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ISOTROPIC DEBYE-WALLER FACTOR AND DEBYE TEMPERATURE OF AISI-430 STEEL

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ABSTRACT

ISOTROPIC DEBYE-WALLER FACTOR AND DEBYE TEMPERATURE OF AISI-430 STEEL. The meagre experimental data on the physical properties of AISI type steel alloys has prompted the authors to undertake an X-ray diffraction study on the alloys belonging to the AISI family, in this case on A430 steel sample. The sample was investigated using two thermal conditions, room-temperature (no heat-treatment) and heat-treated at 540 °C. The main objective was to refine the structural parameters, in particular the Debye-Waller factors in order to be able to calculate the Debye temperature of the alloy system, as well as other physical properties of the system, such as Debye frequency, melting temperature using Lindemann theorem, velocity of sound in the system and the Young modulus of the system. The Rietveld refinement shows that no structural changes have taken place during the 540 °C heat-treatment. However in-depth analysis of the Debye–Waller parameter indicates significant changes in the physical properties of the alloy system. The Debye temperatures are 444 K and 187.1 K after heat treatment respectively. The melting temperature is estimated to be 1200 K, the Debye frequency accordingly vary from 0.427 THz to 0.373 THz (all values in the infra-red portion of the spectrum), the sound velocity has decreased from 4.27 x 10^3 m/s to 1.80 x 10^3 m/s, and the Young modulus has decreased from 14.1 x 10^{10} to 2.51 x 10^{10} N/m^2 respectively.

Key words : Isotropic Debye-Waller factor, debye temperature, AISI-430 steel

ABSTRAK

FAKTOR DEBYE-WALLER DAN SUHU DEBYE BAJA AISI-430. Minimnya ketersediaan data-data fisis logam paduan tipe baja AISI telah mendorong dilakukannya penelitian difraksi sinar-X terhadap logam-logam paduan yang termasuk keluarga AISI, dalam hal ini baja A430. Sample diukur pada dua kondisi termal, suhu ruang (tanpa perlakuan panas) dan perlakuan panas 540 °C. Tujuan utama ialah untuk menghaluskan parameter-parameter struktur, terutama factor-faktor Debye-Waller untuk menghitung suhu Debye sistim logam-paduan, dan besaran-besaran fisis lainnya, misalnya frekuensi Debye, suhu leleh menggunakan teorema Lindemann, kecepatan bunyi pada logam-paduan dan modulus tarik logam-paduan. Penghalusan Rietveld menunjukkan bahwa tidak ada perubahan struktur kristal yang signifikan pada sample. Namun analisis mendalam terhadap parameter Debye-Waller menunjukkan adanya perubahan-perubahan signifikan pada besaran fisis logam-paduan. Suhu Debye menurun dari 444 K menjadi 187.1 K setelah perlakuan panas. Suhu leleh diestimasi sekitar 1200 K ,frekuensi Debye bervariasi dari 0.427 THz menjadi 0.373 THz (kedua harga dalam rentang spectrum infra-merah),kecepatan bunyi telah menurun dari 4.27 x 10^3 m/s menjadi 1.80 x 10^3 m/s, dan modulus Young menurun dari 14.1 x 10^{10} menjadi 2.51 x 10^{10} N/m^2.

Kata kunci : Faktor *Debye-Waller* isotropik, suhu Debye, baja AISI-430

INTRODUCTION

Iron and Steel is one industrial commodity that has found the foremost industrial application among various materials. The economical value is determined by both the wide diversity in steel properties and the ease of formability of steel products in general. Precisely this very high diversity in properties, which has made steel to be very attractive to manufacturers. The meager experimental data on the physical properties of AISI type steel alloys has prompted the authors to undertake an X-ray diffraction study on the alloys belonging to the AISI family, in this case on A430 steel sample. Ferrite stainless-steel AISI 430 (0.11% C and 17%Cr) have excellent corrosion resistance and are respectively inexpensive. The alloy has good strength and moderate ductility. A glance at existing literature [1, 2] turns up that no information on the Debye temperature and mean-square amplitudes of vibration exist for AISI430 alloys. So far only data pertaining to pure elements and some common compounds are presented in the literature [3], an example is shown in Table 1.

