Optimization of process parameters for hot isostatic pressing of Ir–Rh alloys based on first-principles calculations

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Abstract
In this paper, the effect of Rh content on the mechanical properties of Ir–Rh alloys was investigated based on first-principles density functional theory. The calculated results show that when the Rh content is small, the three elastic moduli (elastic modulus (B), shear modulus (G), and Young’s modulus (E)) of Ir–Rh alloy increase rapidly with the increase of Rh content. They reach a maximum value at Ir–10Rh and then decrease, before rising slowly at Ir–40Rh and then gradually decreasing again. This shows that adding a small amount of rhodium to iridium can effectively improve the strength and hardness of iridium. Among all the components of the selected Ir–Rh alloys, Ir–10Rh has the highest hardness and strength. The addition of Rh can cause the embrittlement of Ir–Rh alloys, and its brittleness first increases and then decreases with the increase of Rh content, and reaches the highest at Ir–50Rh. Considering the results obtained from theoretical calculations and experiments, Ir–20Rh was selected as the alloy composition for the study of hot isostatic pressing technology. The effects of mixing time, whether to mix powder with balls, and degassing temperature on the properties of metal powders were studied to find the best mixing and degassing process parameters. In the experiment of mixing powder for the iridium and rhodium alloy, it is found that the time required for mixing powder with balls to reach uniformity was shorter than that without balls. The oxygen content of the final mixed powder obtained by the two processes is the same. The nitrogen content of the metal powder mixed with the ball is slightly higher than that without the ball, but it can be reduced to below 0.001% after the degassing process. During the sintering process, with the increase in temperature, the mutual diffusion speed between iridium powder and rhodium powder increases, the sintering neck grows, the internal pores decrease, and the density of the sintered body increases. Therefore, the final decision process is to select mixing with balls for 10 h, degas at 1200 ℃ for 2 h, and then raise the temperature to 1800 ℃ for sintering. With the increase of hot isostatic pressing temperature and pressure, the density of the alloy increases. When the highest temperature (1300 ℃) and highest pressure (140 MPa) are used for hot isostatic pressing for 2 h, the density can reach 95.7% of the theoretical density.

1. Introduction
High-temperature structural materials have many applications in many modern high-precision fields. They are key materials for hot-end components such as advanced thermal engines, thermoelectric cells (nuclear fuel sealing materials), power station gas turbines, and supersonic wind tunnel nozzles [1, 2]. The most widely used high-temperature structural material today is Ni-based superalloy, whose extreme service temperature has increased by about 300 ℃ over the past 50 years, and is currently close to 1100 ℃ [3]. This is due to the redesign of the face-centered-cubic (fcc)/L12 phase structure in the microstructure of Ni-based superalloys to an ideal
degree [4, 5]. However, because of the lower melting point of Ni (1453 °C), Ni-based superalloys are not destined to be used in higher-temperature environments. In recent years, with the development of China’s aerospace industry, higher requirements are placed on the usable temperature of superalloys, so it is imperative to develop a new generation of structural materials that can work in a high-temperature environment of over 1800 °C to replace Ni-based alloys. Iridium is a platinum group element with a melting point of 2447 °C. It is the noble metal with the highest melting point except osmium. It is the only metal that can be used in an oxidizing atmosphere to 2000 °C without serious loss [6–8]. Iridium alloys have stable chemical properties, high hardness, good high-temperature mechanical properties, excellent corrosion resistance and high-temperature oxidation resistance, and have a similar fcc/L12 phase structure to Ni-based alloys. They are considered perfect candidates for a new generation of superalloys [9, 10]. However, the room temperature brittleness and high-temperature softening properties of iridium limit its development and application considerably. Therefore, the study of new technologies for strengthening and toughening iridium alloys and the development of new high-performance, ultra-high-temperature-resistant iridium alloys have become focuses and hot spots in the research on high-temperature structural materials at home and abroad in recent decades. Because both iridium and rhodium are noble metal elements, they are expensive and the experimental cost is high. Therefore, using the method of computational materials science to calculate its mechanical properties and basic properties can explain its basic principles from a microscopic perspective and effectively reduce the experimental cost. This paper uses the plane wave pseudopotential method of density functional theory, based on the virtual crystal approximation. By calculating the elastic constants and charge densities of iridium–rhodium (Ir–Rh) alloys with different Rh contents, the influence of Rh element content on the mechanical properties of Ir–Rh alloys was analyzed, and finally, the composition of Ir–Rh alloys was screened.

