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ARTICLE

Preparation and Microstructure of Ir-Zr-W Alloys by Powder Metallurgy Route

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Abstract: Iridium alloys doped with approximate 4 at% Zr and 0.3 at% W alloying elements were fabricated for ultra-high temperature applications by powder metallurgy route. The phase compositions and microstructures of the composite powders and the alloy were investigated. It was found that Ir_3Zr phase could not form and no mechanical alloying phenomenon occurred when the composite powder of Ir-ZrH_2-W was prepared by high-energy ball milling even for 24 h, but it could be completely transmitted to Ir_3Zr phase after calcinating at 1300 °C. The average grain size of the alloy prepared by the powder metallurgy route was 4-5 μm, and Ir_3Zr phase was generated *in-situ* in Ir-based alloy during sintering process.

Key words: iridium; microstructure; sintering; powder metallurgy

Iridium has been widely used for making crucibles, thermocouples, rocket parts, gas-turbine blades, equipments for glass making and spark plugs etc. because of its attractive properties, such as high melting point (2443 °C), good oxidation resistance and high strength at elevated temperature[1,2].

Though iridium is a face centered cubic metal, it fractures in a brittle manner similar to that of body centered cubic metal at temperature below 1000 °C [3]. Some alloying elements such as W, Nb, Ni, Zr, and Hf etc. have been doped to prepare Ir-based alloys for improving their high-temperature mechanical performances and workability. Approaches to improve the high-temperature mechanical performance involve two main strengthening mechanisms: solid-solution hardening, coherent and incoherent precipitate hardenings [4,5]. It was found in early studies that the strengthening mechanism of Ir-based alloys containing nominally 0.3 % (mass fraction) W, 60 μg/g Th and 50 μg/g Al is solid-solution hardening which can improve their hot-workability and welding performance. The Ir-based alloy (DOP-26) developed by Liu et al was used to clad the plutonia fuel pellets in radioisotope thermoelectric generators for space power applications [5-7]. However, this Ir-based alloy still fails in a brittle intergranular manner under high-temperature impact conditions. Thus, much researches on doping some microelements have been conducted to change iridium alloys' fracture manners, but the effects are not obvious [1,2,5,6]. Recently, the binary and ternary alloys such as Ir-Zr, Ir-Nb, Ir-Zr-Hf and Ir-Nb-Ni etc. have been developed, and the results reveal that these Ir-based alloys have excellent high-temperature strength. Of then, Ir-Zr, Ir-Hf and Ir-Zr-Hf binary and ternary alloys have attracted more special attention for their coherent dual-phase fcc/$L1_2$ structure, which strongly improve the high-temperature strength of these superalloys[8-10].

As a rule, Ir-based alloys are prepared by arc-melting process. Although high density is achieved, the alloys have very large crystal grains due to high temperature and slow cooling rate during melting. The large crystal grains may lead to intercrystalline cracking under deforming, which is one of drawbacks of arc-melting method. Powder metallurgy (P/M) processing is proved to be an effective method to prepare refractory materials (such as W, Mo etc.) with fine crystal grains and homogeneous structure which is beneficial to deformation working. Therefore, an attempt is made to prepare Ir-4Zr-0.3W alloys by P/M method and to analyse their microstructures in this paper.

1 Experimental

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In the present experiment, P/M processing was employed to prepare Ir-based alloy containing 4% Zr and 0.3% W (at%). Firstly, in order to obtain homogenous alloying powder, a small amount of Ir-ZrH_2-W powder mixture was prepared by blending Ir (purity 99.99%, average particle size 37 μm), ZrH_2 (purity 99%, average particle size 1.04 μm) and W (purity 99.9%, average particle size 3 μm) powders. High-energy ball milling was performed in Certiprep ball mixer (SPEX 8000M) for 2, 4, 8, 12 and 24 h, respectively, using methyl alcohol as a process agent. In addition, the powder ball-milled for 24 h was calcined at 1300 °C for 4 h in vacuum to investigate the phase composition after heat treating. Secondly, Ir-ZrH_2-W powder mixture ball-milled for 24 h was added into a mass of iridium powder to obtain the final composite powder with a composition of Ir-4ZrH_2-0.3W (at%), which was then mixed in a planetary ball mixing attritor for 3 h using methyl alcohol as agent. After dried at 80 °C for 24 h, the mixed powder was packed in a plastic mold and compacted by cold isostatic pressing (CIP) at 200 MPa for 60 s. Finally, the as-prepared greens were pre-sintered at 1500 °C for 4 h in vacuum, and then sintered at 2190 °C for 3 h in hydrogen atmosphere. The powder samples and sintered alloys were characterized by X-ray powder diffraction with CuKα radiation (λ=15.4056 nm). The density of the alloy was measured by Archimedes' method. The microstructures of the samples were observed by scanning electron microscopy (SEM, JSM-6040, 20 kV) and filed emission scanning electron microscopy (FESEM, JSM-6700F, 30 kV). In addition, Ir-Zr-W alloy with the same composition was prepared by arc-melting method in order to compare the microstructure.