In this paper, structural investigation by Rietveld method on AISI430 based alloy is carried out, after the sample was characterized by x-ray diffraction measurements. Using Rietveld refinement method, the crystal structure of both the untreated and the heat treated sample are investigated, beyond mere structural

Table 1. Debye temperatures of various elements and compounds.

Element	Θ_D (°K)
Li	335
Na	156
K	91,1
Cu	343
Ag	226
NaCl	280
KCl	230
CaF_2	470
LiF	680

parameters such as lattice parameters and isotropic temperature factor, but including also other physical parameters such as Debye temperature is also investigated in order to gather information on the physical properties of the sample. The heat treatment temperature of 540 °C was chosen since it represents the highest operating temperature of the SWF-HTGC Reactor [4], which is the final aim of this study.

THEORETICAL

Debye temperature Θ_D is associated with diverse physical properties of a solid alloy. With respect to the electrical property of a metal, according to Matthiessen rule the resistivity of a metal increases proportional to temperature, $\rho \sim T$, at temperatures T above the Debye temperature Θ_D but the resistivity varies as $\rho \sim T^5$ at temperatures below Θ_D. On the atomic scale Debye temperature Θ_D, is associated with the maximum frequency of atomic vibration [5], e.g., Debye frequency ν_D:

$$\nu_D = k/h\ \Theta_D \qquad \text{..... (1)}$$

Here k is the Boltzmann constant and h is the Planck constant. In this aspect $k\Theta_D$ represents the energy of the maximum quantum that can be exited from the solid. The heat capacity C_V of a solid deviates from the Dulong-Petit law and varies according to $\sim T^{-3}$ at temperatures below the Debye temperature Θ_D and this also known as the famous Debye formula which works well for most solids [5]. Θ_D is also related to the average velocity of sound in the solid. According to Lindemann [5], the melting point of a solid is proportional to the square of the Debye temperature Θ_D^2. In this case, the so-called Lindemann melting formula gives the expression,

$$T_m = \frac{\chi_m^2 M k \Theta_D^2 r_s^2}{9\hbar^2} \qquad \text{..... (2)}$$

T_m is the melting temperature, $\hbar$ and k are the Planck and Boltzmann constants, M is the nominal molecular mass in the unit cell, r_s is the radius of the unit cell and χ_m is a fractional number, the ratio of the root-mean-square amplitude of vibration u_{ii} to the lattice parameter a. According to solid-state theory, the temperature factor Q can also be expressed as [6],

$$Q = (6h^2/mkT)\ W(x) \qquad \text{..... (3)}$$

Where m is the mass and T is the absolute temperature. The function $W(x)$ is given by,

$$W(x) = [\varphi(x)/(x^2) + (x/4)] \qquad \text{..... (4)}$$

Where $\varphi(x)$ is an integral and $x = \Theta_D/T$. Based upon Debye approximation, expression (4) could be written as,

$$m_M Q = 6h^2T/k\Theta_D^2\{\varphi(x)/(x^2) + (x/4)\} \qquad \text{..... (5)}$$

Here m_M is the mass of the virtual chemical species in terms of the nominal mole-fractions M of the AISI430-steel. From the works of Shashikala *et al*, Warren and others [6,7] it could be gathered that the terms containing the Debye integral function $\{\varphi(x)$ could be approximated by the following polynomial,

$$\{\varphi(x)/(x^2) + (x/4)\} = 1 + \frac{x^2}{36} - \frac{x^4}{3600} + (\text{higher order terms}) \qquad (6)$$

Therefore equations (5) and (6) could be written as,

$$1 + \frac{x^2}{36} - \frac{x^4}{3600} = Gx^2 \qquad \text{..... (7)}$$

Where G is given by $(kT/6h^2)m_M Q$. Setting the L.H.S. of equation (7) equal to y_1 and the R.H.S. of equation (7) equal to y_2, and then plotting y_1 and y_2 versus x in figure 3, the transcendental equation (7) could be solved using graphical regression analysis to obtain the value of Θ_D for AISI430 steel.