Liu et al [11] successfully developed the Ir–0.3 W alloy, in which a small amount of W dissolves into iridium, which can play the role of solid solution strengthening and increase the recrystallization temperature of iridium, thereby increasing the service temperature of the alloys. The hot working performance and welding performance of the iridium alloy are improved, the alloy can be used for a long time under high-temperature conditions, and it has been successfully applied in the aerospace field. Bao et al [12] from the Institute of Metal Research, Chinese Academy of Sciences added different contents of Al element to iridium, developing Ir–xAl (x = 11, 23, 30, 41, 45) binary alloys by arc melting, and observed the alloys before and after oxidation to study the oxidation resistance of the alloys. Wei Yan et al [13] of the Kunming Institute of Precious Metals conducted oxidation weight loss experiments on pure iridium and iridium–rhodium alloy ingots with different rhodium contents to study the weight loss and crystal structure changes of the samples. The results show that the weight loss rate of iridium and Ir–Rh alloys decreases with the increase of rhodium content; both iridium and Ir–Rh alloy ingots undergo grain boundary oxidation corrosion in a high-temperature oxidation environment. With the increase of rhodium content, the grain boundary oxidation depth becomes shallow and the width narrows. Ir–Rh alloys containing 70% to 80% of rhodium have the least corrosion on the surface. Iridium and iridium-based alloys have been widely used in the field of ultra-high-temperature alloys due to their high melting points, stable chemical properties, good corrosion resistance, and high-temperature oxidation resistance. However, iridium and iridium-based alloys are also among the most difficult metals to process, which greatly limits their development and utilization. At present, the method of preparing Ir–Rh alloy is still based on traditional melting and processing technology. In the traditional smelting and processing technology, it is melted by induction heating, plasma heating, electron beam heating, or arc heating. However, during the smelting process, the Ir–Rh alloy is very easy to inhale, which makes the ingot produce bubbles, porosity, and shrinkage, which seriously affect the quality of the alloy material. In addition, the initial deformation treatment of Ir–Rh alloy can only be completed by the whole process of hot working, including hot forging, hot extrusion, hot rolling, hot drawing, hot stamping, and complex heat treatment. The preparation and processing process is very long. Process control is extremely difficult. Hot Isostatic Pressing (HIP) technology is a new powder metallurgy (PM) technology developed in recent decades. At present, HIP equipment and packaging manufacturing technology are nearly mature. The advantages of near net shape and difficult-to-machine materials are gradually being manifested, and it has become a research hotspot in the world’s industrialized countries. Compared with traditional PM technology, the advantages of HIP are mainly reflected in the following aspects [14, 15]: ☉Excellent material properties. Without subsequent processing, the density of HIP parts can generally reach more than 99%. The composition is uniform, and there is no macroscopic composition segregation in the structure, so the overall mechanical properties are excellent; ☉The dimensional accuracy of the parts is high. The dimensional accuracy and surface roughness of the HIP parts formed by the optimized design can reach the level of precision-casting parts; ☉The material utilization rate is high. Compared with the general process, the HIP pressing near net shape technology can increase the material utilization rate from 10%–20% to more than 50% [15]; ☉The process is simple, and the process cycle is short. In addition to the HIP equipment, no other major equipment is required, which can save a lot of machining workload and reduce the manufacturing cost by 50%–80%; ☉Significant reduction in the molding temperature of materials and devices. Smelting requires heating the metal above its
melting point, and the sintering temperature of traditional PM technology needs to reach about 80% of its melting point. Because of the high pressure of HIP, the pressing temperature is generally only 50%–60% of the melting point. At present, many difficult-to-process high-temperature materials such as high-temperature structural ceramics, titanium alloys, high-temperature alloys, and refractory metals are increasingly prepared using HIP technology, especially in the preparation of complex-shaped devices, which are widely used. With the development of the national defense industry and modern civil high-tech, more demands are put forward for high-temperature precious metal materials used in extreme environments such as high-temperature oxidation and corrosion. It is an inevitable trend to research and develop precious metal HIP technology. We selected Ir–20Rh as the alloy composition for HIP technology research through material science calculations, design of different powder mixing processes, and degassing processes to study the effects of mixing time, pellets, and degassing temperature on the properties of metal powders, and found the optimum powder mixing and degassing process. There are few reports on the PM research and application of precious metals, and the information on the preparation of Ir–Rh alloys by hot pressing and HIP is also less public. In this paper, basic research work is carried out around the preparation of Ir–Rh alloys. Ir–Rh alloys are prepared by cold isostatic pressing–sintering–HIP technology to obtain the best process route. The research results have positive significance for expanding the application field of HIP technology and improving HIP technology and theory.

