Thin film bicrystals have been created using gold, silver, palladium and platinum epitaxially grown single crystals. Low angle twist boundaries in all systems consisted of orthogonal sets of lattice dislocations, whose character is in agreement with the O-lattice theory and earlier less general predictions. High angle boundaries in the Au-Pt system were seen to relax into dislocation networks at temperatures in excess of 600°. However, the
20. Dislocation directions and spacings could not be interpreted in terms of CSL or NCSL relaxations.

All the experiments were rendered more difficult than anticipated because of the difficulties of making the continuous flat single crystals. A critique of the general method of thin film welding for the study of grain boundaries is included.
ABSTRACT

Thin film bicrystals have been created using gold, silver, palladium and platinum epitaxially grown single crystals. Low angle twist boundaries in all systems consisted of orthogonal sets of lattice dislocations, whose character is in agreement with the O-lattice theory and earlier less general predictions. High angle boundaries in the Au-Pt system were seen to relax into dislocation networks at temperatures in excess of 600°C. However the dislocation directions and spacings could not be interpreted in terms of CSL or NCSL relaxations.

All the experiments were rendered more difficult than anticipated because of the difficulties of making the continuous flat single crystals. A critique of the general method of thin film welding for the study of grain boundaries is included.
1. Introduction

The major objective of this programme was to study the effect of a mismatch between the lattice parameters of two grains on the structure of the interface between them. In order to study this in a controlled way the phase boundary was to be created by extending the thin film welding technique, hitherto only used for gold, to the welding of dissimilar crystals. In order to simplify both the crystallography and the experimental technique it was decided to use the f.c.c. noble metals; gold, silver, platinum and palladium. Different pairs of these crystals give a range of lattice parameter mismatch from zero to about 5%.

The success of the programme depended on four consecutive stages of development; the preparation of thin single crystals, welding pairs of these to create the phase boundary, imaging the boundary microstructure in the electron microscope and finally the interpretation of the observations in terms of models of boundary structure. Our achievements under each of these four headings are considered below, followed by an overall critique of the usefulness and potential of this general approach to the study of phase boundaries.

2. Preparation of single crystals

The technique for the preparation of thin (~25nm) single crystals of gold was well established before the start of this work. The conventional technique consists of vapour deposition of the gold onto a relatively thick (~1μm) interlayer of silver, itself epitaxially deposited onto a single crystal substrate.
of sodium chloride. This technique is clearly not suitable for the deposition of thin films of silver or palladium, nor is it even appropriate for gold films if they are subsequently to be welded to silver films, since the acid needed to dissolve the silver interlayer would also remove the other half of the bicrystal.

We therefore developed techniques for growing single crystal thin films of gold, silver and palladium directly onto alkali halide substrates. We were not successful in growing platinum in this way so we could not investigate the silver/platinum bicrystal system. The successful methods involved alternative alkali halide substrates and in some cases required a surface treatment of the substrate prior to deposition using either water vapour or electron bombardment. The full experimental details are given in Appendix 1.

We used (100) oriented single crystals in this work, so the substrates were in all cases cleaved to expose this face. It is important for later stages of the work that the single crystal films are thin enough for the bicrystal to be electron transparent yet they must be absolutely continuous since any holes will open up during the welding process or later anneals. In addition the surfaces of the films should be as flat as possible and the density of growth defects (twins and stacking faults) should be low. It is easy to grow gold films in the conventional manner on a silver interlayer so that they meet all the above criteria. However it was not possible to achieve such all round success with the films needed for this project. Although the major criteria (thin and continuous) were met using the techniques detailed in Appendix 1 even the best resultant films were not ideally flat or defect-free. The characteristics of the best films obtained in this work are summarized in the table.
<table>
<thead>
<tr>
<th>Ag Interlayer</th>
<th>Surface Flatness</th>
<th>Defect Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Yes</td>
<td>Good</td>
</tr>
<tr>
<td>Au</td>
<td>No</td>
<td>Good</td>
</tr>
<tr>
<td>Ag</td>
<td>No</td>
<td>Good</td>
</tr>
<tr>
<td>Pd</td>
<td>No</td>
<td>Fair</td>
</tr>
<tr>
<td>Pt</td>
<td>Yes</td>
<td>Poor</td>
</tr>
</tbody>
</table>

Examples of single crystal films were shown in the first interim report (November 1978).

