

First Trial of Pulse Electric Current Sintering for High-Temperature Material Ir₃Nb

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(Submitted 18 April 2001)

Pulse electric current sintering (PECS) was tried for Ir-25 at.% Nb (Ir₃Nb), which has a high melting temperature of about 2435 °C. Ingot powder was made by crashing an ingot, and the ingot powders were sintered at temperatures between 1700 and 1900 °C up to 2 h under 40 MPa. Pure-metal powder was mixed to achieve a composition of Ir-25 at.% Nb, and the pure-metal powders were sintered at a temperature between 1700 and 1900 °C for up to 1 h. The microstructure and phase structures of sintered samples were investigated by scanning electron microscopy (SEM) and x-ray diffractometry. The sintering mechanism and problems for Ir₃Nb in PECS are discussed.

Keywords electric pulse sintering, iridium, Ir-Nb compound, sintering

1. Introduction

Iridium has been noted as a high-temperature material due to having a high melting temperature (2447 °C), a modulus with the highest elasticity (570 GPa) at room temperature,^[1] and high oxidation resistance.^[2] We developed refractory superalloys with an fcc and L1₂ two-phase coherent structure using Ir as the base material and showed that the strength and creep properties of some of the binary alloys, such as Ir-Nb and Ir-Zr, make them very promising as high-temperature materials.^[3,4] However, polycrystalline Ir cleaves at grain boundaries, similarly to brittle materials after insignificant preliminary deformation but unlike typical fcc metals.^[5] Single-crystal Ir also shows a brittle transgranular mode.^[6] We found that two-phase alloys also fractured by the intergranular fracture mode.^[7] These results suggest that the machinability of Ir or Ir-based alloys will not be satisfactory until the ductility of Ir or Ir-based alloys is improved.

Although machining of Ir or Ir alloys is difficult, Ir and some of the Ir alloys have been used as structural materials, mainly Ir crucibles for the single crystal of high-melting-temperature oxides, such as MgAl₂O₄ or Al₂O₃. These crucibles are made by hot pressing high-purity Ir powder or by welding a hot-rolled Ir sheet.^[8] For Ir alloys, Liu and his colleagues developed ductile Ir-0.3 at.% W including a small amount of Th.^[9] These alloys can be deep-drawn at temperatures between 500 and 600 °C^[10] and are used as a fuel-cladding material in radioisotope thermoelectric generators (the major source of onboard electric power in interplanetary spacecraft). They also investigated the weldability of their alloys.^[11,12]

We tried to make a plate-type tensile test sample using our Ir-based alloys with an fcc and L1₂ two-phase structure. These alloys were easily cracked and fractured under different kinds

of conditions, although pure Ir can be hot rolled under some conditions. We did not find a suitable hot-rolling condition for our alloys. Next, a long rectangular-shaped ingot was made by arc melting, and plate-type tensile specimens were cut using an electric discharge machine. However, the specimens broke easily during cutting because of their brittleness. Another problem was their heterogeneous microstructure. Solid-solution heat treatment cannot be performed on two-phase alloys because the fcc single phase does not expand at high temperatures. Thus, even after heat treatment, the as-cast microstructure remained, causing the fracture of the specimen during cutting or when setting the sample in the tensile test equipment. Therefore, another processing method must be found for our alloy; otherwise, these alloys cannot be used in the application field.

Recently, pulse electric current sintering (PECS) has been noted as a new processing method. It is said that by using PECS, the sample is sintered for a shorter time than hot pressing because the electricity is turned on and off in a pulse-state electric discharge that occurs between powder samples, and also Joule's heat is produced by a large current in PECS. The electric discharge between powders and the large Joule's heat by a large current seem to be suitable for high-melting temperature materials. Furthermore, the sintered sample will be more homogeneous than the ingot by arc melting. When we use a long graphite die, we can sinter a long sample and make a long tensile test sample. To investigate if PECS is a suitable method for Ir-based alloys, we tried to sinter single L1₂ phase Ir-25 at.% Nb (Ir₃Nb), which has a high-melting temperature of about 2435 °C, using PECS.

2. Experimental Procedure

Single-phase Ir-25 at.% Nb, Ir₃Nb with an L1₂ structure, was chosen for the first trial of PECS for the sake of simplicity. Two kinds of samples, namely, powders from an alloy ingot of Ir-25 at.% Nb and mixed pure-metal powder, were prepared. For the first sample, the Ir-25 at.% Nb alloy was prepared by arc melting; then, powder below 150 μm in size was obtained by crashing the alloy ingot. For the second sample, powder samples of pure Ir 5 μm in size and pure Nb 50 μm in size