2. Calculation parameters and theoretical methods

2.1. Calculation parameters

Because Ir and Rh are both fcc structures and have similar lattice constants, the Ir–Rh alloy is an infinite substitution solid solution. To avoid the ‘virtual atoms’ and errors accumulated in the long-range structure generated during modeling using the virtual crystal approximation method, this paper uses a single fcc primitive cell, and uses the virtual crystal approximation on the atoms in the face-centered cube, that is, assuming Ir and Rh are mixed in a certain proportion and occupy atomic positions, and the virtual potential of the mixed atoms can be represented by the algebraic sum of the product of the single-atom potential and its weight. This approximation has been widely used in the calculation of structural properties of disordered systems and solid solutions, and is effective in calculating certain structural properties of crystals [13]. In this paper, the 2 × 2 × 1 supercell substitution solid solution structure of Rh in Ir was constructed, the differential charge density of Rh and Ir was calculated, and the differential charge density map was given. The first-principles density functional theory calculation software used in this paper is the CASTEP module in Materials Studio. Periodic boundary conditions are used in the calculation process, the multielectron system is represented by a plane wave function expansion, and an ultrasoft pseudopotential is used as the plane wave basis set. The interaction between electrons adopts the Perdew–Burke–Ernzerhof exchange-correlation energy function in the generalized gradient approximation. In the reciprocal K space, the plane cut-off energy $E_{cut}$ is selected as 380 eV, the K-point sampling for the calculation of mechanical constants is carried out using the Monkhorst–Pack method, the grid point is 12 × 12 × 12, and the K in the calculation process of charge density and energy density point sampling is 3 × 6 × 3. Before each calculation, the unit cells were geometrically optimized using the Broyden–Fletcher–Goldfarb–Shanno method to obtain their most stable local structures. The basis set correction was used, and the Pulay density mixing method was applied in the calculation of the self-consistent field. In this paper, the unit cells of the selected Ir–xRh (x = 0, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100) alloys were geometrically optimized under the set calculation conditions. x is the mass percentage of the Rh element. The optimized lattice constants, Ir–Rh ratios per atom, and theoretical densities are shown in table 1. The theoretical density calculation formula is [14]:

$$\rho = \frac{ZM}{NV}$$  \hspace{1cm} (1)

In the formula, $Z$ is the number of atoms contained in the unit cell, $M$ is the atomic mass of the atom, $N$ is the Avogadro constant, and $V$ is the unit cell volume. As shown in table 1, the lattice constants of pure iridium and pure rhodium after geometric optimization are 3.9053 Å and 3.8935 Å, and the theoretical densities are 22.733 g cm$^{-3}$ and 11.616 g cm$^{-3}$, respectively, which are close to the theoretical and experimental values [16, 17]. This shows that the physical model and calculation parameters selected in this experiment are reasonable.

$$E(V_0, \varepsilon) = E(V_0, 0) + V_0 \sum \alpha_i \varepsilon_i + \frac{V_0}{2} \sum_{ij} C_{ij} \varepsilon_i \varepsilon_j$$  \hspace{1cm} (2)

2.2. Calculation of the elastic constants

The elastic constants reflect the relationship between stress and strain in the crystal and are used to describe the mechanical properties of the crystal. Ignoring the effect of temperature on the total energy of the system, when
the strain, $\varepsilon$, is small, the elastic constants, $C_{ij}$, can be obtained by the Taylor series expansion of the total energy function of the strained system (ignoring the higher-order $\varepsilon$ terms):