3. **Welding Single Crystals to Create Phase Boundaries**

For many of the bicrystals made during this programme the conventional welding technique was used: pairs of films, still on their substrates, were clamped together face-to-face at the desired misorientation angle. The clamped pair of crystals was then placed in an oven for a short time (e.g. 4 mins at 450°C for gold/gold bicrystals). The conditions necessary to achieve such a weld in the various bicrystal systems used here is detailed in Appendix 2.

However during the course of this work evidence became available that pressure is not necessary to create a weld (1,2) and subsequently we created several crystals which were simply laid on top of each other and then heated in the electron microscope using a hot stage. The disadvantage of this technique is the inaccuracy of predetermining the misorientation between the crystals.

Examples of welded interfaces prepared by the conventional technique were presented in the first annual report (April 1979) and boundaries produced in the hot-stage were shown in the second interim report (October 1979). The major difficulties associated with the welding process are caused by the surface roughness of platinum and palladium films and by the possibility of alloy compound formation at the interface. The former problem restricts the areas of contact between the crystals and hence limits the size of the boundary regions which are created.
This can only be overcome by improvements to the thin film preparation technique: We were eventually successful in obtaining flat enough single crystals to create 100 μm sized interface regions, although this is still far below the size of the boundary regions attainable in gold bicrystals.

The problem of interdiffusion and compound formation during the welding process is difficult to assess because of the lack of data concerning either the diffusion coefficients of each species in the others or the phase diagram of each system at relatively low temperatures. However, the diffraction evidence presented in the second interim report (Oct. 79) strongly suggests that an intermetallic compound is formed in the Au/Pt system and we have seen similar effects in the Ag/Pd system. Our conclusions about the nature of these compounds are discussed in the next sections.

4. Observations of Interfacial Microstructure

We have observed orthogonal sets of dislocations in low angle boundaries in all the systems which we have welded. Examples from the gold-silver system were presented in the first interim report (Nov. 78), from platinum-platinum in the first annual report (April 79) and from gold-platinum in all three reports on this contract (Nov. 78, April 79 and Oct. 79). Further work has shown that low angle boundaries in silver-palladium and gold-palladium also contain very similar microstructures (e.g. Figure 1). The precise interpretation of these observations is made difficult by two factors: The first is the buckling of the thin films which leads to rapid changes in diffraction conditions across the field of view and hence many extinction contours. The second is the presence in the image of many moiré fringes because of the presence of many close pairs of diffraction spots in reciprocal space. Although in principle the presence of moiré fringes could be an advantage, enabling the exact misorientation to be calculated, in practice the presence of so many diffraction spots makes the assignment of any sets of fringes to a particular pair of spots rather difficult.
The difficulty of performing quantitative image contrast experiments means that it is not possible to deduce the Burgers vectors of the dislocations precisely. However it is possible to measure the dislocation line direction more accurately and this parameter has been used in the interpretation of the images (see Second Interim Report, Oct. 79, and section 5 below).

For the study of high angle boundaries the gold-platinum system was chosen for detailed examination because of the magnitude of the lattice parameter misfit and the apparent lack of mutual solubility. As was reported in the second interim report (Oct. 79) no interfacial dislocation structure was seen until hot stage in-situ experiments were carried out at 650°C or above. Figure 2 gives a further example of the small islands of dislocation arrays which are formed as the boundary relaxes.

5. Interpretation of the Observations

5.1 Low angle boundaries

In all the systems which we studied low angle boundaries could be created at a lower temperature or shorter welding time than higher angle boundaries. This is presumably because of the lower energy of a low angle boundary which ensures that the driving force for welding is greater. In the first two reports on this work (Nov. 78 and April 79) we demonstrated that the low angle (001) twist boundary in the Pt-Pt and Au-Ag systems is accommodated by the same sets of screw lattice dislocations that have been reported in the Au-Au interface (3). We could deduce from these observations that the platinum and silver films are flat enough to weld over an appreciable area. Since the lattice parameter mismatch between gold and silver is only of the order of 0.3%, a very small amount of either interdiffusion or elastic strain near the interface will be sufficient to eliminate the mismatch in the boundary plane and hence we should expect the sets of dislocations which accommodate
the misorientation, as observed.