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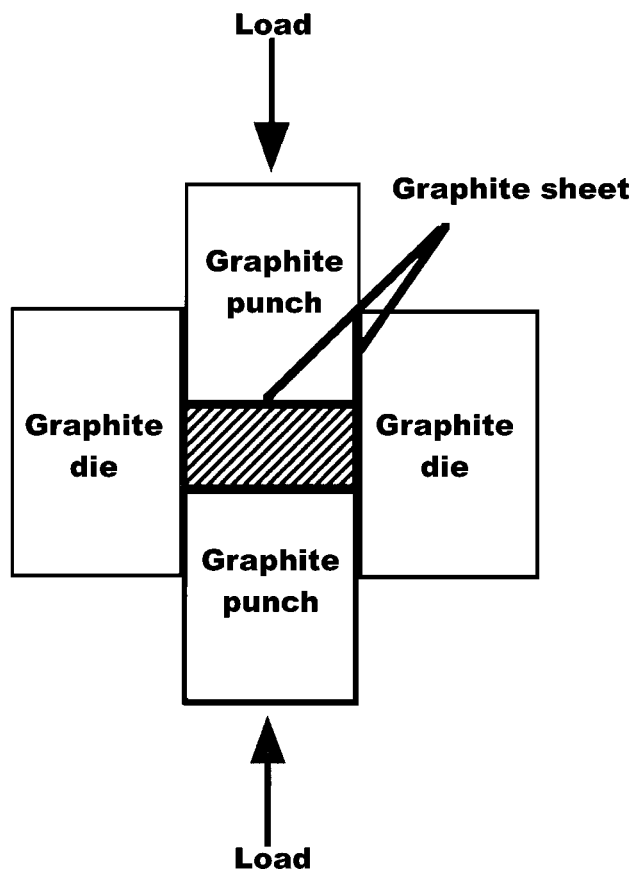


Fig. 1 Schematic diagram of PECS

were measured to obtain the composition of Ir-25 at.% Nb. The total amount of each sample was about 5 g. The measured samples were put in a plastic bottle and then mixed by rotating the bottle on a milling machine for 72 h. These samples were put in a graphite die 15 mm in diameter and 30 mm in height (Fig. 1). Samples were sintered in a vacuum condition under 40 MPa between 1700 and 1900 °C for up to 2 h. To compare with PECS, hot pressing was also carried out at 1800 °C for 4 h. Detailed conditions are summarized in Table 1. During sintering, the temperature and displacement of the die were measured. After the temperature decreased to room temperature, the sintered sample was taken out of the sintering machine. The density of the sintered samples was estimated by measuring their diameter, thickness, and weight. Phase analysis was performed by x-ray diffractometry, and then the microstructure was observed using scanning electron microscopy (SEM). For pure element powder, fluorescence x-ray analyses were performed to analyze composition.

3. Results

3.1 Ingot Powder

The displacement of die and the temperature change during sintering are shown in Fig. 2. Here, the temperature increased at the rate of 2.5 °C/s for all samples. Samples were heated at

Table 1 Sintering condition, composition, and relative density of sintered samples

Ingot powder	Composition (at.%)	Relative density
1800 °C soon/1.25 °C/s	...	70.39
1800 °C 15 min/2.5 °C/s	...	85.63
1900 °C 15 min/2.5 °C/s	...	78.79
1900 °C 1 h/2.5 °C/s	...	89.89
1900 °C h/2.5 °C/s	...	90.32
2000 °C soon/2.5 °C/s	...	89.87
1800 °C 4 h/20 MPa	...	89.82
1800 °C 4 h/20 MPa hot press	...	95.22
Pure-metal powder
1700 °C soon/2.5 °C/s	37.82	92.16
1800 °C 15 min/2.5 °C/s	23.95	107.86
1800 °C soon/2.5 °C/s	24.71	107.41
1800 °C soon/1.25 °C/s	33.4	100.41
1900 °C 1 h/2.5 °C/s	33.45	90.58
1700 to 1800 °C/0.016 °C/s	24.42	97.22

1800 °C for 15 min and 1900 °C for 1 and 2 h. For the condition of 2000 °C, the temperature increased up to 2000 °C and then it was cooled immediately. All samples were expanded during increasing temperature and were still expanded after the temperature reached the setting temperature. When the sintering condition was 1900 °C for 2 h, the sample expansion was stopped 1 h after the temperature reached the setting temperature.

The relative density for each sintering condition is summarized in Table 1 and plotted as a function of the sintering temperature in Fig. 3. The sintering time is also shown close to each symbol. Most samples were sintered under 40 MPa, and the temperature was increased at the rate of 2.5 °C/s. When samples were sintered using a different condition, the condition is shown in the respective figure. The relative densities were between 70 and 90%. At the same sintering temperature, for example, at 1900 °C, the relative density increased with increasing the holding time. However, there was no large difference in the relative density under a holding time between 1 and 2 h. This suggests that the sintering process was saturated after 1 h at 1900 °C. Applied stress was not effective between 20 and 40 MPa. The relative density was higher in the condition under 20 MPa for 4 h than in the condition under 40 MPa for 15 min. This suggests that, when the holding time is long enough, the sintering process progresses under low applied stress. When the rate of increasing temperature changed to half, *i.e.*, 1.25 °C/s, the relative density was at its lowest. Hot pressing was also tried at 1800 °C for 4 h and compared with PECS. The relative density of the hot-pressed sample was the highest among other PECS samples.