In the formula, $V_0$ is the volume of the lattice when it is not deformed and $E(V_0,0)$ is the total energy of the system before strain [18]. There are often three elasticities used to describe the cubic crystal structure ($C_{11}$, $C_{12}$, and $C_{44}$). The bulk elastic modulus $B$ represents the ability of the material to resist elastic deformation, the shear modulus $G$ can measure the material’s ability to shear deformation, and Young’s modulus describes the material’s ability to resist deformation. The bulk modulus, shear modulus, and Young’s modulus can be calculated from the elastic constants. According to the Hill approximation, the bulk modulus, shear modulus, Young’s modulus, and Poisson’s ratio, $\gamma$, can be obtained from the following equations:

$$B = \frac{1}{2}(B_V + B_R)$$

$$G = \frac{1}{2}(G_V + G_R)$$

$$E = \frac{9GB}{2B + G}$$

$$\gamma = \frac{3B - 2G}{2(3B + G)}$$

For the cubic crystal system, the expressions of bulk modulus and shear modulus $B_V$, $G_V$ and $B_R$, $G_R$ in the Voigt approximation and the Reuss approximation have been given in detail in the literature [19, 20], and will not be repeated in this paper. Table 1 lists the calculated values of the elastic constant, bulk modulus, shear modulus, Young’s modulus and Poisson’s ratio for the Ir–Rh alloy. Comparing these mechanical constants for pure iridium and pure rhodium with data reported in the literature [21, 22], they are relatively close, which also shows that the physical model and parameter settings selected in this paper are reasonable. The mechanical stability criteria for the cubic phase structure are [17, 18]: $C_{11} > 0$, $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$. It can be seen from Table 1 that all the alloys satisfy the mechanical stability criteria, from which it can be judged that the established model is mechanically stable.

The anisotropy of structural elasticity can be judged using the anisotropy factor, $A$, of the cubic structure, and the expression is [21]:

$$A = \frac{2C_{44} + C_{12}}{C_{12}} - 1$$

If $A$ is equal to 1, it indicates that the material is isotropic, and if it is not equal to 1, it indicates that the material is anisotropic, and the larger the difference, the greater the anisotropy of the material. Figure 1 shows the $A$ value of Ir–Rh alloys with different Rh contents as a function of Rh content. The $A$ values of all Ir–Rh alloys are greater than 1, and with the increase of Rh content, it first increases and then decreases, reaching a maximum value of 4.782 at Ir–50Rh (figure 1).

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**Table 1.** Atom percentage, lattice parameters, and theoretical density of different Ir–Rh alloys.

| Component   | Atom%  | $a$/Å  | $\rho$/g cm$^{-3}$ |
|-------------|--------|--------|---------------------|
|             | Ir/%   | Rh/%   |                     |
| Ir          | 100    | 0      | 3.9053              | 22.733 |
|             |        |        | 3.8390 [14]         |        |
| Ir–5Rh      | 91     | 9      | 3.9112              | 20.472 |
| Ir–10Rh     | 80.8   | 19.2   | 3.9240              | 19.244 |
| Ir–20Rh     | 68.2   | 31.8   | 3.9487              | 17.689 |
| Ir–30Rh     | 55.5   | 44.5   | 3.9784              | 16.094 |
| Ir–40Rh     | 44.5   | 55.5   | 3.9946              | 14.922 |
| Ir–50Rh     | 34.8   | 65.2   | 3.9932              | 14.015 |
| Ir–60Rh     | 26.3   | 73.7   | 3.9839              | 13.321 |
| Ir–70Rh     | 18.7   | 81.3   | 3.9564              | 12.900 |
| Ir–80Rh     | 11.8   | 88.2   | 3.9312              | 12.418 |
| Ir–90Rh     | 5.6    | 94.4   | 3.9083              | 12.087 |
| Rh          | 0      | 100    | 3.8935              | 11.616 |
|             |        |        | 3.8044 [17]         |        |

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Bulk modulus and shear modulus are two physical quantities that indicate the incompressibility of materials, and Young’s modulus is generally used to measure the hardness of solid materials. The higher the shear modulus and Young’s modulus, the harder the material. Experience has shown that there is an approximate correspondence between the hardness and strength of materials. The hardness value is determined by the initial plastic deformation resistance and the continued plastic deformation resistance. The higher the strength of the material, the stronger the plastic deformation resistance and the higher the hardness value. In general, the greater the elastic modulus ($B$), shear modulus ($G$), and Young’s modulus ($E$), the greater the hardness of the material [23, 24].

