Thermodynamic calculation study on phase structures of Pt-Ir-M(Y, Zr, Mo)

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Abstract. The energy and electronic structure of the solid solutions of Pt-Ir-M (M=Mo, Y, Zr) alloy systems were investigated using the first-principle pseudo-potential plane-wave method. The results show that, adding the same percentage content, 1% Mo doped in Au-Pd solid solution is the most stable phase structure. When doped with Y and Zr, they are likely to react with Au-Pd to form the corresponding intermetallic compounds.

1. Introduction

Electrical contacts mainly undertake connected, points off circuit and load current. Its performance directly affects the safety running for switch apparatus, playing an important role in the service life of electrical appliance as well as reliability and security. In recent years, the requirement of high reliability of contacts which used in control and automobile engineering stimulates research on electrical contact phenomena of the noble metal contact materials. Pt-Ir, as one of them, has high melting point, high hardness, strong corrosion-resistant and low contact resistance. Which is widely used in aircraft engine ignitions, high sensitive relays, micro-motor relays and submarine gravity pendulum relays.

The existing literature more focused on microstructure, mechanical property and physical properties of Pt-Ir in high temperature environment[1–6]. However, as electrical contact material, problems still exist in composition segregation, poor processing performance and performance instability. Recently, it is one of hot spot that improving the above problems through doped other metal. In this work, the phase stability of Pt-Ir-M(M=Mo, Y, Zr) alloy were investigated in order to enhance the understanding of such alloy systems.

2. Calculation Procedure

Phase diagram shows that Pt-Ir alloy is continuous solid solution in high temperature zone under the solidus. Therefore, a solid solution model with Pt as solvent and Ir as solute was constructed, as shown in figure 1. The corresponding models were built with M(M=Mo, Y, Zr)content 1%, 2% and 5%(mass percent) according to the quality of composition proportion. Doping M could be achieved through modifying the atoms of digits.
3. Result and discussion

3.1. Thermal stability of the solid solution model

Cohesive energy (E) and formation enthalpies (H) of Pt-Ir-M (M=Mo, Y, Zr) were calculated. The obtained results are presented in Table 1. It can be seen from Table 1 that all the H of these structures are negative, which means that the structures of these compounds can exist and are thermodynamically stable. With the increasing of doping element, E and H of Pt-Ir-M (M=Mo, Y, Zr) system are becomes higher, which implies that the lower content of doping element, the easier the solid solutions form, and the more stable of them.

| Percentage composition | E (eV/atom) | H (eV/atom) |
|------------------------|-------------|-------------|
| Mo                     |             |             |
| 1%                     | -11.97      | -14.30      |
| 2%                     | -11.74      | -14.02      |
| 5%                     | -11.04      | -13.18      |
| 1%                     | -10.56      | -12.87      |
| Y                      |             |             |
| 2%                     | -10.36      | -12.62      |
| 5%                     | -9.71       | -11.83      |
| 1%                     | -11.78      | -14.24      |
| Zr                     |             |             |
| 2%                     | -11.51      | -13.92      |
| 5%                     | -10.79      | -13.05      |

In the comparison between calculated and experimental lattice parameter of Pt-Ir-M (M=Mo, Y, Zr) alloy phases presented in Section B, C and D, most of the calculated results are in good conformity with the experimental values, confirming that the calculation method and the model selected in this study are adequate.

Compared with three doping elements Mo, Y, Zr in Pt-Ir solid solution, we found that with the same percentage of doping, E and H of Pt-Ir-Mo are lower than the other two, which indicates that Pt-
Ir-Mo is formed more easily than Pt-Ir-Zr and Pt-Ir-Y, in other words, Pt-Ir-Mo is more stable than the other two.

3.2. The stability of Pt-Ir-Mo alloy phases

In Pt-Ir-Mo solid solution, there are four phase structures between Pt and Mo, which are Pt3Mo of P4/MMM, Pt2Mo of IMMM, PtMo of P63/MMC and PtMo3 of PM-3N. Similarly, there are three phase structures between Ir and Mo, which are Ir3Mo of P63/MMC, IrMo of PMMA and IrMo3 of PM-3N. For these seven structures, the related theoretical calculation was done.

