Research Article

INFLUENCE OF TITANIUM DIOXIDE NANOPARTICLES ON MICROSTRUCTURE, ELECTROCHEMICAL CORROSION BEHAVIOR, MECHANICAL AND THERMAL PROPERTIES OF Sn-Al BI BASED ALLOY

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Abstract

Effect of adding titanium dioxide nanoparticles on microstructure, Vickers hardness, internal friction, thermal parameters and electrochemical corrosion behavior of SnAlBiCuZn alloy has been studied using different experimental techniques. Crystallinity (peak intensity), crystal size (peak broadness) and orientations (peak position, 2θ) of SnAlBiCuZn alloy changed after adding titanium dioxide nanoparticles. Corrosion resistance and internal friction of SnAlBiCuZn alloy improved after adding titanium dioxide nanoparticles. Vickers hardness value of SnAlBiCuZn alloy varied decreased after adding titanium dioxide nanoparticles.

Keywords: corrosion parameters; Vickers hardness; internal friction; titanium dioxide nanoparticles

Introduction

Tin- aluminum alloys have good mechanical properties with conformability but these are quite costly. Aluminum-tin alloys have been used as bearing materials (Forrester PG, 1960) which carry a good combination of strength and surface properties (Pratt GC, 1973). Aluminum-tin based alloys are widely used as sliding bearing materials in automobile and shipbuilding industry (Desaki et al., 2000, Lepper et al., 1997). Tin phase in Al-Sn bearing materials can provide suitable friction properties and shear surface during sliding because it’s low modulus, low strength and the excellent anti-welding characteristics with iron (Desaki et al., 2000). Aluminum- tin and lead- aluminum alloys slightly differ in mechanical properties (Pathak and Mohan, 2003). Indium and lead have lowest elastic modulus of all the soft phases alloying with aluminum (Tegart, 1966). The fatigue strength of cold worked and heat treated AlSnZCu alloy having reticular structure is close to that of CuPb alloy with higher seizure resistance (Forrester, 1961). Strength and ductility of SnSb alloy improved after adding Bi or Cu content (Esfandyarpour and Mahmudi, 2011). Elastic modulus and internal friction of SnSbCuX (X = Pb or Ag or Se or Cd- Zn) alloys dependant on alloy composition (El-Bediwi et al., 2011). Effect of adding Cu or Ag or CuAg on structure, electrical resistivity and elastic modulus of SnSb alloy has been studied and the results show, SnSbAgCu alloy has lowest internal friction, cast and adequate elastic modulus (El-Bediwi, 2004). Adding 1 wt. % Cu or Ag improved mechanical properties of SnSb alloy (El-Bediwi, 2004). Both ultimate tensile strength and ductility of SnSb alloy increased after adding Bi or Cu (Esfandyarpour and Mahmudi, 2011). Elastic modulus, internal friction, hardness and thermal conductivity of SnSb alloy improved after adding (CuPb) elements (Kamal, 2006). Elastic modulus, Vickers hardness and thermal diffusivity of SnSbPb3 and SnAl alloy increases after adding TiO2 nanoparticles. Internal friction, thermal conductivity and specific heat of SnSbPb3 and SnAl alloy varied after adding TiO2 nanoparticles. Adding titanium oxide nanoparticles improved strengths and internal friction of SnSbPb3 and SnAl alloy (El-Bediwi, 2015). Strengths of tin- antimony- lead and tin-aluminum- antimony- lead alloys increased after adding niobium oxide. Also stress exponent of tin- antimony- lead and tin- aluminum- antimony- lead alloys decreased after adding niobium oxide (El-Bediwi, 2015). Corrosion parameters, elastic modulus, internal friction, Vickers hardness, electrical resistivity and thermal parameters of SnSb alloy varied after adding Cu, Bi, Al, Zn and Ag element (El-Bediwi, 2015). Melting point, mechanical properties, contact angle and electrochemical parameters of SnZnBi24 alloy varied after adding Cu, In, Al, Se and Ag contents. Adding Cu, Al, Se and Ag content improve mechanical and electrical properties of SnZnBi24 alloy (El-Bediwi, 2015). The aim of this work was to study the...
effect of titanium dioxide on microstructure, electrochemical corrosion behavior, thermal process, internal friction and Vickers hardness of SnAl10Bi10CuZn2 alloy.