The microstructure of the sintered sample was observed by SEM (Fig. 4). Most grains were well sintered; however, some grains were not, as shown by A (Fig. 4a and b). Small holes were also found in the grains. When a sample was sintered at 1900 °C for 2 h, slip lines were observed in many grains (Fig. 4(b)). This shows that the sintering process did not progress after 1 h and grains were just plastically deformed during sintering. When the sintering temperature increased up to 2000 °C, grain growth was observed. Grain size at 1900 °C was about 20 μm but increased to over 50 μm at 2000 °C. However, a gap was also observed at the grain boundary. This suggests

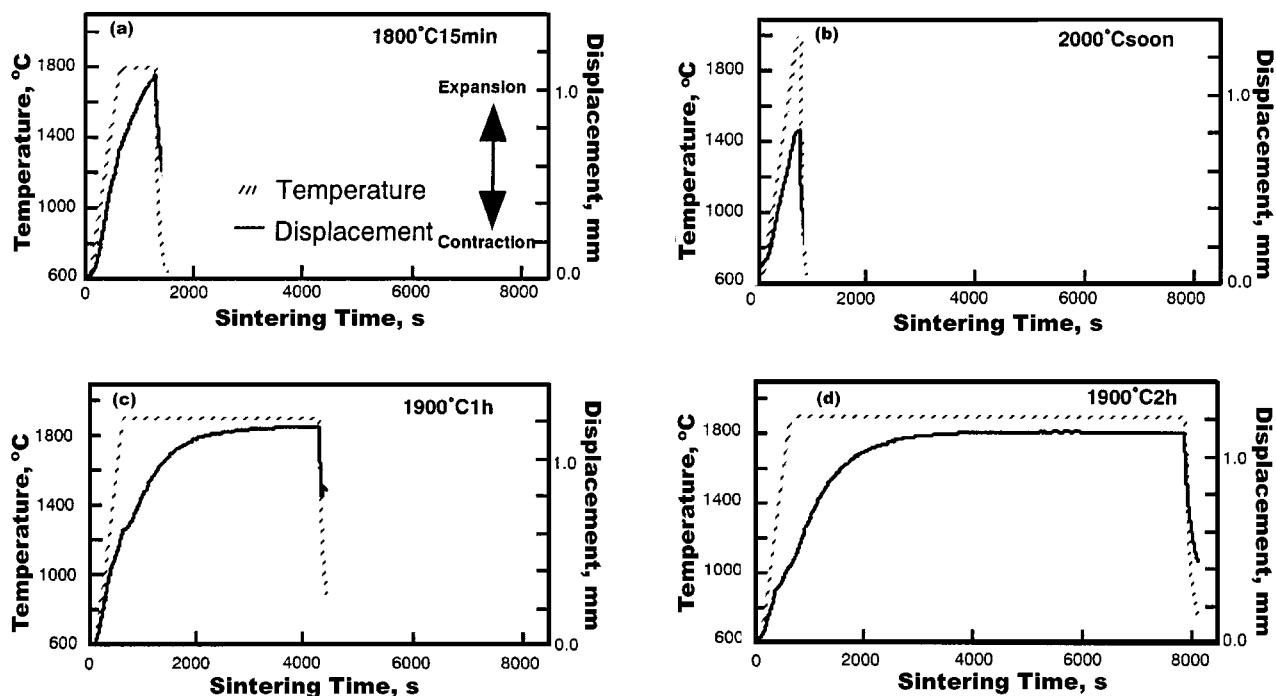


Fig. 2 Displacement of die and temperature change of ingot powder during sintering (a) 1800 °C for 15 min, (b) 2000 °C and immediately cooled down, (c) 1900 °C for 1 h, and (d) 1900 °C for 2 h

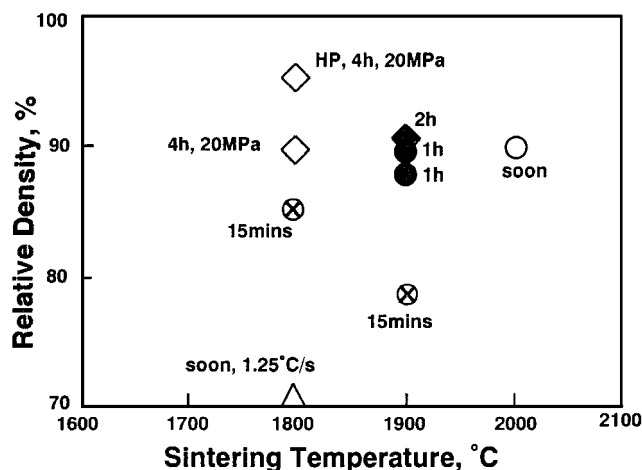


Fig. 3 Relative density as a function of the sintering temperature of ingot powder

that, even at 2000 °C, the sintering process was not perfect. The microstructures of sintered samples by PECS and hot pressing at 1800 °C for 4 h are shown in Fig. 5. Although the hot-pressed sample showed the highest relative density, many more holes were observed in it than in the sample sintered by PECS. This suggests that the sintering process by hot pressing was not perfect either.

