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INTERNAL OXIDATION OF IMPURITIES IN PALLADIUM INVESTIGATED BY X-RAY ABSORPTION SPECTROSCOPY

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Abstract.-
The internal oxidation of dilute Pd alloys has been studied by XAS. Pt, Au, Pb and Bi in Pd form no impurity-oxygen complexes. Y, Nb, Gd, Yb, Lu, Hf, Th, Zr and Mo precipitate at 1050°C as oxides.

In a recent paper /1/ it was shown how X-ray absorption spectroscopy (XAS) can be used to investigate the internal oxidation of impurities in dilute alloys. It was demonstrated in the case of a Zr alloy with 2.8% Zr that oxygen trapped at the Zr shifts the Zr K edge to higher energies. Details of the structure of the Zr-O complex can be deduced from the corresponding EXAFS at the Zr K edge. In this paper the procedure is applied to 13 dilute Pd alloys. The foils were heated for 1 hour in 1 bar of oxygen and quenched into water. Table 1 gives a list of the alloys investigated. The oxygen concentration was determined by weighing. The partial loss of Pb by evaporation during the loading procedure made it impossible to determine the oxygen concentration in PdPb. The X-ray absorption measurements were made at the spectrometer RÖMO of the Hamburger Synchrotronstrahlungslabor. A Si(311) double crystal monochromator was used. All measurements were done in transmission at 77 K.

TABLE 1: Dilute Pd alloys with impurity concentration $c_i$, oxygen concentration $c_0$ taken up at temperature $T_a$ and oxides investigated.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>$c_i$ (a/o)</th>
<th>$c_0$ (a/o)</th>
<th>$T_a$ (°C)</th>
<th>Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1.92</td>
<td>0.31</td>
<td>1037</td>
<td>-</td>
</tr>
<tr>
<td>Nb</td>
<td>2.00</td>
<td>6.05</td>
<td>1053</td>
<td>$\text{Nb}_2\text{O}_3$, $\text{Nb}_2\text{O}_5$</td>
</tr>
<tr>
<td>Gd</td>
<td>2.28</td>
<td>7.18</td>
<td>1053</td>
<td>$\text{Gd}_2\text{O}_3$, $\text{Yb}_2\text{O}_3$, $\text{Lu}_2\text{O}_3$, $\text{HfO}_2$</td>
</tr>
<tr>
<td>Th</td>
<td>1.72</td>
<td>6.97</td>
<td>1051</td>
<td>$\text{Th}_2\text{O}_3$</td>
</tr>
<tr>
<td>Zr</td>
<td>2.06</td>
<td>4.75</td>
<td>1037</td>
<td>$\text{Zr}_2\text{O}_3$, $\text{BaZr}_2\text{O}_3$</td>
</tr>
<tr>
<td>Mo</td>
<td>2.11</td>
<td>6.42</td>
<td>1037</td>
<td>$\text{Mo}_2\text{O}_3$, $\text{Mo}_3\text{O}_3$</td>
</tr>
</tbody>
</table>
The impurities dissolved in Pd can be divided into two groups, as indicated in table 1. The impurities of group 1 do not interact with the oxygen whereas those of group 2 precipitate as oxides or as precursors of oxides. Measurements of the L₃ absorption edges of Pt, Au, Pb and Bi in Pd showed no changes between the oxidized and non-oxidized states. This is demonstrated in the figure 1 for the PdPt. For comparison the edge of PtO₂ is also shown. The edges are identical before and after oxidation and very different from those of the oxides. There is also no difference in the EXAFS above the L₃ edges in the oxidized and non-oxidized PdPt, PdAu, PdPb and PdBi samples. We conclude that Pt, Au, Pb and Bi in Pd do not trap oxygen nor are they precipitated as oxides at 1050 °C. In the case of Au this result is not surprising in view of the small oxygen uptake noted in table 1. In the case of PdPt and PdBi more oxygen is taken up than in pure Pd (0.20 at%). It is not clear what causes the increased oxygen uptake in these alloys. Oxygen in the vicinity of Pt and Bi can clearly be ruled out on the basis of the XAS data.

In a second group of dilute Pd alloys the impurities precipitate as oxides. The group includes PdY, PdNb, PdGd, PdYb, PdLu, PdHf and PdTh. It turned out that for these impurities the oxides precipitated at 1050 °C are those with the highest state of oxidation i.e. Y₂O₃, Nd₂O₅, Gd₂O₃, Yb₂O₃, Lu₂O₃, Ho₂O₃ and ThO₂. In figure 2 is shown the K edge of Y in the oxidized alloy, in the non-oxidized alloy and in Y₂O₃.