Experimental Work
SnAl10Bi10CuZn2(TiO2)x alloys were prepared using tin, aluminum, bismuth, zinc, copper and titanium dioxide with purity better than 99.5 %. The SnAl10Bi10CuZn2(TiO2)x alloys melted in a muffle furnace and the resulting ingots were turned and re-melted again to increase the homogeneity. From these alloys long ribbons of ~ 4 mm width and ~ 90 µm thicknesses were prepared by single roller melt spinning technique. Using double knife cuter the samples cut into convenient shape for all measurements. Microstructure of used alloys was performed using Shimadzu X-ray Diffractometer, (Dx-30, Japan) Cu–Kα radiation with λ=1.54056 Å at 45 kV and 35 mA and Ni–filter, in the angular range 20 ranging from 0 to 100° in continuous mode with a scan speed 5 deg/min and scanning electron microscope (JEOL JSM-6510LV, Japan). The polarization studies were performed using Gamry Potentiostat/Galvanostat with a Gamry framework system based on ESA 300. Gamry applications include software DC105 for corrosion measurements, and Echem Analyst version 5.5 software packages for data fitting. The differential scanning calorimetry (DSC) thermographs were obtained by SDT [Q600 (V20.9 Build 20), U. S. A] instrument with heating rate 10 k/min in the temperature range 0-400 °C. A digital Vickers micro-hardness tester, (Model-FM-7- Japan), was used to measure Vickers hardness values. The internal friction Q−1 was determined using the dynamic resonance method (Cullity, 1959, Schreiber et al., 1973, Timoshenko and Goddier 1951) by plotting the amplitude of vibration against the frequency of vibration. The thermal diffusivity $D_a$ has been derived from resonance peak (Berry and Pritchett, 1973).

Microstructure

X-Ray Analysis
Fig. 1 (a, b, c and d) shows x-ray diffraction patterns of SnAl10Bi10CuZn2(TiO2)x alloys. Fig. 1a shows the SnAl10Bi10CuZn2 alloy has sharp lines corresponding to β-Sn phase and hexagonal Bi phase with started base line ~ 100 counts. SnAl10Bi10CuZn2(TiO2)0.5 alloys have sharp lines corresponding to tetragonal β-Sn phase and hexagonal Bi phase with various started base line (increased started base line up to 1 wt.% TiO2 nanoparticle and then decreased). Also crystallinity (peak intensity), crystal size (peak broadness) and orientations (peak position, 2θ) of SnAl10Bi10CuZn2 alloy changed after adding titanium dioxide nanoparticles as shown in Fig. 1a (a–d). The detail of x-ray analysis of SnAl10Bi10CuZn2(TiO2)x alloys from the x-ray device (2θ, Int. %, d Å, FHWM and area) and from x-ray cards (phase and Miller indices) are listed in Table 1 (a, b, and c). The analysis show that, Al, Cu, Zn atoms and TiO2 nanoparticle dissolved in matrix formed a solid solution and/or undetected phases and changed its microstructure. The estimated crystal size was given through measured diffraction pattern broadening by Scherer formula (Cullity, 1959). Crystal size of β-Sn phase in SnAl10Bi10CuZn2 alloy varied increased after adding titanium dioxide as presented in Table 1d. Lattice microstrain of SnAl10Bi10CuZn2(TiO2)0.5 alloys were calculated from the relation between full half width maximum (FHWM) and 4tanθ as shown in Fig. 1e. Lattice microstrain of SnAl10Bi10CuZn2 alloy decreased after adding titanium dioxide up to 1 wt. % and then increased as listed in Table 1e. The SnAl10Bi10CuZn2(TiO2)1.5 alloy has lower microstrain value.

Fig. 1: x-ray diffraction patterns of SnAl10Bi10CuZn2(TiO2)x alloys (a. SnAl10Bi10CuZn2 alloy; b. SnAl10Bi5Cu2Zn2(TiO2)0.5 alloy; c. SnAl10Bi5Cu2Zn2(TiO2)1.0 alloy; d. SnAl10Bi5Cu2Zn2(TiO2)1.5 alloy)
### Table 1a: x-ray analysis of Sn$_{76}$Al$_{10}$Bi$_{9.5}$Cu$_{2}$Zn$_{2}$(TiO$_{2}$)$_{0.5}$ alloy

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### Table 1b: x-ray analysis of Sn$_{76}$Al$_{10}$Bi$_{9.5}$Cu$_{2}$Zn$_{2}$(TiO$_{2}$)$_{1}$ alloy

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Table 1b: X-ray analysis of Sn$_{76}$Al$_{10}$Bi$_{8}$Cu$_2$Zn$_2$(TiO$_2$)$_1$ alloy

