X-Ray Determination of Debye Temperature and Microhardness of Some HCP Elements Re, Os and Tl

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Abstract. The studies on the microhardness have been calculated the hexagonal close packed metals rhenium (Re), osmium (Os) and thallium (Tl). In this paper, the Vickers’s pyramidal indenter and the true hardness values has been evaluated. Debye temperatures of hexagonal close packed (HCP) of these three metals have been calculated by using X-ray diffraction intensities pattern with Philips 3020 powder diffractometer fixed with a proportional counter using filtered CuKα radiation; all the values have been evaluated at room temperature. In this present work the calculated Debye temperature values θH 338 K, 426 K and 74 for Re, Os and Tl respectively. The calculated Debye temperatures of these hcp metals have been estimated from the hardness H values 135, 400, 27 kg/mm² and are compared with those obtained from Debye temperature of specific heats (θD), Debye temperature of elastic constants (θE) and Debye temperature of X-ray intensity measurements (θM).

Keywords: X-ray diffraction, hardness, Debye temperatures, hcp element

1. Introduction

The hardness of the metal is an significant crystal property. The resistance obtainable by the lattice and its motion of dislocations. The crystal chemical armed forces in a crystal resist motion of dislocations as in it involves the dislocation of atoms/elements. This resistance is known as the intrinsic hardness of a crystal/solid. This crystal microhardness can be correlated by means the strength of interatomic-binding in the crystals.

The previous researchers Abrahams and Hsu [1], Purushotham and Gopikrishna [2, 3] and Denge [4] reported the thermal properties values of some metals and alloys. Mechanical Properties of pure metals and some alloys [5, 6] developed as potential engineering production [7] and thermal, mechanical properties and their applications [8].

2. Experimental

The samples Re, Os and Tl has been obtained from the commercial basis and available in the form of tiny ingots. A fine filing has been obtained in the form of the ingots through facilitate of a jeweller’s file. The filing has been carried out slowly. The filings have passed through a 325-mesh screen. The X-ray Diffraction dimensions have been made with a diffractometer built-in with proportional counter. The X-ray tube was operated at 25 mA and 40 kV and. The XRD patterns of samples have been given in Figure1. The procedure for sample groundwork, have been given in earlier papers [9, 11].
Fig.1. The X-ray patterns of a) Rhenium, b) Osmium and c) Thallium respectively.

3. Characterization Techniques

3.1 Debye model

The Debye model has been applied to examine the temperature variation of several physical properties of solids. One of the earliest applications of the Debye model was in the study of the effect of temperature on X-ray intensities. The treatment of this problem at the hands of Debye himself, led to the formulation of the Debye-Waller factor. The Debye-Waller factor accounts for the reduction in the intensities of the diffracted X-rays with temperature. Its primary use was in correcting the intensities of X-rays diffracted from crystals. However, very soon the relation between the Debye Waller-factor and other crystal properties was identified. Thus, the Debye-Waller factor can be used to calculate the amplitudes of vibration and the Debye temperatures. The Debye-Waller factor can also be theoretically evaluated from the lattice vibration spectrum. A comparison of the theoretically calculated value with the experimentally determined value can be used as a check on the model assumed in the calculation. Similarly, the Debye temperature can be correlated with the bond strength, the melting point and diffusion parameter. Thus, the value of Debye-temperature is no longer
parameter useful only for the correction of intensities or for explaining the specific heats; they have emerged as independent solid state parameter.

3.2 Methods of determining Debye temperatures

The various experimental methods from which Debye temperatures can be determined. These are,

1. $\theta_E$ from elastic constants
2. $\theta_R$ from infrared frequencies
3. $\theta_\nu$ from compressibility
4. $\theta_{\text{tm}}$ from melting points
5. $\theta_{\text{ER}}$ from electrical resistivity
6. $\theta_M$ from X-ray diffraction

The present thesis mainly deals with the experimental determination of mean amplitudes of vibration, Debye Waller factors and also Debye temperature values of some hcp metals, binary alloys with rhombohedral structure, ternary alloys with hcp structure and nano semi-conductors from the measurement of X-ray intensities. In the following section the Debye model, the concept of the Debye temperature and Debye-Waller theory are discussed. This is followed by a review of earlier work on the Debye-Waller factors and also Debye temperature values of metals, alloys and nanoparticles. The chapter concludes with a statement of the scope of the present investigation.

4. Results and discussion

Micro-hardness values have been carried/approved out by a micro-hardness tester fixed/settled with the Vickers’s pyramidal indenter. The micro-hardness shows load dependence on enormously low load values and becomes self-governing of load. The load independence starts around 50gms. In order to find/discover load self-governing standards dimensions on all the three samples have been approved out at different loads up to 120 grams. The micro-hardness (H) is calculated using the equation (1)

$$H = 1.854 \frac{P}{d^2}$$ (1)

Where, P be the load (in grams) and d be the diagonal length (in microns). The micro-hardness falls as load increases and beyond 50gms the load dependence is negligible. In all the three cases the micro-hardness value at 120gms was taken as the accurate microhardness.