Having established the feasibility of the techniques we next studied the Au-Pt system, since the initial lattice parameter mismatch is about 4%. An additional potential advantage of this system is that the reported lattice parameter mismatch between the gold-rich and platinum-rich terminal solid solution is still in the region of 4% (4).

The microstructure observed in low angle Au-Pt interfaces has been reported in all three of the earlier reports on this contract (Nov. 78, April 79, Oct 79) and discrete dislocation networks have been observed up to misorientation angles of 10°. The misfit between the two crystals which was measured from the electron diffraction patterns was always less than that expected from the reported bulk lattice parameter values (4). This might reflect the presence of some elastic strain in the thin crystals or could be the result of modification of the lattice parameter by interdiffusion (although the published phase diagrams would not predict a significant effect). It is interesting to note that other workers have found differences in lattice parameter between bulk specimens and deposited thin films of the same material, which was attributed to the high defect density of the thin films (5).

The dislocation arrays in the low angle bicrystals showed a decrease in spacing with increasing twist angle and a deviation of the line direction from the average [110] of the two crystals. This is qualitatively what would be expected of networks which accommodate both misorientation and misfit. Jesser and Kuhlmann-Wilsdorf (6) developed quantitative equations for dislocation spacing and line direction for the particular case of a low angle twist boundary between two crystals of the same structure but different lattice parameter. It is not difficult to show that the identical equations arise from the more general O-lattice theory developed by Bollman (7).
The quantitative agreement between the measured dislocation spacings and line directions and the predictions of either of the above theories is only fair (2nd interim report, Oct. 79). The reason for this is probably associated with the surface roughness of the initial platinum films: The extent of interdiffusion, and hence variation in lattice parameter, will vary very locally depending on the areas of contact of the two original films. However, the values of misfit determined for the diffraction pattern are derived from a region of the bicrystal which is extensive (100μm diameter) compared to the regions of dislocation (~10μm) and are also representative of the average lattice parameter over the whole thickness of each crystal. Clearly local modifications arising from short range diffusion at the interface will not be detected. Because of the essential inhomogeneity of the interface parameters we can expect no better agreement between theory and experiment than we have found. It seems clear that relaxations at the interface follow the predictions of the O-lattice model and its more restricted precursor the Jesser and Kuhlmann-Wilsdorf analysis.

5.2 High angle boundaries

Although it was possible to make the two single crystals adhere at temperatures as low as 450°C no dislocation structure could be resolved in Au-Pt high angle bicrystals until they had been heated to at least 650°C. It is clear that there must be significant bonding across the interface before the atoms close to the boundary relax into a dislocation array. We presented micrographs in our second interim report (Oct. 79, Figs 5, 6, and 8) which illustrate the absence of resolvable structure in a boundary which relaxed into a dislocation network at a higher temperature. Erlings and Schapink (8) have recently reported a similar lack of resolvable structure in apparently welded bicrystals (their fig. 6b).

Annealing of the high angle Au-Pt bicrystals in the hot stage of the electron microscope frequently caused a dislocation structure to become visible after
heat treatment at 650°C to 900°C. Figure 2 of this report is an example of a 17° twist boundary after in-situ heat treatment to 900°C. Unfortunately although the dislocation networks and several sets of moiré fringes are clearly visible the interpretation is not straight-forward because of the complexity of the diffraction pattern.

We reported in October 79 that at 650°C the spots arising from the platinum crystal split in a way which indicated the nucleation of a third phase, of larger parameter than platinum, epitaxially on the platinum crystal. We have indicated this as phase X in Figure 3 (b). Further heating to 900°C results in a fourth phase appearing, apparently growing epitaxially on the gold crystal but with a lattice parameter close to platinum. We have called this phase Y in figure 3 (c).