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<td>1.29646</td>
<td>13.01</td>
<td>0.1574</td>
<td>8.87</td>
<td>Sn</td>
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<td>79.2891</td>
<td>1.20832</td>
<td>17.06</td>
<td>0.2165</td>
<td>16</td>
<td>Sn</td>
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<td>89.1584</td>
<td>1.09837</td>
<td>8.49</td>
<td>0.3149</td>
<td>11.59</td>
<td>Sn</td>
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<tr>
<td>95.2935</td>
<td>1.04321</td>
<td>7.53</td>
<td>0.2362</td>
<td>7.7</td>
<td>Sn</td>
<td>332</td>
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<tr>
<td>97.3767</td>
<td>1.02552</td>
<td>3.45</td>
<td>0.768</td>
<td>15.53</td>
<td>Sn</td>
<td>521</td>
</tr>
</tbody>
</table>

This paper can be downloaded online at [http://ijasbt.org](http://ijasbt.org) & [http://nepjol.info/index.php/IJASBT](http://nepjol.info/index.php/IJASBT)
of Sn_{76}Al_{10}Bi_{10-x}Cu_{x}Zn_{2}(TiO_{2})_{x} alloys are listed in Table 2. Internal friction of Sn_{76}Al_{10}Bi_{10}Cu_{x}Zn_{2} alloy decreased after adding titanium dioxide nanoparticles. Also thermal diffusivity increased (varied increased) up to 1 wt. % titanium dioxide and then decreased.

**Table 1d**: crystal size of β-Sn in Sn_{76}Al_{10}Bi_{10-x}Cu_{x}Zn_{2}(TiO_{2})_{x} alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>(Sn) τ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}</td>
<td>347.647</td>
</tr>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}(TiO_{2})_{0.5}</td>
<td>387.704</td>
</tr>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}(TiO_{2})_{1}</td>
<td>383.817</td>
</tr>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}(TiO_{2})_{1.5}</td>
<td>352.74</td>
</tr>
</tbody>
</table>

**Table 1e**: lattice microstrain of Sn_{76}Al_{10}Bi_{10-x}Cu_{x}Zn_{2}(TiO_{2})_{x} alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>(g) x10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}</td>
<td>0.9</td>
</tr>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}(TiO_{2})_{0.5}</td>
<td>0.7</td>
</tr>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}(TiO_{2})_{1}</td>
<td>0.4</td>
</tr>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}(TiO_{2})_{1.5}</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Table 2**: internal friction and thermal diffusivity of Sn_{76}Al_{10}Bi_{10-x}Cu_{x}Zn_{2}(TiO_{2})_{x} alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Q_{1}</th>
<th>D_{0} x 10^{9} (m^{2}/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}</td>
<td>0.058</td>
<td>22.65</td>
</tr>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}(TiO_{2})_{0.5}</td>
<td>0.0573</td>
<td>45.9</td>
</tr>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}(TiO_{2})_{1}</td>
<td>0.0496</td>
<td>31.5</td>
</tr>
<tr>
<td>Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2}(TiO_{2})_{1.5}</td>
<td>0.0429</td>
<td>21.9</td>
</tr>
</tbody>
</table>

**Scanning electron microscope analysis (SEM)**

Scanning electron micrographs of Sn_{76}Al_{10}Bi_{10-x}Cu_{x}Zn_{2}(TiO_{2})_{x} alloys are shown in Fig. 2. Sn_{76}Al_{10}Bi_{10}Cu_{2}Zn_{2} has a large dendrite tin structure contained many small grains disturbed in it (white color), slabs from aluminium grain (bright white color) and large bismuth grain (black color). Adding different ratio from TiO_{2} nanoparticles changed the shape and size of dendrite structure and disturbed dissolved atoms as grains in it. SEM analysis for used alloys shows heterogeneity structure and that is agreed with x-ray analysis.

**Internal friction and thermal diffusivity**

Internal friction measurements have been quick fruitful for learning about the behavior of metallic materials. Fig. 3 shows the resonance curves of Sn_{76}Al_{10}Bi_{10-x}Cu_{x}Zn_{2}(TiO_{2})_{x} alloys. Calculated internal friction and thermal diffusivity
Vickers Microhardness and Maximum Shear Stress
Vickers hardness of $\text{Sn}_{76}\text{Al}_{10}\text{Bi}_{10-x}\text{Cu}_{2}\text{Zn}_{2}(\text{TiO}_{2})_x$ alloys at 10 gram force and indentation time 5 sec are presented in Table 3. Also the calculated maximum shear stress of used alloys is presented in Table 3. Vickers hardness value of $\text{Sn}_{76}\text{Al}_{10}\text{Bi}_{10}\text{Cu}_{2}\text{Zn}_{2}$ alloy decreased, (varied decreased), after adding titanium dioxide nanoparticles.