2 Results and Discussion

2.1 Ir-Zr-W alloy powder

Preparation of homogeneous alloy powder is the key step to fabricate high performance Ir-based alloy. Hence, superfine ZrH_2 powder with average particle size 1.04 μm and iridium powder with 37 μm were chosen as starting materials. In the present experiment, the mixing effect of high-energy ball milling for 24 h is quite obvious. Fig. 1 shows the FESEM image of pure Ir powder and FESEM backscattered electron image of Ir-ZrH_2-W mixture powder after 24 h high-energy ball milling. From Fig.1a, it is clear to see that pure iridium powder usually takes on the agglomerates consisting of very fine particles. But after long-time ball milling, the iridium particles were ground and crashed to deform, which can be seen from Fig.1b. In Fig.1b, the white grains are iridium particles and the grey grains are ZrH_2 particles. It is obvious that Ir-ZrH_2-W mixture is very homogeneous and some superfine ZrH_2 granules are embedded in the relative large iridium grains after powerful long-time ball-milling.

However, there was no Ir_3Zr phase formation in Ir-ZrH_2-W mixture even milled for 24 h. The XRD pattern of Ir-ZrH_2-W mixture is shown in Fig. 2a. From the pattern, only Ir and ZrH_2 diffraction peaks were detected, and no Ir_3Zr phase diffraction peak was found within the sensitivity of XRD, indicating that Ir_3Zr phase could not form and no mechanical alloying phenomenon occurred during 24 h ball-milling. From the experimental results, we can know that the mechanical alloying time for high-energy ball-milling need more time because iridium powder not only is very stiff, but also has a relatively high inertia, so it is not easy to react with ZrH_2 powders even the particle size of ZrH_2 powder used in this experiment is superfine. But Ir in the mixture was completely transmitted to Ir_3Zr phase by calcinating at 1300 °C for 4 h under vacuum conditions. Fig. 2b shows the XRD pattern of the powder mixture calcinated at 1300 °C for 4 h. As seen from it, only Ir_3Zr diffraction peaks were detected, which shows the reaction between iridium and ZrH_2 powders occurred during calcining. Though the melting point of Ir_3Zr is as high as 2280 °C, the calcinating temperature of Ir_3Zr in the present experiment was only 1300 °C. At such lower temperature the formation of Ir_3Zr is dominantly attributed to the dehydrogenation of superfine ZrH_2 powder and the solid phase diffusion reaction among the active Zr particles and Ir particles. As we know, ZrH_2 powder begins to dehydrogen at 300 °C and hydrogenation automatically deviate rapidly from ZrH_2 at 600 °C. When hydrogen leaves, new Zr particles with active and large specific surface will appear around the iridium particles. So it is easy to react between iridium and Zr, and finally Ir_3Zr phase would be formed. The phenomenon also occurred in Ir-4Zr-0.3W mixing powder. As shown in Fig. 2c, the final phase compositions include essential component iridium and a small amount of Ir_3Zr, and almost no ZrH_2 phase exists in the mixture powder after calcination.