It appears from this analysis of the diffraction patterns that whereas when creating low angle boundaries relatively little interdiffusion or compound formation occurred, when high angle boundaries are formed higher temperatures are required and fresh phases are nucleated as indicated in Fig. 3. Thus instead of a single interface being formed in the plane of the specimen we have two or three parallel interfaces. We will first consider the possible nature of the phases X and Y and then assess what interfacial microstructure appears in the electron micrographs.

There are brief reports in the literature of the existence of transitory, possible ordered, phases Pt₃Au, PtAu and Au₃Pt (4,9). The only reported lattice parameter measurement indicated that Au₃Pt has a very similar parameter to platinum (4). If one of the other compounds (AuPt or Pt₃Au) has a lattice parameter nearer to that of gold then we could interpret the sequence of events in the following way:
i. In the temperature range 450°C to 650°C the gold and platinum films weld without visible relaxation into dislocation networks.

ii. At about 650°C the phase X, possibly AuPt or Pt₃Au, grows epitaxially on the platinum crystal. There are thus two parallel interfaces: Au/X with a higher angle but only about 1% misfit and X/Pt with a zero angle but about 3% misfit (see table in second interim report, Oct. 79).

iii. At about 900°C the phase Y, probably Au₃Pt, grows at the Au/X interface, forming epitaxially on the gold crystals. We now have three parallel interfaces: Au/Y with zero misorientation and 3% misfit; Y/X with negligible misfit but high angle misorientation and X/Pt as before.

This data is summarized in Figure 3. In order to interpret our micrographs we must establish the various interface structures which could potentially arise. Unfortunately we cannot perform rigorous image contrast analyses on the specimens because of their buckled nature and because of the multiplicity of double diffraction possibilities from a tricrystal. However if all the high angle boundary observations reported in this report and the last (Oct. 79) arise from triple or quadruple crystals (Fig. 3b or c) then we could expect:

a. Edge dislocation arrays and moiré fringes from epitaxial interfaces with misfit but no misorientation (X/Pt or Au/Y).

b. Networks of primary near-screw dislocations and moiré fringes from the medium to high angle interfaces (e.g. Au/X with about 1% misfit and X/Y with near-zero misfit).

c. Networks of secondary DSC dislocations arising from relaxations of high angle boundaries to CSL's (e.g. X/Y, or with some strain Au/X).
or d. Networks of secondary DSC dislocations arising from relaxation to two-dimensional near-coincidence site lattices (NCSLs) (e.g. Au/X). The methods of calculating the properties of these DSC dislocations are treated in the next section.

The table compares the measured properties of the dislocations with the expected behaviour according to the four models a, b, c and d.

**Bicrystal: Au-Pt 13.5° twist**

<table>
<thead>
<tr>
<th></th>
<th>Measured</th>
<th>a</th>
<th>b</th>
<th>12.68°</th>
<th>14.25°</th>
<th>13.57°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dislocation Spacing (Å)</td>
<td>40</td>
<td>95</td>
<td>12</td>
<td>32</td>
<td>20</td>
<td>172</td>
</tr>
<tr>
<td>Line direction (°)</td>
<td>18</td>
<td>7</td>
<td>7</td>
<td>38</td>
<td>38</td>
<td>32</td>
</tr>
</tbody>
</table>

**Bicrystal: Au-Pt 17° twist**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th>16.26°</th>
<th>17.74°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spacing</td>
<td>25</td>
<td>95</td>
<td>10</td>
<td>47</td>
<td>33</td>
</tr>
<tr>
<td>Direction</td>
<td>20</td>
<td>8</td>
<td>8</td>
<td>53</td>
<td>34</td>
</tr>
</tbody>
</table>

**Bicrystal: Au-Pt 20° twist**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th>22.62°</th>
<th>20.22°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spacing</td>
<td>25</td>
<td>95</td>
<td>8</td>
<td>15</td>
<td>36</td>
</tr>
<tr>
<td>Direction</td>
<td>31</td>
<td>10</td>
<td>10</td>
<td>56</td>
<td>18</td>
</tr>
</tbody>
</table>

