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CONDUCTIVITY AND DIELECTRIC PROPERTIES OF A NOVEL FERRITE ALLOY

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ABSTRACT

CONDUCTIVITY AND DIELECTRIC PROPERTIES OF A NOVEL FERRITE ALLOY. The synthesis of a new ferrite alloy with a composition of Fe (73.42 w%), Cr (18.0 w%), Si(1.0 w%), Mn(1.0 w%), C(0.08 w%) and Ti(6.5 w%) has been carried out. The frequency-dependent conductivity and dielectric response of this novel material have been investigated by RLC bridge impedance spectroscopy method. It was verified that the real dielectric constant e¢ of these new F-1 materials show different dielectric behavior with respect to Koops theory of dielectric response in standard ferrite materials. In the F-1 samples, no relaxation peaks are observed for the frequency range below 10 kHz, meaning low frequency behavior such as grain-boundaries effect and space charge polarization has not taken effect. Both dielectric response- and dielectric loss curves show frequency dispersive relaxation peaks, three regions of discontinuity and relaxation peaks were identified in the applied frequency range. The low frequencies up to 10 KHz, intermediate frequencies 10 kHz to 40 KHz, the dielectric constant tend to decrease forming a curve resembling a distorted quarter circle, and higher frequency-range > 40 kHz where a semicircle forms, centered around 60 kHz. Using Nyquist- and Bode plots, these relaxation processes are identified as (beginning of) formation of oxidation-layers at the surface because of sintering, electron transfers between cations and Maxwell-Wagner interfacial polarizations. It is concluded that this is a novel material with its own distinctive dielectric properties.

Key words : Ferrite alloys, novel materials, dielectric relaxation, dielectric properties

ABSTRAK

KONDUKTIVITAS DAN SIFAT DIELEKTRIK PADA LOGAM PADUAN FERIT BARU. Telah dilakukan pembuatan bahan feritik baru yang dinamakan dengan F-1 sebagai bahan studi untuk bahan penukar panas reaktor daya. Pembuatan bahan paduan ini dilakukan dengan teknik metalurgi serbuk. Bahan dibuat dengan komposisi Fe (73,42 w%), Cr (18,0 w%), Si (1,0 w%) , Mn (1,0 w%), C (0,08 w%) dan Ti (6,5 w%). Telah dilakukan pengukuran karakteristik konduktivitas dan dielektrikum bahan baru ini, menggunakan teknik spektroskopi impedansi RLC. Dapat diverifikasi bahwa konstanta dielektrikum riil ε' bahan baru F-1 menunjukkan perilaku relaksasi atau pola respons dielektrikum bahan-bahan feritik yang sedikit berbeda dengan karakteristik yang diajukan oleh teori Koops. Baik kurva respon dielektrik dan rugi dielektrik menunjukkan puncak relaksasi bergantung frekuensi. Telah diamati tiga daerah diskontinyu dan puncak relaksasi pada rentang frekuensi yang digunakan. Frekuensi rendah hingga 10 kHz, frekuensi *intermediate* 10 kHz hingga 40 kHz, disini konstanta dielektrik cenderung menurun dan membentuk suatu kurva seperempat lingkaran yang terdistorsi dan frekuensi tinggi diatas 40 kHz dimana terbentuk sebuah kurva yang mirip sebuah semi-lingkaran dan terpusat pada frekuensi 60 kHz. Melalui plot-plot Nyquist and Bode, proses-proses relaksasi ini teridentifikasi sebagai proses permulaan pembentukan lapisan korosi permukaan, perpindahan elektron antara kation-kation dan polarisasi antar muka Maxwell-Wagner. Kesimpulannya bahan ini material baru (novum) yang memiliki karakteristik sifat dielektrik tersendiri.

Kata kunci : Logam paduan feritik, Bahan-bahan baru (novum), relaksasi dielektrikum, sifat-sifat dielektrikum

INTRODUCTION

Low-carbon ferritic stainless steels contain typically more chromium and/or less carbon than that of martensitic grades. Both changes act towards stabilisation of ferrite against austenite so that ferrite is stable at all temperatures. Therefore, ferritic stainless steels cannot be hardened by heat-treatments as is the case of martensitic ones. They exhibit lower strength but higher ductility/toughness. Typical application may include heat exchanger, appliances, automotive and architectural trim (i.e. decorative purposes), as the cheapest commercial stainless steels are found in this family (AISI 409 as an example) [1]. Other useful industrial application of ferrite materials such as $Ni_xMg_{1-x}Fe_2O_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1.0) is in radio-frequency circuits, operating devices, transformer cores and high quality filters [2]. In this work, a series of new ferrite samples labeled F-1, been prepared. The addition of Ti is a new feature of F-1 samples. The purpose of adding Ti is to prevent sensitization, also F-1 samples contain more Cr element in order to improve the material's resistance with respect to corrosion. This type of sample composition is not available before in the free market [3]. Therefore, these samples and their properties represent a state of the art new development in materials technology.

