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THE LOW TEMPERATURE SPECIFIC HEATS OF TRANSITION METAL ALLOYS

D.E. Moody and M. Huq (+)


Resumé.— Nous donnons de nouvelles mesures de chaleur spécifique à basse température de quelques alliages de métaux de transition. A l'aide des résultats, nous pouvons obtenir des valeurs de la chaleur spécifique électronique, qui sont différentes des prédictions du modèle de Miedema.

Abstract.— New measurements are presented of the low temperature thermal capacity of some transition metal alloys. From the results we have derived values of the electronic specific heat, which are quite different to the predictions of Miedema’s model.

INTRODUCTION.— In the course of developing highly successful rules describing the formation of alloys and intermetallic compounds Miedema /1,2/ introduced an electronegativity scale, based on experimentally determined work functions and adjusted within the experimental error to improve the self consistency of the charge transfer model upon which the rules were based. Estimates of the charge transfer occurring on alloying indicated that this was simply related to the difference in electronegativities of the alloying elements, so that the transfer could now be estimated for any particular alloy.

Subsequently, Miedema showed that both electronic specific heats and superconducting transition temperatures of transition metal alloys could be predicted in terms of electron transfer, and it seemed that the contributions made by each site to the density of states at the Fermi level, the attractive electron-phonon interaction, and the repulsive Coulomb pseudopotential are almost entirely determined by the on-site electron concentration, that is, the atomic number plus the charge transfer on the site /3,4/. In the initial application to γ values /3/, which ignored the electron-phonon enhancement, Miedema suggested that measurements be made on a number of unexplored alloys, chosen on the basis that the rigid band and charge transfer models gave quite different predictions. Although this model was later modified to incorporate electron-phonon enhancement, the predictions of γ values were substantially unchanged. Some of the suggested alloys have now been measured and these and other results are reported in the following.

EXPERIMENTAL RESULTS.— Specimens were formed by argon arc melting, using Johnson Matthey 'Specpure' materials, and were vacuum annealed at 900°C prior to measurement in our computer controlled calorimeter /5,6/, operated in the temperature range 1.4 - 4.2 K. The results are presented in the conventional graphical form in figure 1 and are shown as smooth curves since the scatter is imperceptible on this scale. Most of the curves show some upward curvature and in these cases the results have been parametrised by fitting the equation $C = A + \gamma T + BT^2$ rather than the usual $\gamma T + BT^3$, and the coefficients derived by minimising $\sum(C - C_{\text{calc}})^2$ are presented in table I. The relationship of the derived γ values to the experimental results is also shown in figure 1 by plotting the line of $YT + BT^2$ for each alloy. Apart from five of the alloys suggested by Miedema, results are also included for Pd5Mo and Pd5Nb, which extends earlier work at lower concentrations /7/.

It is not clear at this stage what significance should be attached to the constant term A in the specific heat of most of the alloys, but it can be seen from figure 1 that the only γ value which might be seriously in error is that for Pt30W.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Concentration (if analysed)</th>
<th>γ (all in mJ for 1 mole)</th>
<th>A (all in mJ for 1 mole)</th>
<th>rms dev (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt17Ti</td>
<td>18.3</td>
<td>2.21</td>
<td>0.068</td>
<td>0.65</td>
</tr>
<tr>
<td>Pt30W</td>
<td>29.8</td>
<td>3.6</td>
<td>0.01</td>
<td>4.2</td>
</tr>
<tr>
<td>Ir10Hf</td>
<td>-</td>
<td>2.70</td>
<td>0.026</td>
<td>-</td>
</tr>
<tr>
<td>Pt20V</td>
<td>20.7</td>
<td>3.28</td>
<td>0.058</td>
<td>0.74</td>
</tr>
<tr>
<td>Pd20Ti</td>
<td>-</td>
<td>1.80</td>
<td>0.037</td>
<td>0.16</td>
</tr>
<tr>
<td>Pd5Mo</td>
<td>-</td>
<td>4.47</td>
<td>0.067</td>
<td>-</td>
</tr>
<tr>
<td>Pd5Nb</td>
<td>-</td>
<td>4.88</td>
<td>0.072</td>
<td>-</td>
</tr>
</tbody>
</table>

(*) Now at University of Mosul, Iraq.
DISCUSSION.- To effect a comparison between the present results and those considered previously by Miedema, they are shown in figure 2 superimposed on a copy of figure 7 from reference /4/. One is immediately tempted to conclude that the predictive capabilities of the model compare very badly with its ability to fit existing data, but it should be borne in mind that, of the non-ferromagnetic transition metal alloys to which the model applies, relatively few have been studied calorimetrically, those that have tending to be either isoelectronic or have similar electron/atom ratios. Since the present investigation has already doubled the number of experimental γ values for transition metal alloys in which the electron/atom ratio differs by five or more, it is perhaps not surprising that the predictions are rather poor. It might be possible to revise the model parameters to incorporate the new data, but since the development of our computer controlled calorimeter has removed all impediments to experimental progress save that of specimen preparation any possible revision is likely to be a continuing process.

The main need now is to extend the experimental work to include many more alloys characterised by a large electron/atom difference between the constituents, in the course of which we hope to see, for example, whether the very low γ value found in Pd20Ti and probably occurring in a number of other Pd based alloys (indicating a split band regime) will appear at some higher concentration in Pt alloys.

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References