Table 2 shows the calculated and experimentally determined lattice parameter of Pt-Ir-Mo alloy phases. Compared the calculated lattice parameters with the experimental values, it shows that the calculated results of lattice constants are in good conformity with the experimental values, confirming that computation parameters selected in this study are suitable.

**Table 2. Lattice constants, cohesive energy and formation enthalpies of Pt-Ir-Mo.**

| Structure | Method | Space Group | Lattice constant, a (Å) | Lattice constant, b (Å) | Lattice constant, c (Å) | cell volume, V (Å³) | Cohesive energy, E (eV/atom) | Formation enthalpies, H (eV/atom) |
|-----------|--------|-------------|-------------------------|-------------------------|-------------------------|-----------------------|-------------------------------|---------------------------------|
| Ir3Mo     | Cal    | P63/MMC     | 5.462                   | –                       | 4.370                   | 112.91                | -11.73                        | -11.26                          |
|           | Exp    |             | 5.487                   | –                       | 4.385                   | 114.33                | –                            | –                              |
| IrMo      | Cal    | PMMA        | 3.863                   | 3.854                   | 3.859                   | 57.44                 | -12.10                        | -11.62                          |
|           | Exp    |             | 2.752                   | 4.804                   | 4.429                   | 58.55                 | –                            | –                              |
| IrMo3     | Cal    | PM-3N       | 4.921                   | –                       | –                       | 119.19                | -12.22                        | -11.72                          |
|           | Exp    |             | 4.968                   | –                       | –                       | 122.62                | –                            | –                              |
| Pt3Mo     | Cal    | P4/MMM      | 3.914                   | –                       | 3.913                   | 59.95                 | -8.96                         | -8.66                           |
|           | Exp    |             | 3.897                   | –                       | 3.936                   | 59.77                 | –                            | –                              |
| Pt2Mo     | Cal    | IMMM        | 2.745                   | 8.259                   | 3.923                   | 88.93                 | -9.65                         | -9.32                           |
|           | Exp    |             | 2.765                   | 8.296                   | 3.938                   | 90.33                 | –                            | –                              |
| PtMo      | Cal    | P63/MMC     | 4.450                   | 2.713                   | 4.903                   | 59.20                 | -10.42                        | -10.04                          |
|           | Exp    |             | 4.475                   | 2.729                   | 4.914                   | 60.01                 | –                            | –                              |
| PtMo3     | Cal    | PM-3N       | 4.944                   | –                       | –                       | 120.86                | -11.39                        | -10.93                          |
|           | Exp    |             | 4.987                   | –                       | –                       | 124.03                | –                            | –                              |

The obtained E and H of Pt-Ir-Mo alloy phases are also presented in table 2. All H of these structures are negative, which means that the structures of these compounds can exist and are thermodynamically stable. The E and H of Ir-Mo alloy phases are higher than the other, which indicates that alloy phases of Pt-Mo system are formed more easily than Ir-Mo system at ambient conditions, in other words, Ir-Mo is more stable than the other. The H of IrMo3 is –11.72eV/atom, the lowest in the seven alloy phases and a similar situation is found of E. All this indicates that the IrMo3 has the strongest alloying ability among these alloy phases.

3.3. The stability of Pt-Ir-Y alloy phases

In Pt-Ir-Y solid solution, there are three phase structures between Pt and Y, which are Pt3Y of PM-3M, Pt4Y5 of PNMA and Pt2Y of FD-3M. Moreover, there are only two phase structures between Ir and Y, which are Ir2Y of FD-3M, IrY of PM-3M. For these five alloy phases, the related theoretical calculation was done.

The calculated lattice constants are listed in table 3, along with the experimental results. It can be seen that calculated lattice parameters are similar to experimental values. So a very good agreement is reached between calculated results and the experimental values.
It can be predicated that the Ir2Y structure has the highest stability than among these structures.

Similar to Pt-Ir-Mo, all H of Pt-Ir-Y are negative, which also means that the structures of these compounds can exist and stable. The E and H of these five alloy phases are listed in table 3, too. The H of Pt-Y alloy phases in our calculation are −9.56, −9.34 and −9.54 eV/atom separately. Such results are all lower than those results of Ir-Y. It means that Ir-Y alloy phases are more stable than Pt-Y. The E were calculated to further estimate the stability of the above alloy phases. By comparing the value of E with the H, we can fine that the structural stability of five alloy phases based on the E has the same tendency as that based on the H. The E and H of Ir2Y are respectively −9.39 and −10.74 eV/atom, which are the highest among the five alloy phases. From the viewpoint of thermodynamics, it can be predicated that the Ir2Y structure has the highest stability than among these structures.