A.C. impedance spectroscopy has been used successfully applied among other things for characterizing the electrochemical properties of electrodes, coating materials, mechanism of chemical reactions, measuring sensing characteristics of capacitance or conductance based sensors, and mechanism of electric conduction and dielectric polarization in ferrites [4]. In the present work, results of dielectric and dielectric loss factor (*tan d*) room-temperature measurements on new ferrite materials are presented and discussed. The main objective was to check on any significant frequency-dependent changes in the dielectric characteristics of the samples. Dielectric variation with frequencies could provide information on the free and localized electrical charges in the materials.

THEORY

Impedance spectroscopy (IS) is an electrical technique for characterizing the microstructure and physical properties of materials. The measured parameters could include electrical parameters such as complex impedance (Z), admittance (Y), complex capacitance (C^*) and modulus (M). In most materials, these quantities are frequency dispersive or dependent. The object of an impedance measurement may be to determine the values of the various elements in the equivalent circuit or simply to confirm that a given electrochemical system fits a particular equivalent circuit model. By studying how these parameters, vary with frequency, substantial information could be gained about dielectric, dipolar characteristics of the materials, and many behaviors of interest in these materials, such as charge layer formation, corrosion rate, corrosion inhibitor performance, electro deposition mechanism, coatings evaluation etc could be studied. IS experiments are conducted by applying a small amplitude a.c. voltage to the material and measuring the resultant current. By sweeping the frequency of the applied signal impedance over a wide range of frequencies could be determined. The values of the capacitance (C_p) and resistance (R_p) in parallel configuration are measured simultaneously [5]. The phase angle *tan f* (for the parallel configuration) is expressed as,

$$\tan\phi = 2\pi f R_p C_p \quad \text{...} \quad (1)$$

f is the frequency and the dielectric loss factor is

$$D = \tan\delta = (\tan\phi)^{-1} \quad \text{......................................} \quad (2)$$

The absolut dielectric constant *e* is calculated from the measured capacitance by the relationship

$$\varepsilon = \frac{C_p\, h}{A} \quad \text{...} \quad (3)$$

The real component of the dielectric constant,*e¢*, is then calculated using the relationship,

$$\varepsilon' = \frac{\varepsilon}{(1+D^2)^{1/2}} \quad \text{...} \quad (4)$$

The imaginary component is given by the expressio

$$\varepsilon'' = D\varepsilon' \quad \text{...} \quad (5)$$

The other electrical parameters are calculated via the processor once the impedance is obtained. For a parallel (R_p),(C_p) configuration the equivalent substitutional impedance is expressed:

$$Z = \frac{R_p^2}{1+4\pi^2 f^2 R_p^2 C_p^2} \quad \text{.................................} \quad (6)$$

An appropriate electrode is used to apply the electric field to the material of interest. One popular technique for evaluating the a.c. impedance data is the Nyquist plot or the Cole-Cole plot of a complex impedance plane diagram. The imaginary component such as Z'' or ε'' is plotted versus the real component of Z' or ε' for each excitation frequency. Please note that at high frequencies only the uncompensated resistance contributes to the this measurement, while at low frequencies the polarization resistance also contributes to this measurement. Polarization resistance could be used to calculate the corrosion rate of an electrode material.

EXPERIMENTAL METHOD

Materials

In this work, the new alloy codenamed F-1 has been prepared. The alloy is comprised of six different elements, iron, chrome, titanium, manganese, silicon, carbon each with a specified weight-percentage tabulated in Table-1. For experimental purpose three identical pellet samples have been prepared, codenamed F11, F12 and F13. The dimensions of the pellets are described below.