The Debye temperature of a solid can be calculated from the equation (2)

$$\theta_\nu = CV^{1/6}M^{-1/2}\psi^{-1/2}$$ (2)

Plendl [12] have been calculated micro-hardness (H) of a crystal, now substituting for $\psi$ in equation 2, the following relation is calculated for Debye temperature ($\theta_H$) in terms of hardness by using equation (3)

$$\theta_H = CV^{1/6}M^{-1/2}H^{1/2}$$ (3)

Where, $C'$ is a new proportionality constant. Seigal [13], Gopi Krishna and Kishan Rao [14] and Shankarnarayana [15] established the above equation for several hcp metals.
The above equation (3) represents the between Debye temperature ($\Theta$) and micro-hardness (H) has been calculated the values on the Re, Os and Tl by resources of the obtainable micro-hardness data in (Hand book of the Physicochemical properties of the elements, 1968) and the obtainable data on thermal properties like Debye temperatures have been calculated in the investigation by the X-ray method and also compared with the specific heat and elastic constant values, these values have been agreed well with each other. Used for this reason the constant C’ has been chosen to be $5 \times 10^{-7}$. The value of the constant is used for measuring the Debye temperature of all the present work Re, Os and Tl metals from the microhardness information. All the values have been summarized in Table 1. Gschneidner [16] have been considered Debye temperature from specific heats and elastic constant, these values also included in Table 1.

**Table 1.** Values of Debye temperatures calculated from Eq.(3), specific heats, elastic constants and X-ray diffraction intensities for Re, Os and Tl.

| Metal | H (kg/mm$^2$) | $\Theta_H$ (K) Eq. (3) | $\Theta_D$ (K) | $\Theta_E$ (K) | $\Theta_M$ (K) Present work | $E_f$ (eV) |
|-------|---------------|----------------------|----------------|----------------|----------------------------|------------|
| Re    | 135           | 388                  | 429            | 421            | 413                        | 5.00       |
| Os    | 400           | 426                  | 467            | 431            | 443                        | 5.59       |
| Tl    | 27            | 74                   | ...            | ...            | 88                         | 0.39       |

$\Theta_H$ - From hardness values (calculated)

$\Theta_D$ - From specific heats (Gschneidner 1964)

$\Theta_E$ - From elastic constants (Gschneidner 1964)

$\Theta_M$ - From X-ray intensities (Present work)

Experimental values of formation energies of metals may be obtained from quenching studies. A measurement of the quenched-in electrical resistivity as a function of quench temperature yields a value for the formation energy as residual electrical resistivity is proportional to the total number of defects frozen in by the quench. Experimental values of the formation energy are available for several metals (Peterson, 1968). The values of formation energies from experiment are not known for many hcp metals and it is desirable to obtain the formation energy from any other known physical quantity. An attempt has been made here to obtain the information from temperatures.

Mukherjee [17] empirically obtained the relation

$$\Theta = C \left( \frac{E_f}{2MV} \right)^{1/2}$$  \hspace{1cm} (4)

Where $\Theta$ is the Debye temperature, $E_f$ the vacancy formation energy, $M$ and $V$ are the mass and volume per atom of the crystal and $C$ is a constant which is the same for all metals. From his empirical calculation Mukherjee suggested a value of 34 for the constant C.

Glyde [18] relation is given by
\[ E_f = A \left( \frac{k}{\hbar} \right)^2 M \theta^2 a^2 \] 

(5)

Where \( a \) is the inter-planar spacing, \( A = 1.17 \times 10^{-2} \), \( M \) be the molecular weight and \( h \) and \( k \) are the Planck and the Boltzmann constants respectively. Purushotham [19, 25] have been used the above equation (5) and calculated vacancy formation energy for several metals and alloys. The calculated values of vacancy formation energies for Re, Os and Tl are also included in Table 1.

Conclusions

In the resent study, the micro-hardness has been calculated the three hexagonal close packed metals Using Vickers’s pyramidal indenter and the true hardness has been estimated. In this present work the calculated Debye temperature values 338 K for Re, 426 K for Os and 74 K for Tl metals. Debye temperatures values of these three hcp metals were measured from the hardness values 135, 400, 27 kg/mm\(^2\) and are compared with those obtained from Debye temperature of specific heats (\( \theta_d \)), Debye temperature of elastic constants (\( \theta_e \)) and Debye temperature of X-ray intensity measurements (\( \theta_\alpha \)). The microhardness of three hcp metals been calculated. The thermal properties of these hcp metals have been measured using the present micro-hardness values and also compared with Debye temperature values calculated from specific heats, elastic constants and X-ray diffraction studies.

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