Table 2 shows the change in $B$, $G$, and $E$ of Ir–Rh alloy with Rh content. It can be seen that the changing trends of the three elastic moduli are almost the same. When the Rh content is small, the three elastic moduli of the Ir–Rh alloy increase rapidly with the increase of the Rh content, and reach the maximum value at Ir–10Rh, and then a rapid decline until a slow rise and then a slow fall at Ir–40Rh. This shows that adding a small amount of rhodium element to iridium can effectively improve the strength and hardness of iridium. Among all the components of the selected Ir–Rh alloy, Ir–10Rh has the highest hardness and strength, and its shear modulus can reach 234.8038 MPa. As the strength and hardness of the Ir–Rh alloy increase, its processing difficulty and manufacturing cost also increase accordingly. Liu Yi et al [21] of Kunming Institute of Precious Metals used an arc melting–high-temperature die forging–hot rolling–hot drawing process to process pure Ir and Ir–40Rh into Φ0.5 mm wire, and tested their tensile properties and found that for Ir–40Rh, the tensile strength (1765 MPa) was lower than that of pure iridium (2151 MPa), which is consistent with the variation trend of Young’s modulus of Ir–Rh alloys with Rh content calculated here.
2.3. Density and energy state density

To understand better the reasons for the change in mechanical properties of Ir–Rh alloys, several components with outstanding performance in the above calculations were selected to calculate their charge density and state density, and their charge density distribution map and state density distribution map were produced. Figures 3(a)–(d) are the charge density distribution diagrams of Ir, Ir–10Rh, Ir–50Rh, and Rh, respectively, and the brighter area in the figure represents the higher charge density. From the charge density map, it can be seen that the macroscopic distribution of the extranuclear charges of the four alloys with different compositions is relatively close, which is different from the spherically symmetric distribution of the extranuclear charges of traditional metal bonds. Its distribution is extremely uneven and has obvious directionality. However, the charge distribution of silicon, which is a typical covalent bond material, is relatively close, that is, a directional chemical bond is formed with the nearest four atoms, and part of the charge is localized between the gaps of the atoms. It can be seen from figures 3(a)–(c) that with the increase of rhodium content, the bond axis of the chemical bond formed between atoms becomes wider, the charge density at the center of the atom becomes larger, and the charge distribution anisotropy increases. Comparing figures 3(c) and (d), it can be seen that the charge density in the center of the atom in (d) is further increased, and the bond axis of the chemical bond...
between atoms is narrowed again. This is consistent with the changing trend of hardness and elastic constant anisotropy factor with rhodium content in the previous material.

Figure 4(a) shows the partial density of states (PDOS) of Ir and Rh, and figure 4(b) shows the total DOS of Ir–10Rh, Ir–50Rh, Ir–70Rh, and Ir–90Rh. It can be seen from the figure that the DOS of all Ir–Rh alloys spans the Fermi level, and there are more electrons at the Fermi level, and the outer electron orbitals have higher energy and stronger bonds. The main peaks near the Fermi surface of the Ir–Rh alloys are mainly contributed by the electrons of the 5d orbital of the Ir atom and the 4d orbital of the Rh atom, and the peaks of each alloy are approximately the same. When the Rh content is lower than 50%, with the increase of Rh content, the total DOS of Ir–Rh alloy tends to move to lower energy levels, and the peak width increases slightly. When the Rh content exceeds 50%, with the increase of Rh content, the total DOS of Ir–Rh alloy tends to move in the direction of higher energy level, and the peak width of the total energy density decreases slightly at this time. High bond energies correspond to low and broad DOS peaks, and low bond energies correspond to high and narrow DOS peaks [25, 26]. It can be seen that when the Rh content is lower than 50%, the bond energy of the Ir–Rh alloy is slightly enhanced with the increase of the Rh content. When the Rh content exceeds 50%, the bond energy of the Ir–Rh alloy decreases slightly with the increase of the Rh content, which directly affects the plastic deformation of the Ir–Rh alloy, causing its brittleness to increase at first and then decrease with the increase of Rh content. The concept of ‘pseudogap’ can also be introduced when analyzing the DOS diagram, that is, there are two peaks on both sides of the Fermi level, and the DOS between the two peaks is not zero. The pseudo-energy gap directly reflects the strength of the covalent bond of the system: the wider it is, the stronger the covalent bond is [21, 27]. From figure 4(b), it can be seen that the pseudogap of Ir–10Rh, Ir–50Rh, Ir–70Rh, and Ir–90Rh are 0.87, 1.09, 0.85, and 0.71 eV, respectively. It can be seen that Ir–50Rh has the strongest covalency, which is consistent with the above conclusion.

Through comparative analysis, it can be seen that the chemical bond of the Ir–Rh alloy is not a typical metal bond, it has obvious anisotropy and has the characteristics of a covalent bond. Because of the directionality of covalent bonds, the relative positions between atoms are not easily changed, which gives covalent bond materials low plasticity and rigidity. It is precisely because the chemical bonds of Ir–Rh alloys have this covalent bond feature that causes the unusual properties of Ir–Rh alloys.