3.2 Pure-Metal Powder

The displacement of the die and the temperature change for sintering of pure-metal powder are shown in Fig. 6 for some

conditions. In contrast to ingot powder, the pure-metal powder sample shrank while the temperature was increasing and then started to expand after the temperature reached the setting temperature. Expansion continued for 1 h at 1900 °C (Fig. 6c). Sudden shrinkage was also observed between 1700 and 1800 °C when the temperature increased at a rate of 2.5 °C/s (Fig. 6a and c). However, when the temperature-increase rate between 1700 and 1800 °C decreased to 0.016 °C/s, sudden shrinkage was not observed (Fig. 6(d)). Instead, the sample gradually expanded.

The relative density of the sintered sample and the alloy composition after sintering are shown in Table 1. The relative density was between 90 and 100%. Some samples showed relative density over 100%. After sintering, the alloy composition greatly shifted from the nominal composition, 25 at.% Nb. We observed that the powder was observed to spill from the die during sintering around 1750 °C. Thus, the alloy composition deviated from the nominal composition, and then the relative density showed over 100% for some samples.

X-ray analysis is shown in Fig. 7. For all samples, peaks from pure Ir, pure Nb, and Ir₃Nb (L1₂) were observed. This shows that alloying progressed partially; however, it was not perfect. At 68 and 82 deg (arrow in Fig. 7), the L1₂ peak increased with increasing the sintering temperature. Compared with samples sintered at 1800 °C, the L1₂ peak was larger when the holding time was longer. This suggests that higher sintering temperature and longer holding time allow alloying to progress. The same was observed in the microstructure of the sintered sample (Fig. 8). When the sample was heated to 1700 °C and then immediately cooled (Fig. 8a), the Nb phase was observed. By EDS (Energy Dispersive Spectrometer) analysis, some particles were almost pure Nb, including 3 at.% Ir, while some of

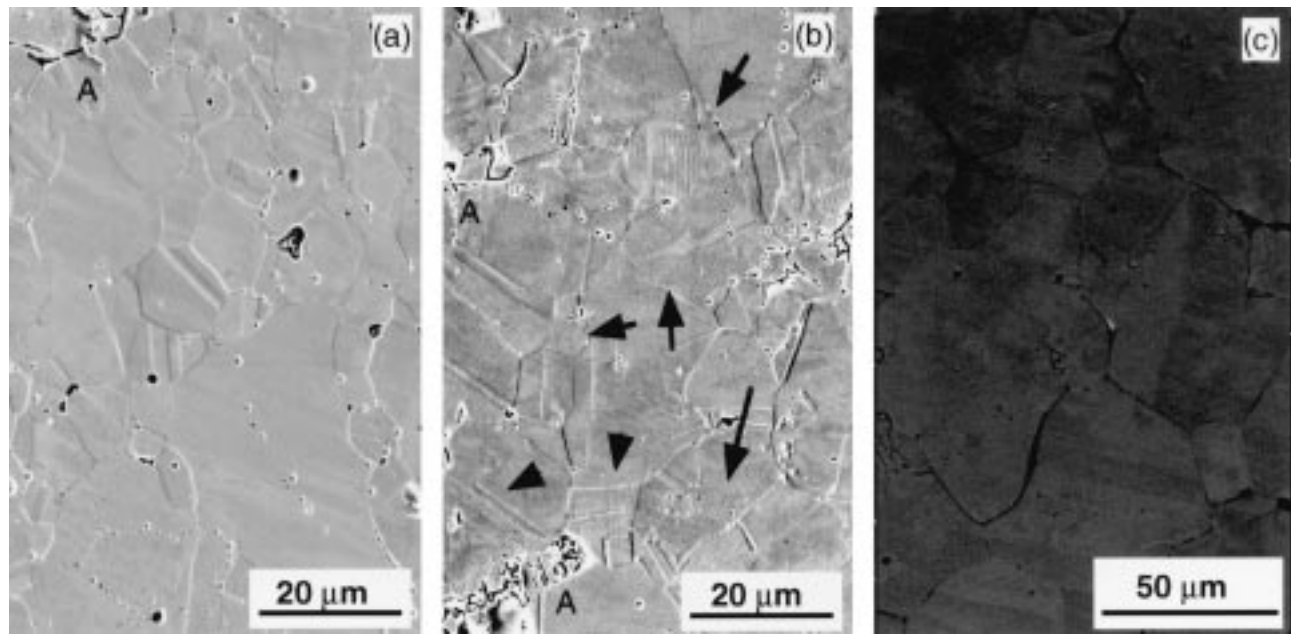


Fig. 4 Microstructure of ingot powder sintered at (a) 1900 °C for 1 h, (b) 1900 °C for 2 h, and (c) 2000 °C and immediately cooled down