### 3.4. The stability of Pt-Ir-Zr alloy phases

| Structure | Method | Space Group | Lattice constant, a (Å) | Lattice constant, b (Å) | Lattice constant, c (Å) | cell volume, V (Å³) | Cohesive energy, E (eV/atom) | Formation enthalpies, H (eV/atom) |
|-----------|--------|-------------|------------------------|------------------------|------------------------|----------------------|--------------------------------|----------------------------------|
| Pt3Zr     | Cal    | PM-3M       | 3.983                  | –                      | –                      | 63.20                | -8.92                          | -8.66                             |
|           | Exp    | 3M          | 3.990                  | –                      | –                      | 63.52                | –                              | –                                 |
| PtZr      | Cal    | PM-3M       | 3.340                  | –                      | –                      | 37.26                | -8.56                          | -10.87                           |
|           | Exp    | 3M          | 3.310                  | –                      | –                      | 36.26                | –                              | –                                 |
| Pt11Zr9   | Cal    | I4/M        | 10.518                 | –                      | 6.748                  | 746.61               | -8.60                          | -10.88                           |
|           | Exp    | I4/M        | 10.297                 | –                      | 6.888                  | 730.32               | –                              | –                                 |
| Ir3Zr     | Cal    | PM-3M       | 3.913                  | –                      | –                      | 59.90                | -11.13                         | -10.72                           |
|           | Exp    | 3M          | 3.943                  | –                      | –                      | 61.30                | –                              | –                                 |
| Ir2Zr     | Cal    | FD-3M       | 8.933                  | –                      | –                      | 712.84               | -7.85                          | -7.45                            |
|           | Exp    | 3M          | 7.359                  | –                      | –                      | 398.53               | –                              | –                                 |
| IrZr      | Cal    | PM-3M       | 3.241                  | –                      | –                      | 34.05                | -10.43                         | -10.05                           |
|           | Exp    | 3M          | 3.318                  | –                      | –                      | 36.53                | –                              | –                                 |
| IrZr2     | Cal    | I4/MCM      | 6.812                  | –                      | 10.429                | 483.99               | -9.42                          | -9.07                            |
|           | Exp    | 428.37      | 6.512                  | –                      | 5.673                  | 240.57               | –                              | –                                 |

There are three phase structures between Pt and Zr, in Pt-Ir-Zr alloy, which are Pt3Zr and PtZr of PM-3M, Pt11Zr9 ofI4/M. And there are four phase structures between Ir and Zr, which are Ir3Zr of PM-
3M, Ir2Zr of FD-3M, IrZr of PM-3M and IrZr2 of I4/MCM. For these seven alloy phases, the related theoretical calculation was done.

The calculated lattice parameters are listed in Table 4, along with the experimental result. Similar to those of Pt-Ir-Mo and Pt-Ir-Y, the calculated lattice constant of Pt-Zr and Ir-Zr are a close approximation to the experiment results, confirming that the present calculations are reliable. However, it worth mentioning that the calculated cell volume V of Ir2Zr is approximately twice the experimental one which likely means that existing model will most likely need to be adjusted for Ir2Zr.

The value of the H and E of Ir3Zr in our calculation are −10.72eV/atom and −11.13eV/atom, both of which are lowest in seven alloy phases. This result implies Ir3Zr is the most stable, IrZr comes second, whose H= −10.05eV/atom and E is −10.43eV/atom.

4. Conclusions

The phase stability of the Pt-Ir-M(M=Mo, Y, Zr) have been investigated by the method of the first-principle pseudo-potential plane-wave. Comparison between theoretical results of E and H with Pt-Ir-M(M=Mo, Y, Zr) solid solutions show that the stability is aligned as Y < Zr < Mo with the same percentage of doping.

The H and E results show that the nineteen phase structures of Pt-Ir-M(M=Mo, Y, Zr) are all thermodynamically stable structures, among which the IrMo3 has the greatest alloying ability and the highest structural stability, and the Ir2Y is second.

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