3. Study on the process parameters of hot isostatic pressing

3.1. Iridium–rhodium alloy mixed powder experiment

Mixing refers to the process in which the moving speed and direction of the material change under the action of gravity, external force, and mechanical force, so that the component particles in each system are evenly distributed. This process is also called the homogenization process. Powder mixing is one of the most basic process operations in PM production, and its mixing quality (the uniformity and state of distribution of each component of the final mixture) will directly affect the performance of sintered products. Through calculation and analysis, Ir–20Rh has the best overall performance. In this experiment, Ir–20Rh was used as the experimental object. The loose packing density method was used to judge the degree of mixing of the powder. The standard GBT-1479–198 was used for the loose packing density measurement method. The experimental results are shown in figure 5. Figure 5(a) is mixing with the ball, and figure 5(b) is mixing without the ball. It can be seen from figure 5 that the bulk density of both mixing methods increases with the prolongation of mixing time, and finally reaches a stable value. During the mixing process, the time for the bulk density of the powder mixed with the ball to reach a stable value is much shorter than the time required for the mixed powder without the ball to reach the stable value, and the bulk density is higher. Among them, the stable value of the loose packing density of mixing with balls is 2.894 g cm$^{-3}$, and the mixing without balls is 2.214 g cm$^{-3}$. This is because the metal powder used in this experiment is an amorphous powder made using a chemical method, and the particle sizes
of iridium powder and rhodium powder are quite different, and there are defects such as microcracks, cavities, and voids inside the powder (figure 6(a)). During the mixing process with the balls, there is friction and extrusion between the pellets, the powder, and the powder particles, which causes the powder to move violently in the mixing tank, the particles become smaller, and the internal voids are bridged (figure 6(b)), so that the bulk density increases more. In the process of mixing without the ball, the movement degree and amplitude of the powder are small, so the mixing time is long, and the bulk density is small.

3.2. Iridium–rhodium alloy vacuum degassing experiment
As can be seen from figure 6(a), the iridium powder used in the experiment has a small particle size, many internal voids, and many gas molecules adsorbed on the surface, which will seriously affect the density and performance of the sintered sample. Therefore, vacuum degassing is necessary. In this experiment, the powder was predensified using a hydraulic press at 15 MPa, and then put into a high-vacuum tungsten wire furnace for sintering and degassing at different temperatures. Table 3 lists the oxygen and nitrogen content of the mixed powder obtained under different mixing process conditions after degassing for 2 h at different temperatures. After degassing for 2 h under all the selected temperature conditions, the nitrogen content in the metal powder decreased to less than 0.001%, and the oxygen content decreased gradually with the increase in temperature. In addition, the oxygen content of the metal powder mixed with the ball was lower than that without the ball. It can be seen from table 3 that the oxygen content of the alloy powder decreased by 37.7% compared with the original metal powder after degassing at 1200 °C for 2 h. However, the oxygen content after degassing at 1400 °C for 2 h is basically the same as that at 1200 °C or even slightly increased. This may be because the metallurgical reaction and diffusion in the metal powder are accelerated at 1400 °C, and the pore-closing speed is increased so that the gas inside the metal cannot be discharged in time. When the temperature rises to 1600 °C and 1800 °C, the metallurgical and diffusion reactions are faster, and the voids are closed more rapidly, but as the temperature increases, the atomic oxygen in the alloy also has higher energy, which makes it diffuse to the metal surface faster. The oxygen content of the alloy decreased further after heat treatment at 1600 °C and 1800 °C for 2 h.

3.3. Iridium–rhodium alloy sintering experiment
Figure 7 shows the microstructure of the predensified alloy powder after sintering at different temperatures for 2 h, the sintering temperatures being 1200 °C, 1400 °C, 1600 °C, and 1800 °C. It can be seen from figures 7(a)–(d) that when sintered at 1200 °C and 1400 °C, the iridium powder and rhodium powder inside the sintered body can diffuse into each other, but the diffusion speed is slow. After sintering for 2 h, there is an interdiffusion layer on the contact surface of the iridium powder and the rhodium powder, also called the bonding layer. This is because, under high-temperature conditions, the atomic energy inside the alloy powder increases, the amplitude increases, the movement to the adjacent crystals diffuses, and more atoms enter within the range of atomic force...
Table 3. The oxygen and nitrogen content of the mixed powder obtained under different mixing conditions after 2 h of gas removal.