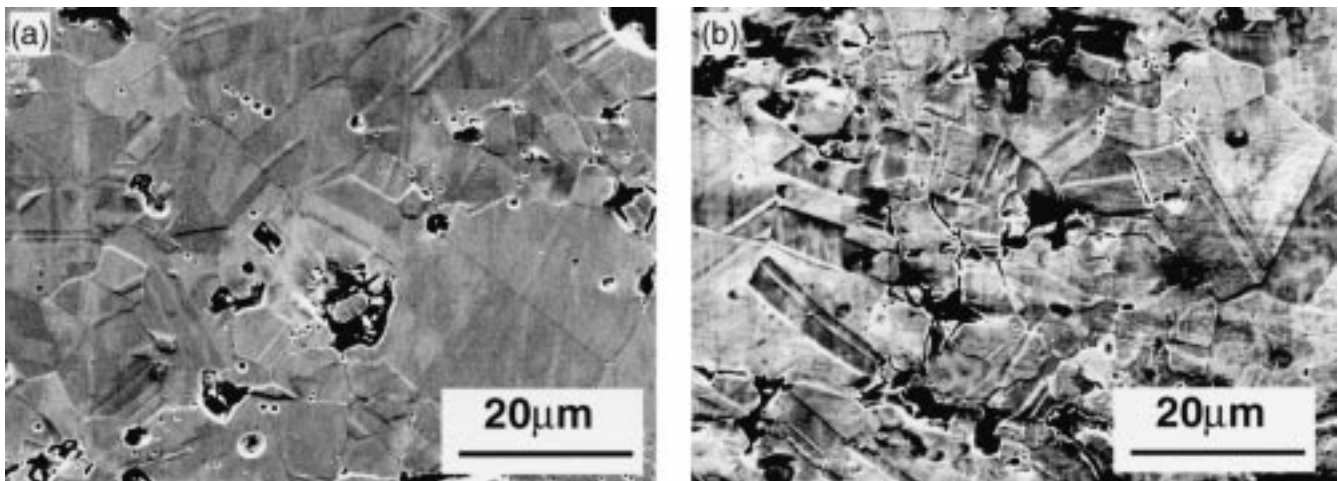


Fig. 5 Microstructure of ingot powder sample sintered by (a) PECS and (b) hot pressing at 1800 °C for 4 h

them included 45 at.% Ir. The matrix showed Ir-12.5 at.% Nb. When the sintering temperature was 1800 °C (Fig. 8b), the amount of Nb decreased, and diffusion of Nb progressed. Thus, we found some particles with Ir-23.6 at.% Nb. This is close to the composition of Ir₃Nb (Ir-25 at.% Nb). The composition of the matrix was 11.1 at.% Nb. When the sintering temperature was 1800 °C, but the temperature-increase rate was half (Fig. 8c), we still found pure Nb. However, the matrix composition was about 20 at.% Nb. This is close to the Ir₃Nb composition. When sintering was held at 1900 °C (Fig. 8d), the matrix was Ir₃Nb (about 23 at.% Nb), although we still observed pure Nb. When the sample was heated very slowly between 1700 and 1800 °C at about 0.016 °C/s, Ir₃Nb (20 at.% Nb) was formed, but the matrix showed Ir-46.5 at.% Nb. From these results, it appears that the best condition is 1900 °C for 1 h. A slow

temperature-increase rate was also effective, but the sintering temperature was more effective for alloying. However, for all conditions, we found that pure Nb or Ir included a high amount of Nb. This suggests that Nb powder did not mix homogeneously, and thus, the alloying process did not finish perfectly.

4. Discussion

4.1 Ingot Powder

The displacement of the die expanded after the temperature reached the setting temperature in PECS, in which the sample is heated directly. This suggests that the sample temperature did not reach the setting temperature during sintering. That is,