Table 1. *Composition of ferritic material alloying elements.*

Elements	Fe	Cr	Si	Mn	C	Ti
w. %	73.42	18.0	1.0	1.0	0.08	6.5

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Equipments and Methods

In this work several equipments and instruments were used. For sample preparation spatula, light-resistant plastic container, ball milling machine, dies, press-machine, furnace BIPs 395204 ball milling machine fabricated in 1996. Further, quenching hardened NKL steel-dies in cylindrical form with an outside diameter of 7 cm, and an inside diameter of 1,5 cm was used. For sintering, a furnace of the type thermoline model F47920-26-80. Press machine with a maximum pressure of 20.000 psi, is a Carver model 3912 S/N: 40.000-LOG 10785 constructed by Fred S. Carver Inc. are also used. Difraction intensity for phase verification are obtained using the Shimadzu X-ray diffractometer XD-610. Analysis of diffraction pattern indicates that F-1 ferrite samples prepared and studied here have a single phase cubic structure [6].

AC impedance spectroscopy is utilized to obtain dielectric and dielectric loss factor data, measured using the computerized Hioki RLC spectrometer located at the AKN-PTBIN laboratory. The samples are prepared in the form of discs of thickness *h* of 5,0 mm and cross-sectional area *A* (diameter 1,5 mm) using powder metallurgy method. The disc-shaped samples are placed between two electrodes. An ac signal of $V = 1$ V with various frequencies from 100 Hz to 100 kHz is applied. The values of the capacitance (C_p) and resistance (R_p) in parallel configuration are measured simultaneously [5]. The surface microstructure is observed using the Phillips SEM microscope and the composition is analyzed using the SEM-EDAX instrument.

RESULTS AND DISCUSSION

SEM Results

SEM results are presented in Figure 1. The overall SEM result in Figure 1a. and the partial area SEM result of Figure 1b. show that corrosion has not yet affected the sample. The EDS composition analysis (partial and on the spot) is presented in Table 2 below.

Table 2. Composition of ferritic material alloying elements by SEM-EDAX

Elements	Fe	Cr	Si	Mn	C	Ti
w. %	66.08	16.16	5.84	0.78	(undetected)	10.98

EDS result in Table 2 clearly shows the existence of Cr element on this spot, although this small spot does not represent the whole bulk material, so it does not equal to Table 1.

Resistance Measurement

In Figure 2, the characteristic resistance versus frequency plot reveals an unusual pattern, namely that

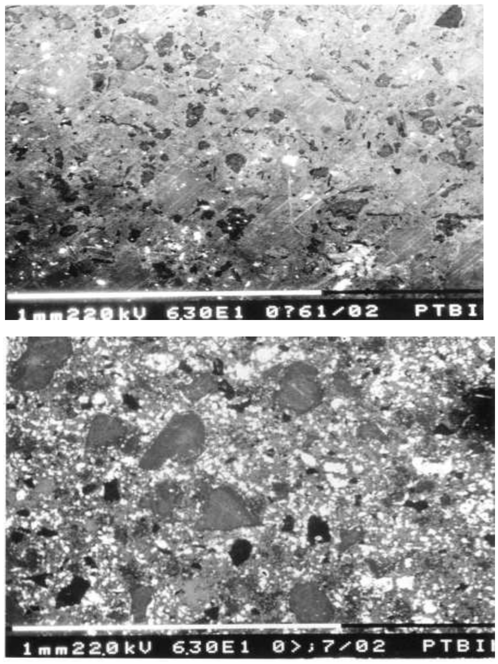
(a)
(b)


Figure 1. Scanning Electron Microscope (SEM) results of new ferrite materials.

the plot consists of three different patterns, an increasing curve up to frequency of 1,0 kHz followed by a decreasing curve of up to 10 kHz, and finally a distorted semicircle curve for frequencies above 10 kHz. This behavior is unusual, and could be attributed to bulk-interface interaction in the samples.

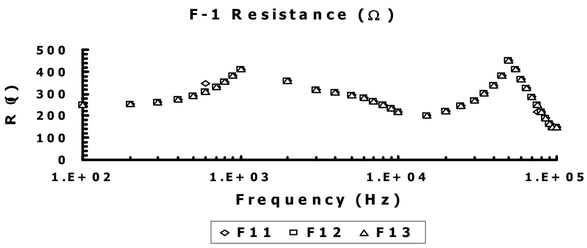


Figure 2. Measured resistance in parallel configuration for three F-1 samples.