**Bicrystal: Au-Pt 30° twist**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th>30.51°</th>
<th>29.74°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spacing</td>
<td>25</td>
<td>95</td>
<td>5</td>
<td>41</td>
<td>69</td>
</tr>
<tr>
<td>Direction</td>
<td>44</td>
<td>15</td>
<td>15</td>
<td>30</td>
<td>0</td>
</tr>
</tbody>
</table>

**TABLE 1**

It can be seen that there is no satisfactory agreement between the observed dislocation networks and the predicted interfaces. However, in support of the interpretation of the diffraction patterns in terms of three or four crystals we can invoke the moiré contrast in Fig. 2. : There are clearly
very widely spaced fringes arising from an interface of small misfit or misorientation together with much finer fringes which must arise from a high angle interface. Any further interpretation is rendered virtually impossible in these specimens because of the complexity of the interference effects between three or four buckled crystals.

6. The near-coincidence site lattice model

There are very few (if any) true coincidence site lattices between two crystals with the same structure but different lattice parameters. However there will in general be many two-dimensional coincidence site lattices which can be created on particular boundary planes by applying a small strain to one crystal. These we have termed near-coincidence site lattice (NCSLs): They are true CSLs once a uniform strain has been applied to one lattice. The concept of a planar two-dimensional NCSL has been recognised by a number of workers (10,11,12,13) but no direct evidence for the relaxation of atoms at a boundary to an NCSL by means of arrays of DSC dislocations has been obtained. It was one of the major objectives of this work to look for such evidence and we chose to study planar (100) interfaces in order to maximise the chance of finding such a boundary.

We devised a simple computer programme to search for NCSLs between crystals of specified lattice parameters. The multiplicity of possibilities is illustrated by the single page of output shown in Fig. 4. We can define many boundary parameters which are analogous to those in common use with conventional CSLs. Thus we refer to \( \frac{1}{2} \), the two-dimensional reciprocal density of coincident sites, and to the two-dimensional DSC lattice which defines the Burgers vectors of perfect interfacial dislocations.

Once the strain indicated in the last column of Fig. 4 is applied then a
true two-dimensional CSL exists and we can therefore define a DSC lattice as indicated by Bollmann (7). The easiest way to do this in practice is to use Grimme's theorems (14): this states that the DSC lattice is the reciprocal of the CSL of the two reciprocal lattices of the crystals. For two cubic crystals this is very easy to calculate and hence the basic DSC vectors can be found. These were used to compute the data in Table 1. An example of one of the NCSLs referred to in the table is plotted in Fig. 5.

7. A Critique of the Welded Thin Film Phase Boundary Approach

As is evident from much of this report the experimental approach employing the welding of two thin film single crystal of different materials has not proved as fruitful for the study of phase boundaries as had been hoped. It remains, in principle, one of the few ways in which the interface parameters can be controlled to permit a systematic study of interface boundaries. However the method encounters three types of problem:

i. Production of specimens: It is not always possible to make single crystal films which are thin, continuous and flat enough on a sub-1µm scale to be welded successfully.

ii. Many experimentally suitable alloy systems (e.g. Au-Ag) are ruled out metallurgically because of the complete solubility shown by their phase diagrams. In addition, as we found for Au-Pt, the heat treatment requirements needed to create a boundary may permit the nucleation of a third phase at the designed interface.

iii. Even the best specimens (from the point of view of i and ii above) are extremely buckled and hence the control of diffraction conditions in the electron microscope is very difficult. The successful interpretation of the sort of structural information found in this
project cannot be achieved under such imprecisely known crystallographic and electron diffraction conditions.

The pre-requisites for any future study based on this experimental approach are therefore:

a. The production of thin, continuous, flat (on both fine and coarse scales) single crystals of the intended materials
b. Electron microscopy using microdiffraction from very small areas of the specimen
c. The choice of an alloy system without undesirable compounds.

Nonetheless, as we emphasised above, the approach is still one of the only ways by which we will learn more about how the structure of interphase boundaries depends on the properties and orientations of the two lattices.