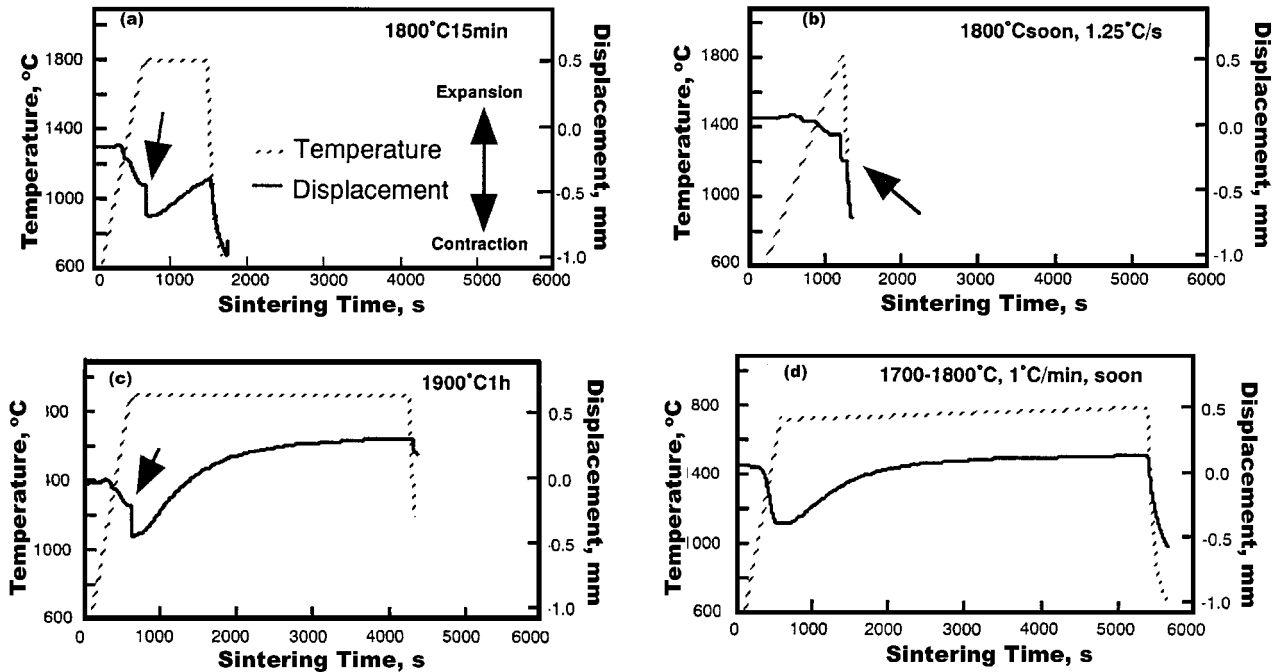


Fig. 6 Displacement of die and temperature change of pure-metal powder during sintering (a) 1800 °C for 15 min, (b) 1800 °C and immediately cooled down, (c) 1900 °C for 1 h, and (d) 1800 °C and immediately cooled down but at a temperature increase rate between 1700 and 1800 °C of 0.016 °C/s

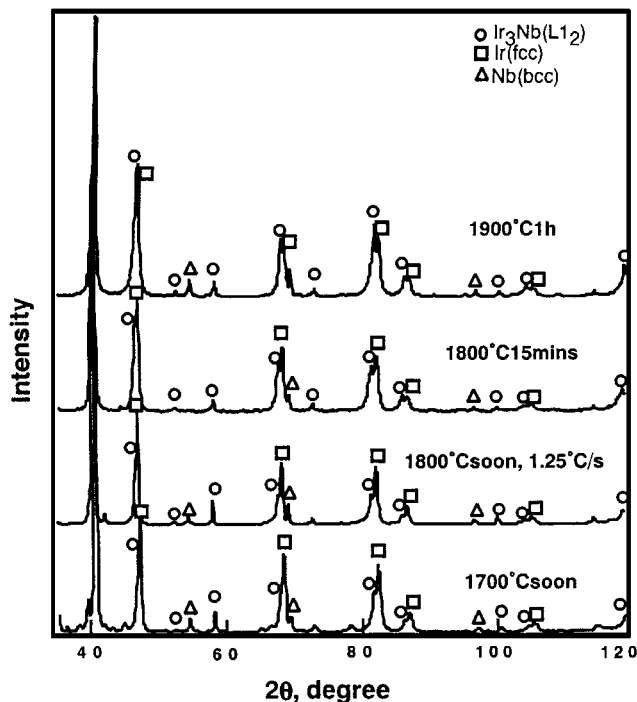


Fig. 7 X-ray analysis of pure-metal powder after sintering

the sample temperature still increased during sintering; then, the sample continued to expand. On the other hand, the sample shrank in hot pressing, in which the sample is heated indirectly.

Thus, the sample temperature seemed to reach the setting temperature. These results show that, although heating the sample directly is an advantage of PECS because the temperature should increase quickly, it is not effective for Ir₃Nb.

The heat conductivity of Ir₃Nb decreases from 100 W m⁻¹ K⁻¹ above 200 °C.^[13] According to Wiedemann-Franz's law, the heat conductivity is in inverse proportion for electric conductivity at constant temperature:

$$\chi/\sigma T = \text{const}$$

where χ is the heat conductivity, σ is the electric conductivity, and T is the absolute temperature. When the heat conductivity becomes low at a high sintering temperature, the electric conductivity becomes low. In this case, it will be difficult for electrons to pass through into the sample. Thus, the sample temperature did not increase as quickly as we expected.