It is obvious that the edges of the oxidized samples are identical with those of Y₂O₃ and very different from that in the non-oxidized state. Similar results were observed for the other alloys of this group. The EXAFS X "k² of the oxidized samples are also identical to those of the oxides, as is shown in the figure 3 for oxidized PdY and Y₂O₃. The same is true for the other alloys of this group. In the case of PdNb we have compared the edges of the oxidized and non-oxidized alloys with those of Nb₂O₅ and NbO₁.₀₃. The edge of the oxidized sample is identical with that of Nb₂O₅ whereas there is no resemblance with that of NbO₁.₀₃. The EXAFS of the oxidized PdNb alloy is also identical with that of Nb₂O₅.

In the case of PdZr and PdMo the analysis was less straightforward.
Figure 2: Y K edge in Pd Y 2 % (*), in oxidized Pd Y (-) and in Y2O3 (+).

Figure 3: EXAFS $\chi \cdot k^2$ above the Y K edge in oxidized Pd Y (-) and in Y2O3 (+).

Figure 4 shows the edges of the oxidized alloy, of the non-oxidized alloy and of monoclinic ZrO2. There is clear indication of an interaction of the oxygen with the Zr atoms. Otherwise the edges of the oxidized and non-oxidized alloy would be identical. The edge of the oxidized alloy is very similar to that of monoclinic ZrO2 indicating tetravalent Zr in the oxidized sample. On the other hand the EXAFS of the oxidized alloy is completely different from that of monoclinic ZrO2. We have analyzed the EXAFS of the oxidized alloy in detail. In the non-oxidized sample the first four Pd shells around the Zr atoms are visible. In the oxidized alloy the signal is weaker indicating a poorly crystallized state around the Zr atoms. Two shells are nevertheless visible. The first shell is attributed to oxygen. It has been analyzed with the amplitudes and phases transferred from the cubic perovskite BaZrO3, giving a shell of 4 oxygens at a distance of (2.06 ± 0.02) Å from Zr. The second shell has been analyzed in two ways, once with Pd (model ZrPd$_3$) and once with Zr (model metallic Zr) as backscatterers. Zirconium as a backscatterer gave the better fit. We found (12 ± 1) Zr.
atoms at a distance of \((3.60 \pm 0.01) \text{ Å}\) from another Zr atom. As is visible from the EXAFS the Zr-O complex is obviously not monoclinic ZrO\(_2\). It is also not cubic ZrO\(_2\) which has 8 oxygens at \(2.21 \text{ Å}\) and 12 Zr at 3.59 Å. It is rather a poorly crystallized complex showing only one oxygen and one Zr shell.

In the case of PdMo the edges and the amount of oxygen uptake indicate a strong interaction of the oxygen with Mo atoms. The Mo K-edge of the oxidized sample has strong resemblance to that of MoO\(_3\) and no resemblance to that of MoO\(_2\). Again the impurities have reached the highest state of oxidation. But the EXAFS in the oxidized alloy was too weak to be analyzed. Only a first shell of oxygens is visible. In PdMo only a poorly crystallized Mo-O precipitate forms in oxygen at 1037°C.

X-ray absorption spectroscopy has been applied to the internal oxidation of impurities in thirteen dilute Pd alloys. Impurity-oxygen interactions are indicated by shifts in the position of the K and L\(_3\) impurity edges. Details of the nature of the precipitates are obtained from the EXAFS. It turned out that Pt, Au, Pb and Bi in Pd are not oxidized at 1050°C. Y, Nb, Gd, Yb, Lu, Hf and Th precipitate at 1050°C as oxides Y\(_2\)O\(_3\), Nb\(_2\)O\(_5\), Gd\(_2\)O\(_3\), Yb\(_2\)O\(_3\), Lu\(_2\)O\(_3\), HfO\(_2\) and ThO\(_2\), respectively. This are the oxides with the highest state of oxidation of the corresponding metal atoms. Zr and Mo in Pd are also converted to the highest state of oxidation (4 and 6 valent, respectively). But the precipitates are only poorly crystallized showing only 1 or 2 shells around the impurities. One more point is noteworthy. In all alloys where fully crystallized oxides precipitate (group 2a in table 1), the oxygen uptake is systematically larger than that corresponding to the oxygen to metal ratio of the oxides. This might be due to the finite size of the precipitates, which could be surrounded by a cloud of oxygen. Further work is needed to test this hypothesis.

REFERENCES