| Temperature | Original gas content | 1200 °C/2 h | 1400 °C/2 h | 1600 °C/2 h | 1800 °C/2 h |
|-------------|---------------------|-------------|-------------|-------------|-------------|
| technology  | with ball           | with ball   | with ball   | with ball   | with ball   | with ball   | with ball   | With ball   | without ball |
| oxygen content | 0.053 | 0.054 | 0.033 | 0.035 | 0.036 | 0.038 | 0.018 | 0.025 | 0.0090 |
| nitrogen content | 0.0024 | 0.0015 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
on the powder contact surface to form a bonding surface. With the increase in time, the bonding surface becomes larger, which increases the strength of the sintered body. As shown in figures 7(e) and (f), when the temperature rises to 1600 °C, the bonding surface further expands to form a sintering neck, so that the original particle interface forms a grain interface, and as the sintering continues, the sintering neck grows. The originally interconnected voids between the particles gradually shrink into closed cells. It can be seen that the number of pores with ball mixing is much less than that without ball mixing. This is because the metal powder in the ball-mixing process is ground and extruded by small balls, the particle size becomes smaller, the pores inside the powder are bridged, and the tap density increases, thereby reducing the porosity. It can be seen from figures 7(g) and (h) that when the temperature rises to 1800 °C, with the further increase in the temperature, the mutual diffusion speed between the iridium powder and the rhodium powder further increases, and the sintering neck continues to grow. As a result, the number of internal pores is reduced, and the density of the sintered body is further increased. It can be seen that after sintering at 1800 °C for 2 h, the sintered body can basically achieve the purpose of homogenization. Therefore, the process scheme selected in this paper is: degassing at 1200 °C for 2 h and then increasing the temperature to 1800 °C for 2 h of sintering.

3.4. Hot isostatic pressing experiments

In terms of densification of refractory alloys, HIP technology uses high temperature and isostatic pressure to heal defects such as pores, shrinkage porosity, and cracks in the material using plastic deformation similar to creep mechanism and compression. While using the equalization characteristics of pressure to bridge the internal defects of the material, the changes in the shape and size of the parts are very small, and sometimes even cannot be measured. In this section, Ir–20Rh alloy degassed at 1200 °C and sintered at 1800 °C for 2 h is used as HIP material. Using different HIP temperatures (1100 °C–1300 °C) and pressures (100–140 MPa), the effects of different HIP processes on the alloy density and microstructure were analyzed, and the optimal process parameters were determined. The parameters of the HIP experiment and the density of the final sample are shown in table 4. Because the wrapping material used in the experiment was 314 stainless steel, the selected temperatures were

![Figure 7. The microstructure of the alloy after 2 h sintering at different temperatures.](image-url)
1100, 1200, and 1300 °C to ensure that the wrapping did not leak. The heating and boosting method of the HIP experiment is to increase the pressure first, to ensure that the envelope will not be crushed under the condition of low temperature. It can be seen that with the increase of the HIP temperature in figure 8(a), the density of the alloy gradually increases, and within this temperature range, it presents an approximately linear relationship. With the increase in temperature, the strength of the Ir–Rh alloy decreases, plastic deformation occurs under the action of external pressure, the internal pores gradually heal, and the density increases. The variation of alloy density with HIP pressure is shown in figure 8(b). At 1300 °C, the density of the alloy will increase with the increase of the HIP pressure, and the higher the pressure, the faster the density increase, but the increase is small, only about 1%. Compared with the effect of HIP temperature on material density, the effect of pressure is small.

Figure 9 shows the original state of the alloy after sintering and the metallographic microstructure of the alloy after HIP at different temperatures. The sintering was divided into two stages, the first was degassing at 1200 °C for 2 h, and then the temperature was raised to 1800 °C for 2 h sintering. After sintering, there are a large number of pores in the alloy, which are amorphous in shape and different in size. After the alloy was electrolytically corroded, there were tiny cracks inside. These positions may be the boundaries of the metal powder before sintering, which have not completely disappeared or are not very strong during the sintering process.

