated during air quenching from high temperature. The samples were aged at 475 °C for various lengths of time up to 1000 hrs in high vacuum. Magnetic measurement, hardness measurement and microstructural characterizations were carried out during interruption. The MHL measurements were carried out at a maximum field of 6 kAm⁻¹ and frequency of 50 mHz. Transmission Electron Microscopy (TEM) was used to investigate the microstructural modifications during thermal ageing. An automatic Vickers hardness measurement tester was used to measure the micro-hardness of the samples at a load of 100 g.

3. Results
3.1. Change in properties by tempering
Change in hardness of the Fe-Cr alloys against Cr content before and after tempering is shown in figure 1. The hardness of the alloys was increased with increase in Cr content due to the solid solution hardening. With tempering no significant change in hardness was found.

![Figure 1](image1.png)

**Figure 1.** Change in hardness of the Fe-Cr alloys against Cr content before and after tempering.

The change in coercivity and remanence of the Fe-Cr alloys before and after tempering is shown in figure 2. Before tempering, coercivity of the alloys was increased and a corresponding decrease in remanence was observed with Cr content. After tempering, the coercivity of all the alloys was dropped significantly whereas remanence of the alloys was increased. The result indicated that the difference in coercivity in the four samples before tempering was due to the difference in their thermal stress imposed during air-quenching. The removal of thermal stress after tempering was resulted in drastic decrease in coercivity and increase in remanence in the alloys.

![Figure 2](image2.png)

**Figure 2.** Change in coercivity and remanence of the Fe-Cr alloys against Cr content before and after tempering.
3.2. Change in properties by thermal ageing

Change in hardness of the alloys with ageing time is shown in figure 3. In Fe-20% Cr alloy, it was found that the hardness increased slowly up to 50 hrs of ageing and then increased rapidly. In Fe-15% Cr alloy after 100 hrs hardness was found to increase. However, hardness of Fe-5% Cr and Fe-10% Cr alloys did not show any change with ageing time.

\[ \text{Micro vickers hardness, Hv} \]

\[ \text{Ageing time, t / h} \]

Coercivity and remanence of the alloys with ageing time is shown in figure 4 and figure 5 respectively. In Fe-20% Cr alloy, the coercivity was increased from the beginning of the ageing and the rate of increase was enhanced after 50 hrs of ageing which was very similar to the change in hardness in the alloy. In Fe-15% Cr and Fe-10% Cr alloy the coercivity was decreased initially up to 50 hrs and after that it was increased. The remanence of the three alloys decreased with ageing time whereas the rate of decrease depends on the Cr content. In Fe-5% Cr alloy, the behavior was completely different than the other three alloys. The coercivity was increased from the beginning of ageing and falls down after 50 hrs. There was no significant change in the remanence found in the alloy containing 5% Cr in the entire period of ageing.

\[ \text{Coercivity, Hc / Am}^{-1} \]

\[ \text{Ageing time, t / h} \]

\[ \text{Remanence, Br / T} \]

\[ \text{Ageing time, t / h} \]

Figure 3. Change in hardness of the Fe-Cr alloys with ageing time.

Figure 4. Change in coercivity of the Fe-Cr alloys with ageing time.

Figure 5. Change in remanence of the Fe-Cr alloys with ageing time.
4. Discussion
The coercivity in Fe-20% Cr alloy was increased substantially and remeance was decreased sharply than the other alloys possibly due to the formation of Cr rich α′ phase precipitations. The TEM study could not able to detect such precipitations in the present study due to similar lattice structure of Fe and Cr. However, results from atom probe field ion microscopy on Fe-Cr alloy shows that the nanometer size precipitations of Cr-rich α′ phase are either isolated or interconnected depending on the Cr content and heat treatment conditions [6, 7]. In alloy containing 24% Cr, formations of interconnected precipitates are seen after 500 hrs aging at 500 °C [7]. Since the ageing conditions and Cr content are almost similar, formation of Cr-rich α′ phase and their growth to form interconnected region are also expected in the present Fe-20% Cr alloy. Formation of the coherent precipitates is responsible for the increase in hardness in the alloy due to their local strain field whereas with the increase in volume fraction of the precipitates and their interconnected network enhanced the hardness furthermore. The local residual stress around the coherent precipitates is quite higher as previously reported in Fe-Cu alloy. The coherent Cu precipitation produces magnetic hardening in the alloys due to hindrance of domain wall motion [17, 18]. In Fe-20% Cr alloy, the increase of volume fraction of Cr rich precipitates and their interconnection lead to the increase of coherent strain field and its enhancement. This is one of the promising mechanisms to explain the behavior of coercivity and remanence of thermally aged Fe-20% Cr alloy. In addition to the strain effect, it would be noticeable to consider the change of chemical composition of the matrix. During the Cr precipitation, reduction of Cr content also occurs in the matrix. Such change in matrix conditions also alters the magnetic hysteresis properties of the alloys through change in intrinsic parameters such as crystalline anisotropy and magnetostriction coefficient.