For the sintering process, two kinds of models are suggested. The first model is that, when the average powder size is constant during sintering, the relative density increases with increasing applied stress. This suggests that the plastic flow around the surface of each powder is a strong factor to the sintered sample. This model can be shown as follows:^[14]

$$\ln(1 - D) = Kt \quad (\text{Eq 1})$$

where D is the relative density, t is the holding time, and K is the constant. The second model is that pores shrink by the diffusion effect in the final stage of sintering. This can be shown as follows:^[15]

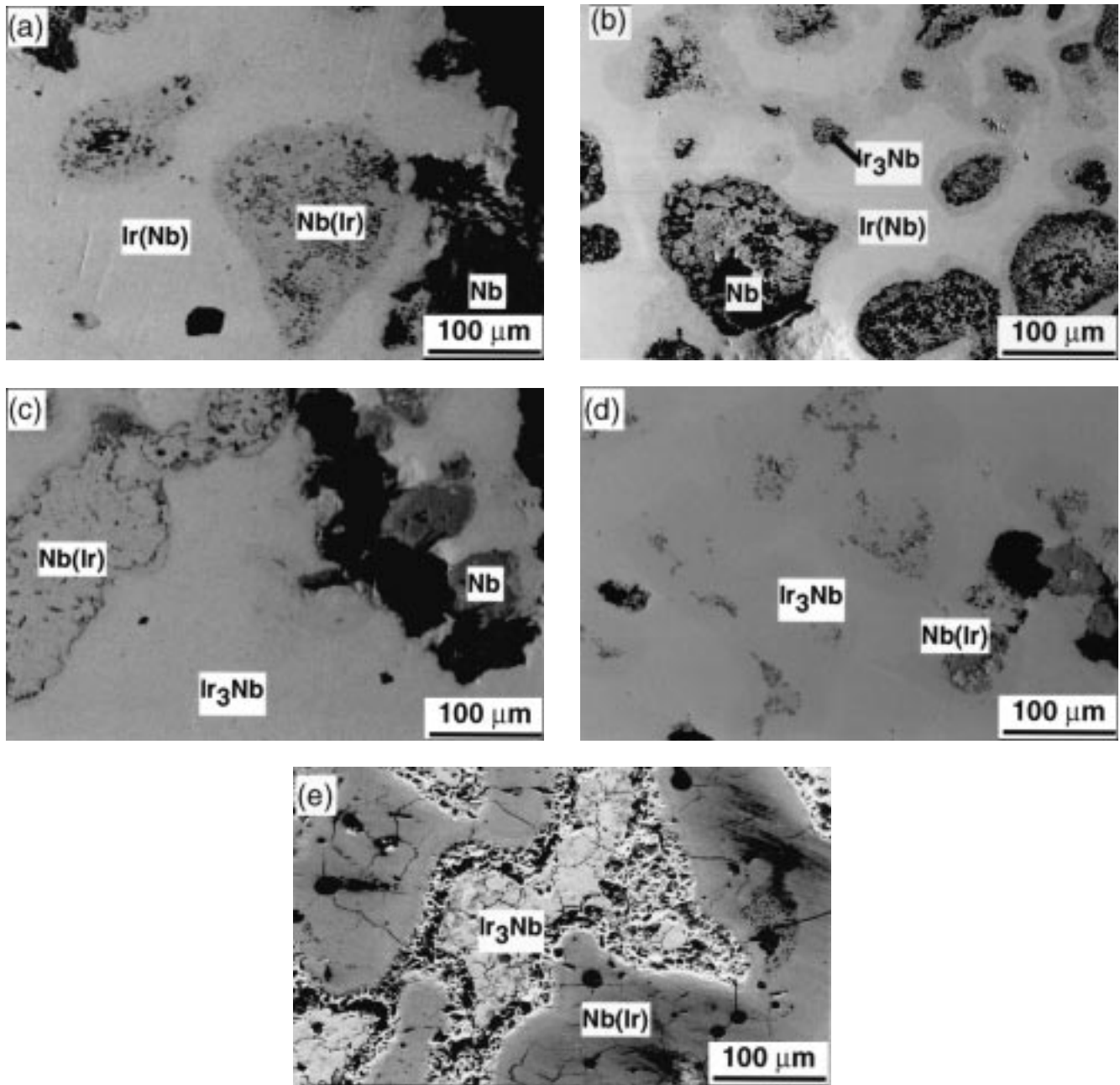


Fig. 8 Backscattered images of a pure-metal powder sample sintered at (a) 1700 °C and immediately cooled down, (b) 1800 °C for 15 min, (c) 1800 °C and immediately cooled down but at a temperature increase rate of 1.25 °C, (d) 1900 °C for 1 h, and (e) 1800 °C and immediately cooled down but at a temperature increase rate between 1700 and 1800 °C of 0.016 °C/s

$$r_0^3 - r^3 = kt \quad (\text{Eq 2})$$

where r_0 is the initial pore size, and r is the pore size at time t . Only the first model was confirmed for our alloy because pore size is difficult to measure. Figure 9 shows relative density change as a function of holding time. The relative density and the holding time are proportionate to each other. This suggests that the sintering process of Ir_3Nb was controlled by the plastic flow around the surface of each powder. When sintering is controlled by the diffusion process, the relationship between

the relative density and the holding time deviates from the proportionate relationship in Eq 1.^[15] Figure 4 also supports this model. After the sample had been sintered for 2 h at 1900 °C, slip lines were observed inside the grains. This shows that each powder deformed plastically and that plastic flow occurred around the powder during sintering.