| Sample | Temperature/°C | Pressure/MPa | Time/h | Density/g·cm⁻³ | Consistency |
|--------|----------------|--------------|--------|----------------|-------------|
| 1#     | 1100           | 140          | 2      | 16.907         | 87.60%      |
| 2#     | 1200           | 140          | 2      | 17.756         | 92.14%      |
| 3#     | 1300           | 140          | 2      | 18.468         | 95.70%      |
| 4#     | 1300           | 120          | 2      | 18.326         | 94.20%      |
| 5#     | 1300           | 100          | 2      | 18.006         | 93.31%      |
After HIP at 1100 °C and 140 MPa for 2 h, the number and diameter of pores were reduced, and no small cracks appeared after corrosion (figure 9(b)). After HIP at 1200 °C and 140 MPa for 2 h, compared with figure 9(b), the diameter and number of internal pores further decreased, and the large pores gradually became elongated (figure 9(c)). When the temperature rose to 1300 °C, the large pores inside the alloy basically disappeared, leaving only a small number of small pores evenly distributed inside the alloy, and the shape of the holes is approximately spherical because the spherical shape is the state with the lowest surface energy (figure 9(d)).

The mechanism of alloy densification in the HIP process is that the compressive stress on the alloy during the HIP process exceeds its yield limit, resulting in slippage. The stress is not uniform, and part of the alloy is extruded into the inside of the pores where the stress is concentrated, resulting in plastic deformation, which reduces the alloy voids and improves the density. Under the three conditions of HIP, the compact could not reach a fully dense state, and its porosity can be obtained by calculating the ratio of the surface area of the pores to the area of the whole picture. The calculated porosities in figures 9(a)–(d) are 12.9%, 10.9%, 5.6%, and 1.5%, and their densities are 87.1%, 89.1%, 94.3%, and 98.5%, respectively. It can be seen that the alloy has the least defects and the best mechanical properties after HIP at 1300 °C and 140 MPa for 2 h.

Figure 10 shows the metallographic structure of the alloy after HIP at the same temperature and different pressures. It can be seen from figure 10(a) that there are a large number of holes in the Ir–Rh alloy before HIP, and the shapes of these holes are different, and some holes are clustered together. After HIP, most of the pores inside the alloy can be healed, leaving only some small voids. When the HIP temperature remains unchanged and the pressure increases, the internal microstructure of the alloyed gold is also greatly improved, and the internal pores are greatly reduced (figures 10(b)–(d)). Under the three HIP conditions, the green compact could not reach a fully dense state, and its porosity can be obtained by calculating the ratio of the surface area of the pores to the area of the whole picture. The calculated porosities in figures 10(a)–(d) are 11.9%, 4.1%, 2.8%, and 1.1%, and their densities are 88.1%, 95.9%, 97.2%, and 98.9% of the total theoretical density, respectively. In the HIP process, under the condition of constant temperature, with the increase of pressure, the fewer the internal defects of the alloy after HIP and the denser the alloy.

4. Conclusions

(1) The strength and hardness of Ir–Rh alloys increase first and then decrease with the increase of Rh content, reaching the maximum value at Ir–10Rh. They then decrease rapidly, and then decrease slowly after reaching a plateau around Ir–40Rh.

(2) The addition of Rh can cause the embrittlement of Ir–Rh alloys. The brittleness increases first and then decreases with the increase of Rh content, and the brittleness is the highest at Ir–50Rh. This trend is consistent with the variation trend of the elastic constant anisotropy factor of the alloy with Rh content.

(3) The charge density and energy state density of the alloy indicate that there is a ‘pseudo-covalent bond’ in the Ir–Rh alloy, which has strong anisotropy. Among the alloy compositions studied, the chemical bond of Ir–50Rh has the strongest anisotropy, which may be the reason why it appears to be the most brittle.
Combining with first-principles calculations, it can be seen that Ir–20Rh alloy has both high strength and good high-temperature oxidation resistance, so this study chose Ir–20Rh as the raw material for HIP preparation research.

The final mixed powder obtained by mixing with balls not only has a higher bulk density than mixing without balls but also takes much less time to achieve uniformity than mixing without balls. The final mixing process was 10 h with balls.

After the Ir–Rh alloy was sintered at 1800 °C for 2 h, the alloying process was basically completed, and the structure and composition were uniform. Therefore, the optimal process scheme was finally determined in this paper: degassing at 1200 °C for 2 h and then increasing the temperature to 1800 °C for 2 h sintering.

The density of the alloy increases with the increase of HIP temperature and pressure. When the HIP temperature and pressure are both selected to the maximum value, the final density of the alloy reaches 95.7% of the total theoretical density.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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