In Fe-15% Cr and Fe-10% Cr alloys, it was found that coercivity decreased up to 50 hrs. Such behavior of magnetic softness was due to the recovery of dislocation structures in the alloys [19]. Although such effect was also expected to be present in the Fe-20% Cr alloy, the production of more number of precipitates and their increased in volume fraction overwhelmed the effect of recovery of dislocations. There was an increased in the coercivity after 50 hrs in Fe-15% Cr alloy which was more than the Fe-10% Cr alloy. Such behavior can be corroborated with the more volume fraction of Cr-rich precipitates in Fe-15% Cr alloy.

The magnetic properties changed in Fe-5% Cr alloy were quite different than the alloys having higher Cr content. The Fe-5% Cr alloy is below the solubility limit of Fe in Cr, hence there is no possibility of Cr rich α′-phase. In Fe-Cr alloy with Cr concentration ≤ 5%, the short range ordering is strong [20]. Due to such strong short range ordering, the change in magnetic properties in Fe-5% Cr alloy was different from the other alloys.

![Figure 6. Change in hardness against coercivity in Fe-20% Cr alloy.](image-url)
The change in hardness with the coercivity in Fe-20% Cr alloy is shown in figure 6. A linear relationship between the hardness and coercivity has been found with the embrittlement. Many reports say that the effect of embrittlement is enhanced by radiation environment and observed at much lower temperature than 475 °C. The change in hardness and hence coercivity in radiation embrittlement materials are expected to be quite more. So the alloys having lower Cr content is expected to be harden more in radiation embrittlement than the present study and can be detected by MHL technique.

5. Conclusion
Hardness of Fe-Cr alloys particularly with higher Cr content was found to increase due to the increase in volume fraction of Cr-rich α’-phase. A linear relationship was found between the hardness and coercivity during thermal ageing in Fe-20% Cr alloy. With increase in volume fraction of the Cr rich α’-phase the remanence was decreased substantially. Due to low volume fraction of such phase the change in properties was not very significant in the alloys having lower Cr content. The results enables that the Magnetic Hysteresis Loop technique would be a good NDE tool for the evaluation of embrittlement in nuclear power plant components made up of Fe-Cr alloys.

Acknowledgements
This work was supported in part by Japan Society for the Promotion of Science and Korea Science and Engineering Foundation under the contract of the Japan-Korea Basic Scientific Cooperation program.

References
[1] Mathon M H, De Carlan Y, Geoffroy G, Averty X, Alamo A, De Novion C H 2003 J. Nucl. Mater. 312 236.
[2] Brenner S S, Miller M K and Sofa W A 1982 Scr. Metall. 16 831.
[3] Grobner P J 1973 Metall. Trans. 4 251.
[4] Y. De Carlan, A. Alamo, M.H. Mathon, G. Geoffroy, A.Castaing 2000 J. Nucl Mater. 672 283.
[5] Soriano-Vargas O, Avila-Davila E O, Lopez-Hirata V M, Cayetano-Castro N, Gonzalez-Velazquez J L 2010 Mater. Sci. & Eng. A 527 2910.
[6] Miller M K, Hyde J M, Cerezo A, Smith G D W 1995 Appl. Surface Sci. 87/88 323.
[7] Miller M K, Hyde J M, Hetherington M G, Cerezo A, Smith G D W and Elliott C M 1995 Acta Metal. Mater. 43 3385.
[8] Yustinovshikov Y, Shirobokova M and Pushkarev B 1996 Acta Mater. 44 5021.
[9] Little E A, Stoter LP 1982 STM-STM 782 207.
[10] Miller M K, R E Stoller, K F Russell 1996 J. of Nucl. Mater. 230 219.
[11] Bonny G, Terentyev D, Malerba L, 2008 Scripta Mater. 59 1193.
[12] Mohapatra J N, Panda A K, Mitra A, 2009 J.Phys.D: Appl. Phys. 42 095006.
[13] Mitra A, Mohapatra J N, Swaminathan J, Ghosh M, Panda A K, Ghosh R N 2007 Scripta Mater 57 813.
[14] Mohapatra J N, Ray A K, Swaminathan J, Mitra A 2008 J.Magn. and Magn.Mater. 320 2284.
[15] Moorthy V, Choudhary B K, Vaidyanathan S, Jayakumar T, Rao K B S and Raj B 1999 Int. J. of Fatigue 21 263.
[16] Lo C C H, Tang F, Jiles D C, Biner S B 1999 Magnetics IEEE Trans. 35 3977.
[17] Aleshin N P, Altpeter I, Dobmann G, Kroening M, Reddy A 2002 National Seminar of ISNT 5-7 12.
[18] Kamada Y, Takahashi S, Kikuchi H, Kobayashi S, Ara K, Echigoya J, Tozawa Y, Watanabe K, 2009 J. Mater. Sci. 44 949.
[19] Martinez-de-Guerenu A, Arizti F, Diaz-Fuentes M, Gutierrez I Acta Mater. 2004 52 3657.
[20] Erhart P, Caro A, Caro M S D, Sadigh B 2008 Phys. Rev. B 77 134206.