EXPERIMENTAL

AISI430 solid sample was cut into two equal size pieces, and one piece was heated at the rate of 14 °C to 540 °C, which is the highest operating temperature in steam working fluids of the power plant reactor namely HTGCR [2], with holding time of 24 hours; in order that the effects of heat-test on the materials can be observed. Both pieces of the sample are then mounted by first adding resin as a glue-material, followed by polishing to smooth out the sample surface, in compliance with the standard protocols in x-ray diffraction measurements. The sample then was put in XRD-sample holder before exposure to the radiation of the x-ray diffraction apparatus. Diffraction intensity was measured using the step counting method with a 0.05° step-scan and the preset time of 2 seconds. The data and results presented herein were obtained on a routine basis as part of laboratory runs. This is to say, no special optimized calibrations were performed. The intensities data collected in this experiment is then analyzed by least-square refinements using the *Rietveld method*, which can handle whole pattern refinements with structural constraints [8]. To characterize the goodness

of the calculation, the usual reliability criteria were looked at, that is, the mean 2θ deviations for cell parameter refinements and the profile intensity *R-value*, the weighted profile *R-value* and the expected *R*-value (calculated for regions containing significant contributions to the peak intensities and with background-corrected counts).

RESULT AND DISCUSSION

Rietveld Refinement and Debye Temperature

The unit cell parameters are calculated using the nominal wavelength of the x-ray diffraction and the results compared to literature [9]. The experimental parameters will be used as the initial (*guessed*) input parameters in the Rietveld refinement procedures. It was evident from the initial (manual) analysis of the cell parameters that the crystal structure of the sample phase is based on a base-centered-cubic (bcc) unit cell. In Figure 1 the refinement results on the diffraction pattern of untreated AISI430 sample is presented.

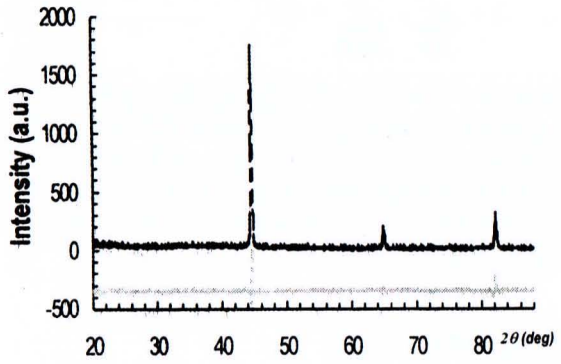

Figure 1. Refined diffraction pattern of untreated AISI430 sample

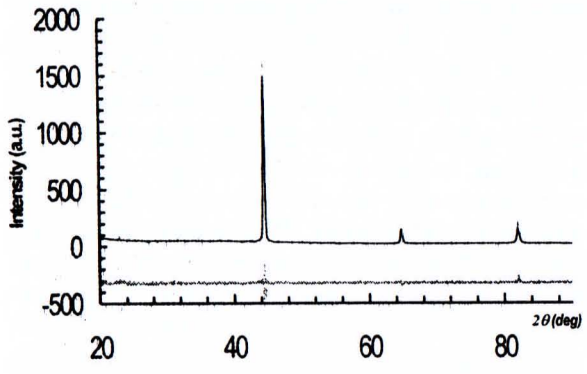

Figure 2. Refined diffraction pattern of heat-treated AISI430 sample

The refinement of the structural parameters using x-ray diffraction intensity is carried out by employing the specially developed computer application code *RIETAN* attributed to F. Izumi [8]. *Pseudo*-Voigt profile function and conjugate-direction iteration method were used in the refinement process. Final Rietveld refinements, including profile parameters, and phase-dependent parameters, such as lattice-parameters and isotropic thermal factor rapidly converged to the reliability factors presented in Table 2. The lattice parameter in both thermal conditions agrees within the range of statistical errors (standard deviation).

Table 2. Refined structural parameters of AISI430 based alloy (No heat treatment and 540 °C heat treated condition).

Phase*) M (Fe-Cr-C) Condition	Lattice parameter a (Å)**)	Q (Å^2)	R_{wp} (%)	R_p (%)	R_F (%)	R_I (%)	"Goodness of Fit S"
Untreated	2.874 (2)	0.5 (2)	20.5	15.60	2.08	2.68	1.22
Heat-treated	2.872 (4)	2.7 (2)	17.9	14.05	2.50	2.94	1.18

*) An imaginary chemical species M(Fe-Cr-C) was input.
**) Numbers in parentheses indicate standard deviation in the last significant digit of refined parameters.
SG. Im3m (vol. *I-129*); 1401 data points, 3 reflections (110), (200) and (211).