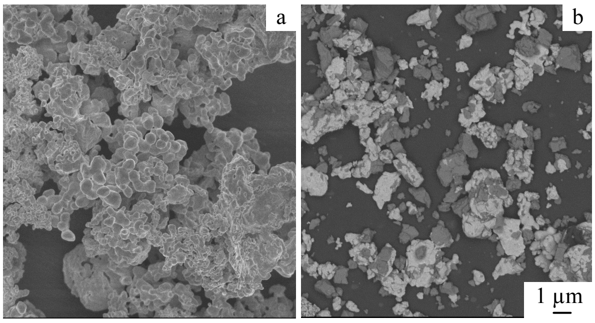

Fig.1 FESEM image of pure Ir powder (a) and FESEM backscattered electron image of Ir-ZrH_2-W mixture powder after 24 h high-energy ball milling (b)

2.2 Microstructure of Ir-Zr-W alloy after pre-sintering and sintering

In this investigation, two-step sintering was performed to improve the density of Ir-based alloys. Upon pre-sintering in vacuum at low temperature and sintering in hydrogen at high temperature, ZrH_2 reacted with iridium completely, and no ZrH_2 existed in the finally alloy according to XRD pattern of the Ir-based alloy, shown in Fig. 3. Because of the small content of W, no characteristic peaks of W were detected in the alloy. But SEM EDS analysis result shows that there is approximate 0.228 at% tungsten in the alloy, which can be seen from Fig.4. Fig.5a shows the typical image of the fracture surface of the alloy sintered at 1500 °C. During the pre-sintering, Ir_3Zr phase was formed when ZrH_2 was decomposed to Zr and hydrogen. It can be seen from the Fig. 5a that the sintering necks of Ir/Ir, Ir/Ir_3Zr particles appeared and grew below 1500 °C. The relative density reached 85% and there still were a few pores. After sintering at 1500 °C for 4 h, the average grain size increased to 3 μm. Fig.5b shows the morphology of the cross-section of Ir-based alloy sintered at 2190 °C. When the sintering temperature was elevated to 2190 °C, the grains grew obviously and their average grain sizes increase to 4-5 μm. The gas pores decreased obviously with the growth of the crystal grain and the relative density increased to 95%. In spite of that the density of Ir-Zr-W alloy by P/M processing is relatively lower than that of Ir-Zr-W alloy by arc-melting, the grain size of Ir-Zr-W alloy prepared by P/M method is only 1/10 of that by arc-melting, shown in Fig.5b and c, and it shows the advantage of P/M processing. From Fig. 5b, it can be further seen that no obvious cracking occurred in the cross-section of the alloy by P/M processing when the alloy was fractured by hammering, while there was obvious intergranular cracking in the cross-section of the alloy by arc-melting process under the same failure condition.

According to the Ir-Zr binary phase diagram, the addition of more than 3 at% Zr will lead to forming of an Ir_3Zr intermetallic phase for the low solubility of Zr in Ir, which is consistent with our X-ray diffraction results shown in Fig.3[5]. Fig. 6 shows the backscattered electron image of Ir-Zr-W alloy sintered at 2190 °C. From the figure, it can be seen that Ir_3Zr particles, the relative black granules, are homogeneously embedded in the matrix of Ir, which means that Ir_3Zr phase can be generated *in-situ* in the alloy.

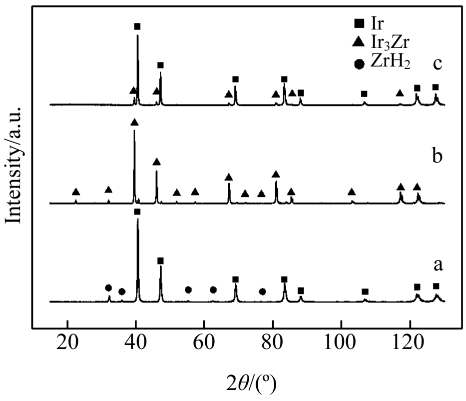

Fig.2 XRD patterns of Ir-ZrH_2-W powder ball-milled for 24 h (a), Ir-ZrH_2-W powder ball-milled for 24 h and calcined in vacuum for 4 h (b), and Ir-4ZrH_2-0.3W powder calcined in vacuum for 4 h (c)