Table 3: Vickers hardness and maximum shear stress of used alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$H_v$ kg/mm$^2$</th>
<th>$\mu_s$ kg/mm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sn}<em>{76}\text{Al}</em>{10}\text{Bi}<em>{10}\text{Cu}</em>{2}\text{Zn}_{2}$</td>
<td>46.6±8.1</td>
<td>15.38</td>
</tr>
<tr>
<td>$\text{Sn}<em>{76}\text{Al}</em>{10}\text{Bi}<em>{10-x}\text{Cu}</em>{2}\text{Zn}<em>{2}(\text{TiO}</em>{2})_{0.5}$</td>
<td>24.4±1.4</td>
<td>8.05</td>
</tr>
<tr>
<td>$\text{Sn}<em>{76}\text{Al}</em>{10}\text{Bi}<em>{10-x}\text{Cu}</em>{2}\text{Zn}<em>{2}(\text{TiO}</em>{2})_{1}$</td>
<td>39.43±2.3</td>
<td>13.012</td>
</tr>
<tr>
<td>$\text{Sn}<em>{76}\text{Al}</em>{10}\text{Bi}<em>{10-x}\text{Cu}</em>{2}\text{Zn}<em>{2}(\text{TiO}</em>{2})_{1.5}$</td>
<td>42.2±4.2</td>
<td>13.93</td>
</tr>
</tbody>
</table>

Electrochemical Corrosion Behavior
Electrochemical polarization curves of $\text{Sn}_{76}\text{Al}_{10}\text{Bi}_{10-x}\text{Cu}_{2}\text{Zn}_{2}(\text{TiO}_{2})_x$ alloys in 0.25 M HCl are shown in Fig. 4. The corrosion potential of $\text{Sn}_{76}\text{Al}_{10}\text{Bi}_{10-x}\text{Cu}_{2}\text{Zn}_{2}(\text{TiO}_{2})_x$ alloys exhibited a negative potential. Also the cathodic and the anodic polarization curves exhibited similar corrosion trends. The corrosion current ($I_{\text{Corr}}$), corrosion potential ($E_{\text{Corr}}$) and corrosion rate (C. R) of $\text{Sn}_{76}\text{Al}_{10}\text{Bi}_{10-x}\text{Cu}_{2}\text{Zn}_{2}(\text{TiO}_{2})_x$ alloys in 0.25 M HCl are presented in Table 4. Corrosion rate and corrosion current values of $\text{Sn}_{76}\text{Al}_{10}\text{Bi}_{10-x}\text{Cu}_{2}\text{Zn}_{2}$ alloy decreased after adding 0.5 and 1.5 wt. % titanium dioxide nanoparticles but they increased after adding 1 wt. %.
Table 4: $E_{corr}$, I$_{corr}$ and C. R of Sn$_{76}$Al$_{10}$Bi$_{10}$
$\times$Cu$_{2}$Zn$_{2}$(TiO$_{2}$)$_{x}$ alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$E_{corr}$ mV</th>
<th>I$_{corr}$ μA</th>
<th>C. R mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$<em>{76}$Al$</em>{10}$Bi$<em>{10}$Cu$</em>{2}$Zn$_{2}$</td>
<td>-943</td>
<td>3.69</td>
<td>3.861e3</td>
</tr>
<tr>
<td>Sn$<em>{76}$Al$</em>{10}$Bi$<em>{9.5}$Cu$</em>{2}$Zn$<em>{2}$(TiO$</em>{2}$)$_{0.5}$</td>
<td>-873.0</td>
<td>3.27</td>
<td>3.424e3</td>
</tr>
<tr>
<td>Sn$<em>{76}$Al$</em>{10}$Bi$<em>{9}$Cu$</em>{2}$Zn$<em>{2}$(TiO$</em>{2}$)$_{1}$</td>
<td>-704.0</td>
<td>9.05</td>
<td>9.475e3</td>
</tr>
<tr>
<td>Sn$<em>{76}$Al$</em>{10}$Bi$<em>{8.5}$Cu$</em>{2}$Zn$<em>{2}$(TiO$</em>{2}$)$_{1.5}$</td>
<td>-875.0</td>
<td>2.92</td>
<td>3.085e3</td>
</tr>
</tbody>
</table>

The results of EFM experiments are a spectrum of current response as a function of frequency. Fig. 5 shows the intermodulation spectrum of Sn$_{76}$Al$_{10}$Bi$_{10}$xCu$_{2}$Zn$_{2}$(TiO$_{2}$)$_{x}$ alloys in 0.25 M HCl solutions. The larger peaks were used to calculate the corrosion current density and the corrosion rate which presented in Table 5. Corrosion rate value of Sn$_{76}$Al$_{10}$Bi$_{10}$Cu$_{2}$Zn$_{2}$ alloy decreased, varied decreased, after adding titanium dioxide nanoparticles but corrosion current density increased, varied increased, after adding titanium dioxide nanoparticles.