We could not find a suitable sintering condition for ingot powder. The reason is that neither powder size nor powder shape was homogeneous. By using a mill with a mill ball, we can achieve spherical and homogeneous size powder and may

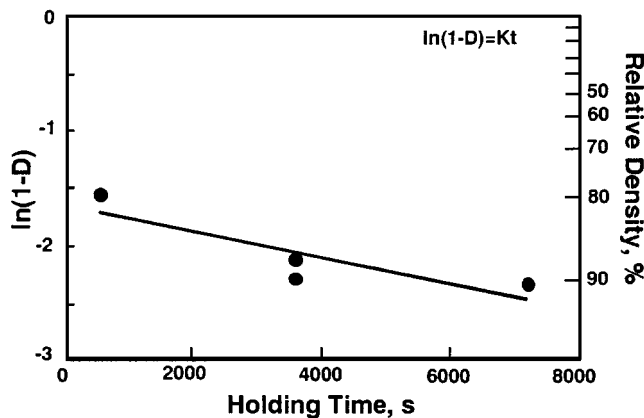


Fig. 9 Relative density change as a function of the holding time

then succeed in sintering. However, Ir is a very precious and expensive material, so we used only a 5 g sample, an amount that is not enough for milling. Among Ir-based alloys, Ir-50 at.% Al with a B2 structure was tried for hot pressing.^[16] The ingot was prepared by the arc-melting method and then mechanically crushed into powder with a size smaller than 50 μm . Hot pressing at 1800 °C for 4 h was carried out. Some voids and pure Ir were observed because of the narrower phase region of B2 IrAl or extremely low diffusivity.

4.2 Pure-Metal Powder

Compared with ingot powder, the pure-metal powder sample showed very few pores. However, the alloying process did not finish perfectly. One reason is that both Ir and Nb have a very high melting temperature of around 2450 °C. Diffusion at 1800 °C must be very slow for the alloying process. Another reason is that Nb powder distribution is not homogeneous, as shown by pure Nb in the sintered sample. This is because of the powder size difference or the weight difference between the Ir and Nb powder. The weight of Nb is half that of Ir. However, mechanical alloying is difficult for the limited sample used (5 g). In this case, the heat of formation may be helpful for sintering to succeed. If we add a third element with a low melting temperature, large heat reaction may occur, and this reaction may allow the alloying process to progress at the low melting temperature. We hope to conduct this work in the future.

4.3 Pulse Electric Current Sintering

In this study, we could not succeed in sintering using PECS. Generally, it is considered that when high voltage is intensively applied to a sample in PECS, spark plasma generates between each powder, which is covered by a thin insulator-like oxidation layer, and then the powder surface becomes clean, allowing sintering to progress.^[17] Pulse electric current sintering is sometimes called plasma-activated sintering or spark plasma sintering. The sintering process is considered to work as follows. (1) The oxidized layer of the metallic sample surface is broken. (2) An electric current and heat are concentrated at the point where the powders connect, and then, the connecting area (neck) grows thicker. (3) The temperature difference between the connecting point of the powders and the center of the powder

allows atomic diffusion to progress. Thus, the metallic sample can be sintered at relatively low temperature and for a short time by PECS. However, the sample temperature did not reach the setting temperature, and we found many pores inside the sample. This suggests that the preceding advantage of PECS did not occur for Ir₃Nb. To date, no clear evidence of plasma between powders has ever been obtained. Thus, we also doubt that plasma generates between powders during sintering.

5. Conclusions

Pulse electric current sintering was tried for Ir₃Nb, which has a melting temperature of about 2450 °C. Powder made by crashing an alloy ingot (ingot powder) and sample mixed-pure metal to become Ir-25 at.% Nb (pure-metal powder) were tried.

- *Ingot powder.* After sintering at 1900 °C for 2 h, the relative density was about 95%. Microstructure showed that plastic deformation occurred during sintering. This shows that the sintering process was controlled by the plastic flow around the powder surface.
- *Pure-element powder.* The alloying process did not finish perfectly, and pure Nb still existed after sintering.

The advantage of PECS, namely, that plasma breaks the insulator of the metallic powder, or that the short sintering time is enough for direct heating of sample, was not effective for Ir₃Nb.

Acknowledgment

We thank Drs. S. Nishimura and N. Hirosaki, NIRIM, for supporting the PECS.

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