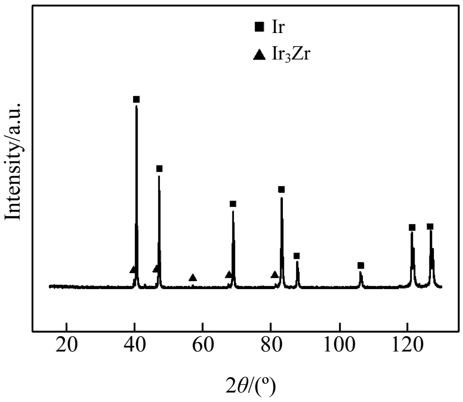

Fig.3 XRD pattern of Ir-based alloy sintered at 2190 °C for 3 h

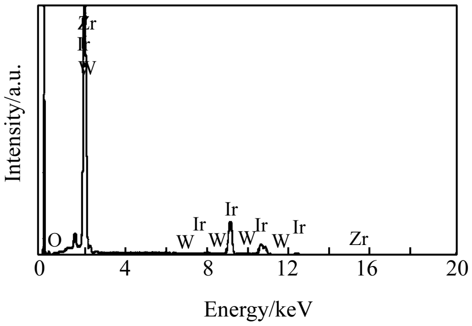

Fig.4 SEM EDS of Ir-Zr-W alloy sintered at 2190 °C for 3 h

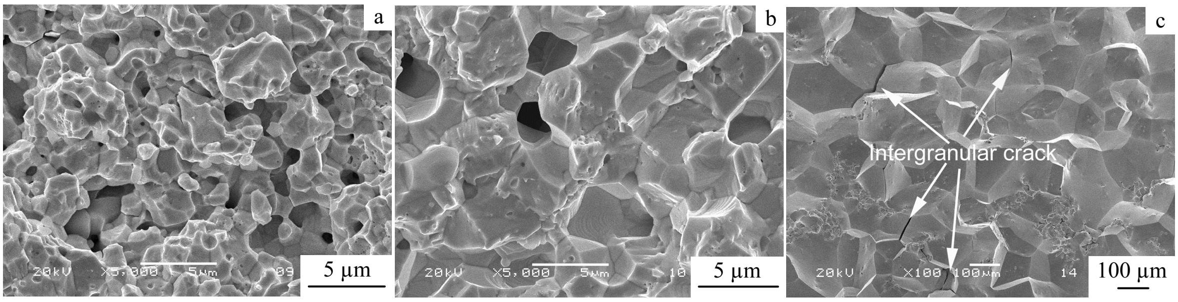

Fig.5 Fractographs of Ir-Zr-W alloys: (a) pre-sintered at 1500 °C, (b) sintered at 2190 °C and (c) prepared by arc-melting method

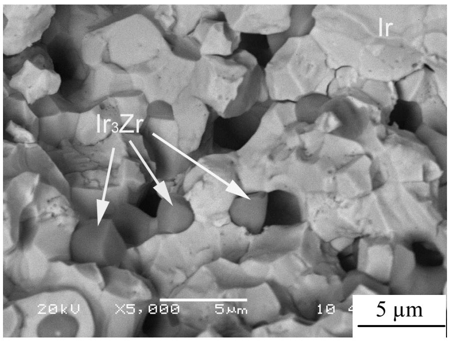

Fig.6 SEM backscattered electron image of Ir-Zr-W alloy sintered at 2190 °C

3 Conclusions

1) Ir-4Zr-0.3W (at%) alloys can be fabricated by P/M processing.

2) As-prepared Ir-ZrH_2-W mixture has high reactivity after 24 h ball milling, and Ir-ZrH_2 in the mixture will be completely transmitted into Ir_3Zr phase during calcinating below 1300 °C in vacuum.

3) The relative density of Ir-based alloys can reach 85% after pre-sintering at 1500 °C and finally 95% after sintering at 2190 °C.

4) The average grain size of Ir-based alloy prepared by P/M method is within 4-5 μm, and Ir_3Zr phase can be generated *in-situ* in the alloy.

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粉末冶金工艺制备 Ir-Zr-W 合金及其显微结构研究

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摘　要：采用粉末冶金工艺制备 Ir-4Zr-0.3W (at%)合金，并对合金粉末和合金的相组成和显微结构分别进行了研究。发现，即使对合金粉末高能球磨 24 h，也无法生成 Ir_3Zr 相，不发生机械合金化现象。但是，当合金粉末经 1300 °C 煅烧后，完全转变为 Ir_3Zr 相。采用粉末冶金工艺制备的铱合金晶粒尺寸细小，约 4~5 μm，并且在铱合金中原位生成 Ir_3Zr 相颗粒。

关键词：铱；微结构；烧结；粉末冶金

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