Table 5: $i_{corr}$ and C. R of Sn$_{76}$Al$_{10}$Bi$_{10}$xCu$_{2}$Zn$_{2}$(TiO$_{2}$)$_{x}$ alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$i_{corr}$ μA</th>
<th>C. R mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$<em>{76}$Al$</em>{10}$Bi$<em>{10}$Cu$</em>{2}$Zn$_{2}$</td>
<td>29.92</td>
<td>31.33e3</td>
</tr>
<tr>
<td>Sn$<em>{76}$Al$</em>{10}$Bi$<em>{9.5}$Cu$</em>{2}$Zn$<em>{2}$(TiO$</em>{2}$)$_{0.5}$</td>
<td>161.6</td>
<td>169.3</td>
</tr>
<tr>
<td>Sn$<em>{76}$Al$</em>{10}$Bi$<em>{9}$Cu$</em>{2}$Zn$<em>{2}$(TiO$</em>{2}$)$_{1}$</td>
<td>62.44</td>
<td>65.38</td>
</tr>
<tr>
<td>Sn$<em>{76}$Al$</em>{10}$Bi$<em>{8.5}$Cu$</em>{2}$Zn$<em>{2}$(TiO$</em>{2}$)$_{1.5}$</td>
<td>66.74</td>
<td>69.89</td>
</tr>
</tbody>
</table>

Fig. 5: The intermodulation spectrum of Sn$_{76}$Al$_{10}$Bi$_{10}$
$\times$Cu$_{2}$Zn$_{2}$(TiO$_{2}$)$_{x}$ alloys

Thermal Behaviour and Parameters
Thermal analysis is used to study solid state transformations as well as solid liquid reactions. They depend on the nature of solid phase and on its temperature. The DSC thermographs were obtained with heating rate 10 °C/min in the temperature range 0-400 °C. Fig. 6 shows the DSC thermographs of Sn$_{76}$Al$_{10}$Bi$_{10}$xCu$_{2}$Zn$_{2}$(TiO$_{2}$)$_{x}$ alloys. No significant effect on melting temperature value of Sn$_{76}$Al$_{10}$Bi$_{10}$Cu$_{2}$Zn$_{2}$ alloy after adding titanium dioxide nanoparticles as presented in Table 6.

Fig. 6: DSC graphs of used alloys
Conclusion
Lattice microstrain of Sn76Al10Bi10Cu2Zn2 alloy decreased after adding titanium dioxide up to 1 wt. % and then increased. Internal friction of Sn76Al10Bi10Cu2Zn2 alloy decreased after adding titanium dioxide nanoparticles. Corrosion rate and corrosion current values of Sn76Al10Bi10Cu2Zn2 alloy decreased after adding 0.5 and 1.5 wt. % titanium dioxide nanoparticles but they increased after adding 1 wt. %. Corrosion rate value of Sn76Al10Bi10Cu2Zn2 alloy decreased, varied decreased, after adding titanium dioxide nanoparticles but corrosion current density increased, varied increased, after adding titanium dioxide nanoparticles. No significant effect on melting temperature value of Sn76Al10Bi10Cu2Zn2 alloy after adding titanium dioxide nanoparticles.

Table 6: Melting temperature of used alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Melting temperature °C</th>
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</thead>
<tbody>
<tr>
<td>Sn76Al10Bi10Cu2Zn2</td>
<td>212</td>
</tr>
<tr>
<td>Sn76Al10Bi9.5Cu2Zn2(TiO2)0.5</td>
<td>210.1</td>
</tr>
<tr>
<td>Sn76Al10Bi9Cu2Zn2(TiO2)1</td>
<td>212.3</td>
</tr>
<tr>
<td>Sn76Al10Bi8.5Cu2Zn2(TiO2)1.5</td>
<td>213.8</td>
</tr>
</tbody>
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References


Cullity BD (1959) *Element of x-ray diffraction*, Ch.10: 297


Schreiber E, Anderson OL and Soga N (1973) *Elastic Constants and their Measurement*, McGraw-Hill Book Company Ch. 4