Dielectric Measurement

In Figure 3 the dielectric constant versus frequency curve is shown for the standard A-430 ferrite. In the standard sample three relaxation peaks are present at frequencies of 3 kHz, 15 kHz and 35 kHz, and the

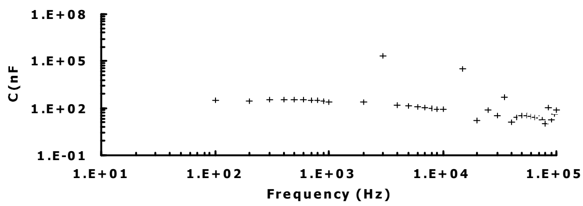


Figure 3. Measured capacitance in parallel configuration for a standard A-430 ferrite samples.

semicircular curve at the high frequency region is not very pronounced.

In Figure 4, the parallel capacitance versus frequency data for the three different ferrite samples is presented. The data for each sample differ only very slightly (≈ 1% or less) from one another. There fore, the three samples could be analyzed as one, and no need to present separate analysis for each sample, which is also an experimental indication that sample preparation was carried out in a uniform and consistent manner.

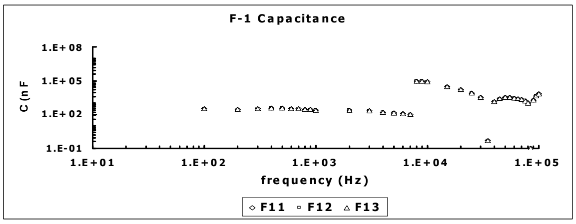


Figure 4. Measured capacitance in parallel configuration for three F-1 samples.

In Figure 5, the curve of dielectric constant versus frequency is shown for the three samples. As is obvious from Figure 5, the dielectric constant show a relatively large value (up to 10^{-3} F/m) and a wide range of variation (10^{-8} F/m to 10^{-3} F/m). The ferrite F-1 samples show normal dielectric behavior up to frequencies of 10 kHz. In comparison to the standard ferrite sample A-430 no relaxation peaks are observed for this frequency range, meaning low frequency behavior such as grain-boundaries effect and space charge polarization has not taken effect at this frequency-range. Above 10 kHz, relaxation behavior in the dielectric constant becomes more obvious, the pattern is a decreasing curve (rather resembling a quarter circles) up to 40 kHz, followed by a depressed semicircle with a peak centered around 60 kHz. This is generated by any defect that may arise through abrasion-layers at the surface of the samples, especially during sintering. However according to Koops theory for ferrite materials, at lower frequency range, the real dielectric constant and the dielectric loss factor should have a higher value and should decrease with decreasing frequency [2].

In addition, the absence of dielectric relaxation peaks at lower frequencies indicate that corrosion have

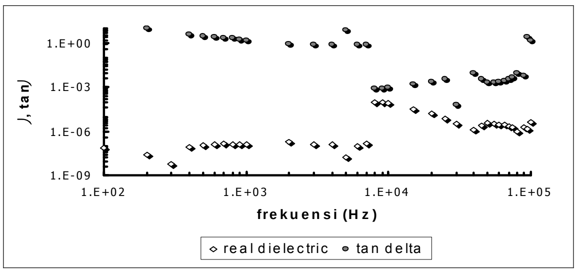


Figure 5. Plot of real dielectric constant and ε' *tan* δ versus frequency for three F-1 samples.

not yet affected the samples, this also supported by SEM microgram in Figure 1. The Koops theory was based on the Maxwell-Wagner model for the inhomogeneous double layer dielectric structure. This inhomogeneous dielectric structure was considered as consisting of two layers. The first layer comprises of fairly well conducting large ferrite grains, which are separated by the second thin layer of poorly conducting grain boundaries. The grain boundaries could be formed by the superficial reductions or oxidation of crystallites in the porous materials as a result of their direct contact with the firing athmosphere, especially at higher sintering temperatures. However, behavior as predicted by Koops theory is shown instead by the imaginary dielectric constant ε" in Figure 6, and not by the real dielectric constant ε' plot in Figure 5. Therefore, the dielectric behavior of these new F-1 materials is considerably different compared to conventional ferrite alloys, and represent a new finding in a new (novel) material .

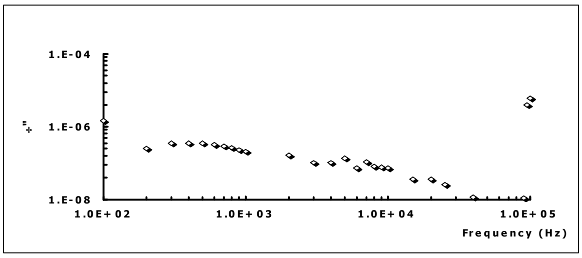


Figure 6. Plot of imaginary dielectric constant ε" versus frequency for three F-1 samples.