8. Conclusions

i. Continuous thin single crystals of platinum, palladium and silver can be grown in a similar manner to that used for gold.

ii. Low angle twist grain boundaries in platinum bicrystals relax into the same dislocation networks as have been observed in gold.

iii. Low angle (001) twist boundaries between dissimilar fcc metals appear to relax into networks of dislocations whose properties are predicted by the O-lattice model or by the theory of Jesser and Kuhlmann-Wilsdorf.

iv. At least two compounds of Au and Pt form between 650°C and 900°C.

v. There is still no direct evidence for the relaxation of a phase boundary to a nearby NCSL.

vi. It is easily possible to construct two-dimensional DSC networks for NCSL interfaces.
Appendix 1

Preparation of thin single crystals

All materials were vapour deposited in a vacuum bell jar at a pressure of \(10^{-5}\) torr onto a substrate at 300°C. The details are as follows:

<table>
<thead>
<tr>
<th>Material</th>
<th>Evaporation System</th>
<th>Substrate</th>
<th>Substrate Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td></td>
<td>KBr</td>
<td>Electron Bombardment*</td>
</tr>
<tr>
<td>Ag</td>
<td>Mo Boat</td>
<td>NaCl</td>
<td>Water vapour +</td>
</tr>
<tr>
<td>Pd</td>
<td></td>
<td>KBr</td>
<td>Water vapour +</td>
</tr>
<tr>
<td>Pt</td>
<td>W wire</td>
<td>Ag/NaCl and Ag/KBr</td>
<td>-</td>
</tr>
</tbody>
</table>

* Electron bombardment was achieved by exposing the substrate surface for at least 6 hours to a 20 millicurie source of \(^{90}\)Sr.

* The water vapour treatment is achieved by covering the substrate and a few drops of water with a Petri dish cover for a few minutes.

Appendix 2

Welding of bicrystals

The conditions needed to create a weld by clamping the two crystals together were:

<table>
<thead>
<tr>
<th>System</th>
<th>Time</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/Au</td>
<td>5 mins</td>
<td>400°C</td>
</tr>
<tr>
<td>Au/Ag</td>
<td>8-10 mins</td>
<td>450°C</td>
</tr>
<tr>
<td>Au/Pd</td>
<td>8-10 mins</td>
<td>500°C</td>
</tr>
<tr>
<td>Ag/Pd</td>
<td>8-10 mins</td>
<td>500°C</td>
</tr>
<tr>
<td>Au/Pt</td>
<td>8-10 mins</td>
<td>450°C (Low angle)</td>
</tr>
<tr>
<td>Pt/Pt</td>
<td>7 mins</td>
<td>650°C</td>
</tr>
</tbody>
</table>

For systems containing Pt or Pd higher temperatures were generally needed to create high angle boundaries.
Appendix 3

Staff working on the project:
Dr. Z. H. Luklinska March 1978 - March 1980
Associate student (not paid by the contract)
P. Maheswaran.

Appendix 4

Publications arising from this work.
One written publication based on this work is in press and two further papers are in preparation.

i. 'The relationship between structure and energy in grain boundaries'  

ii. 'Phase boundaries in welded bicrystals'. Z.H. Luklinska, P. Maheswaran and P. J. Goodhew.

iii. 'The NCSL and its application' P.J. Goodhew and R.F. Scott.

Verbal accounts of parts of the work have been presented at:


REFERENCES

7. W. Bollmann 'Crystal defects and crystalline interfaces' Springer Verlag 1970
13. V.M. Ievlev, A.V. Bugakov and V.A. Ammer phys stat sol. (a) 49 413 (1978)
Dislocation arrays in a low angle (001) twist boundary between silver and...
Dislocation arrays in a high angle ($17^\circ$) (001) twist boundary between gold and platinum. The dislocations were not evident until the specimen had been heated to above $650^\circ$C in the electron microscope.
Figure 3

The probable sequence of phase formation in the thin film specimens. The original two crystals are shown in (a). Subsequent heat treatment causes the growth of phase X epitaxially on the platinum, followed by the nucleation of phase Y on the gold.
A small section of the output of the computer programme which searches for CSL and NCSL boundaries. Where a zero misfit is shown a CSL is generated. A non-zero misfit indicates the difference in lattice parameter needed to create the listed two-dimensional NCSL.
FIGURE 5

The unrelaxed atom positions in a $17.74^\circ (0.52/53)$ NCSL.