

# 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

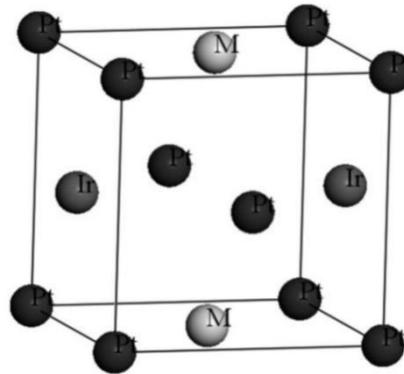
Electrical contacts mainly undertake connected, points off circuit and load current. Its performance directly affects the safety running for switch apparatus, playing an important role in the service life of electrical appliance as well as reliability and security. In recent years, the requirement of 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-resistance 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.





**Figure 1.** Crystal structure of Pt-Ir-M.

All calculations were performed in CASTEP program which is based on density functional theory (DFT) of first-principles total energy pseudo potential plane wave method. CASTEP process was completed commonly used approximate energy density functional with the local density approximation(LDA)and generalized gradient approximation(GGA). Geometric optimization of lattice parameters was performed in original cell. The energy cut-off of the plane wave basis was all set as 340eV, which is sufficient for fully converge. The K-points were sampled by  $6 \times 6 \times 6$ . Other parameters were all set as fine.

### 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.

**Table 1.** Cohesive energy and formation enthalpies of Pt-Ir-M(M=Mo, Y, Zr) with different composition ratio.

Percentage composition		E (eV/atom)	H (eV/atom)
Mo	1%	-11.97	-14.30
	2%	-11.74	-14.02
	5%	-11.04	-13.18
Y	1%	-10.56	-12.87
	2%	-10.36	-12.62
	5%	-9.71	-11.83
Zr	1%	-11.78	-14.24
	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 Pt<sub>3</sub>Mo of P4/MMM, Pt<sub>2</sub>Mo of IMMM, PtMo of P63/MMC and PtMo<sub>3</sub> of PM-3N. Similarly, there are three phase structures between Ir and Mo, which are Ir<sub>3</sub>Mo of P63/MMC, IrMo of PMMA and IrMo<sub>3</sub> 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 (Å <sup>3</sup> )	Cohesive energy, E (eV/atom)	Formation enthalpies, H (eV/atom)
Ir <sub>3</sub> Mo	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	–	–
IrMo <sub>3</sub>	Cal	PM-3N	4.921	–	–	119.19	-12.22	-11.72
	Exp		4.968	–	–	122.62	–	–
Pt <sub>3</sub> Mo	Cal	P4/MMM	3.914	–	3.913	59.95	-8.96	-8.66
	Exp		3.897	–	3.936	59.77	–	–
Pt <sub>2</sub> Mo	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	–	–
PtMo <sub>3</sub>	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 IrMo<sub>3</sub> is -11.72 eV/atom, the lowest in the seven alloy phases and a similar situation is found of E. All this indicates that the IrMo<sub>3</sub> 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 Pt<sub>3</sub>Y of PM-3M, Pt<sub>4</sub>Y<sub>5</sub> of PNMA and Pt<sub>2</sub>Y of FD-3M. Moreover, there are only two phase structures between Ir and Y, which are Ir<sub>2</sub>Y 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.

**Table 3.**Lattice constants, cohesive energy and formation enthalpies of Pt-Ir-Y.

Structure	Method	Space Group	Lattice constant, a (Å)	Lattice constant, b (Å)	Lattice constant, c (Å)	cell volume, V (Å <sup>3</sup> )	Cohesive energy, E (eV/atom)	Formation enthalpies, H (eV/atom)
Pt3Y	Cal	PM-	4.108	–	–	69.34	-7.54	-9.56
	Exp	3M	4.075	–	–	67.67	–	–
Pt4Y5	Cal	PNMA	7.471	14.706	7.539	828.84	-7.23	-9.34
	Exp		7.458	14.546	7.519	815.69	–	–
Pt2Y	Cal	FD-	7.684	–	–	453.61	-7.50	-9.54
	Exp	3M	7.576	–	–	434.93	–	–
Ir2Y	Cal	FD-	7.538	–	–	428.37	-9.39	-10.74
	Exp	3M	7.524	–	–	425.94	–	–
IrY	Cal	PM-	3.399	–	–	39.28	-8.61	-10.21
	Exp	3M	3.400	–	–	39.30	–	–

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 be 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 find 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 predicted that the Ir2Y structure has the highest stability than among these structures.

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

**Table 4.**Lattice constants, cohesive energy and formation enthalpies of Pt-Ir-Zr.

Structure	Method	Space Group	Lattice constant, a (Å)	Lattice constant, b (Å)	Lattice constant, c (Å)	cell volume, V (Å <sup>3</sup> )	Cohesive energy, E (eV/atom)	Formation enthalpies, H (eV/atom)
Pt3Zr	Cal	PM-3M	3.983	–	–	63.20	-8.92	-8.66
	Exp		3.990	–	–	63.52	–	–
PtZr	Cal	PM-3M	3.340	–	–	37.26	-8.56	-10.87
	Exp		3.310	–	–	36.26	–	–
Pt11Zr9	Cal	I4/M	10.518	–	6.748	746.61	-8.60	-10.88
	Exp		10.297	–	6.888	730.32	–	–
Ir3Zr	Cal	PM-3M	3.913	–	–	59.90	-11.13	-10.72
	Exp		3.943	–	–	61.30	–	–
Ir2Zr	Cal	FD-3M	8.933	–	–	712.84	-7.85	-7.45
	Exp		7.359	–	–	398.53	–	–
IrZr	Cal	PM-3M	3.241	–	–	34.05	-10.43	-10.05
	Exp		3.318	–	–	36.53	–	–
IrZr2	Cal	I4/MCM	6.812	–	10.429	483.99	-9.42	-9.07
	Exp		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 of I4/M. And there are four phase structures between Ir and Zr, which are Ir3Zr of PM-

3M, Ir<sub>2</sub>Zr of FD-3M, IrZr of PM-3M and IrZr<sub>2</sub> 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 is worth mentioning that the calculated cell volume V of Ir<sub>2</sub>Zr is approximately twice than the experimental one which likely means that existing model will most likely need to be adjusted for Ir<sub>2</sub>Zr.

The value of the H and E of Ir<sub>3</sub>Zr in our calculation are  $-10.72\text{eV/atom}$  and  $-11.13\text{eV/atom}$ , both of which are lowest in seven alloy phases. This result implies Ir<sub>3</sub>Zr is the most stable, IrZr comes second, whose H =  $-10.05\text{eV/atom}$  and E is  $-10.43\text{eV/atom}$ .

#### 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 IrMo<sub>3</sub> has the greatest alloying ability and the highest structural stability, and the Ir<sub>2</sub>Y is second.

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