A Nyquist plot or complex-plane-plot of the dielectric constant is shown in Figure 7. As is evident from the diagram, the data is widely scattered. To make data interpretation simpler, the Bode plot of log *Z* versus log *f* is plotted after calculating Z_{abs} using equation (6). The results are plotted in Figure 8.

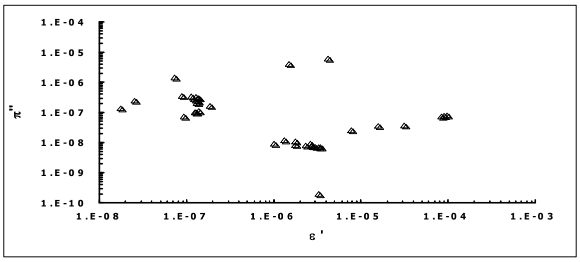


Figure 7. Complex-plane plot of real part ε ' and imaginary part ε " of the dielectric constant.

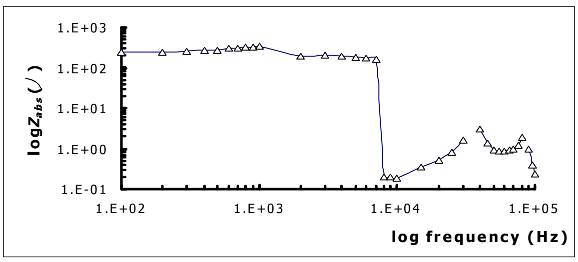


Figure 8. Bode-plot of log Zabs versus log frequency. Note the appearance of relaxation peaks at 40 kHz and 85 kHz.

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The slope centered around 8.5 kHz indicates the existence of double-layer capacitance in the interface between electrode and ferrite material. The overall plot also distinguishes between several steps in the electrochemical process contributing to the process, as indicated by the appearance of peaks at 40 kHz and 85 kHz. The first peak could be due to electron transfers between cations, and the second peak may be due to Maxwell-Wagner interfacial polarizations [7]. Both peaks border an inverted semicircle. Therefore, the Bode plot provides a clearer description of the electrochemical system's frequency dependent behavior compared to the Nyquist plot, since the frequency values are explicit.

CONCLUSIONS

A new (novel) ferrite material has been synthesized and its dielectric properties investigated. The dielectric spectrum shows considerable difference when compared to the same spectrum belonging to standard AISI 430 ferrite sample. Three regions of discontinuity and relaxation peaks were identified in the applied frequency range. The low frequencies up to 10 KHz, where the curve is almost flat indicating low frequency behavior such as grain-boundaries effect and space charge polarization has not taken effect in the samples at this frequency-range. From 10 kHz to 40 KHz, the dielectric constant tend to decrease forming a curve resembling a distorted quarter circle.

This is caused by the inability of the jumping frequency of electric charge carriers to follow the alternation of the applied electric field. At 40 kHz a semicircle forms, centered around 60 kHz. Relating to the Bode plot, this is the frequency region where oxidation-layers induced by sintering are formed at the surface, and where electron transfers between cations and Maxwell-Wagner interfacial polarizations occur.

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REFERENCES

[1]. www.Key-to-Steel.com, 2005; www.knight-group.co.uk, (2005)

[2]. M.A. EL-HITTI AND M.A. AHMED, *Mat. Sci. Tech.*, **14** (1998) 19-24

[3]. NURDIN EFFENDI, AZIS K. JAHJA, MARZUKI, dan TRI DARWINTO, Synthesis Of Ferritic Alloys as a Candidate Material for Power Reactor Heat Exchanger, submitted to *MESIN journal of Trisakti University Mechanical Engineering Department*, (2006)

[4]. F. JOSSE, R. LUKAS, RN ZHOU, S. SCHNEIDER and D. EVERHART, *Sensors and Actuators*, **B 35-36** (1996) 363-369

[5]. A.K. JONSCHER, *Dielectric Relaxation*, Chelsea Dielectric Press, London, (1983)

[6]. ASM Vol. 3, *Alloy Phase Diagram*, The Mater. Information Soc., 1990; P. Villars and L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases 2nd Ed.*, **2 B**, ASM International (1991)

[7]. K. IWAUCHI AND N. IKEDA, *Phys. Stat. Solid (a)*, **93** (1986) 309