The graphical solution of the transcendental equation (7) is presented in Figure 3.

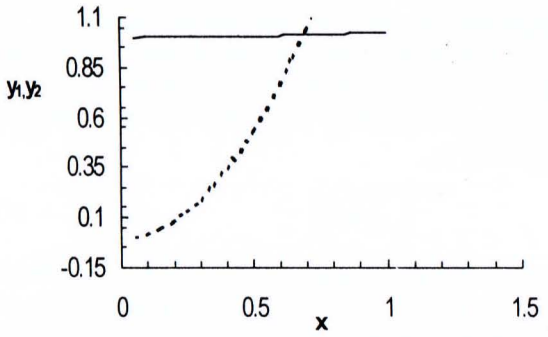

Figure 3. Calculation of the Debye-temperature using Debye method of approximation.

In Table 3, Debye-Waller factor Q, Debye temperature Θ_D, Debye frequency ν_D and isotropic vibration amplitude u_{ii} of AISI430 based alloy are shown.

Table 3. Calculated values of G, x, Q_1, Debye frequency and isotropic vibration amplitude u_{ii} of AISI430 based alloy

AISI 430	Debye Waller Factor Q (Å^2)	G	x	ν_D (THz)	u_{ii} (Å)	Θ_D (K)
Untreated	0.5	0.481	1.48	0.427	0.08	444
treated	2.7	2.600	0.624	0.373	0.17	187

Estimate of Melting Temperature Using Lindemann Formula

The melting temperature could be estimated using the Lindemann formula (equation 2). The parameter χ_m is taken to be 0.108 and the calculated

unit cell mass M is 1.841 x 10^{-25} kg, k = 1.381 x 10^{-23} JK^{-1}, Θ_D is the calculated Debye temperature here 444 K respectively, the refined unit cell radius r_s is 1.436 Å and the Planck constant h is 1,055 x 10^{-34} Js. a value of around 1200 K is obtained [10].

Estimate of Sound Velocity in the Samples and the Young Modulus

In an isotropic solid [11] the sound velocity v_s is related to the Debye temperature as follow,

$$\Theta_D \approx \frac{v_s\, h\, (3/4\pi)^{1/3}}{\Omega^{1/3}\, k_B} \qquad \text{..... (8)}$$

and Ω is the atomic volume.
And the Young modulus Y is given by the expression,

$$v_s = \sqrt{Y/\rho} \qquad \text{..... (9)}$$

Here ρ is the samples' density, from RIETAN results.

In Table 4, the mass density and the estimated melting temperatures, the velocity of compressed wave and the Young modulus are presented.

Table 4. Mass density r and estimated values of sound velocity v_s and Young modulus Y of AISI430 based alloy

AISI 430	ρ (g/cm³)	v_s x 10^3 (m/s)	Y x 10^{10} N/m²
Untreated	7.773	4.27	14.1
Treated	7.738	1.80	2.51

CONCLUSION

The crystal structure of the AISI-430 based alloy is preferably the body centered cubic (bcc) model, crystallographically represented by the *Im3m* space group. Refinement results show that no crystallographic changes have been observed in the sample after heat treatment at 540 °C and quenching. However an extended analysis of the structural data obtained from Rietveld refinements, show that the isotropic structure-factor has changed after heat treatment, and consequently this change would lead into changes in the physical properties, such as Debye temperature, velocity of sound, Debye frequency and Young modulus as well. The reason maybe that if an isotropic material is heated unequally and slowly thermal stress may occur, and when the sample is suddenly cooled (quenched) thermal shock may occur in the sample. However thermal shock in most metals is not a problem, because metals normally have sufficient ductility to permit deformation rather than fracture.

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TANYAJAWAB

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Pertanyaan

1. Apakah ada perbedaan yang signifikan hasil analisis pada kedua faktor tersebut dan berapa parsen perbedaannya.

Jawaban

1. Perbedaan parameter fisik yang ada cukup signifikan mencapai 50% sampai dengan 100%.

Patrisius Purwanto, P3IB-BATAN

Pertanyaan

1. Apa manfaat faktor Debye Waller.

Jawaban

1. Faktor Debye Waller berpengaruh pada suhu Debye yang menentukan sifat termal dan konduktivitas listrik bahan.