Creep Behavior of Ir-Nb and Ir-Zr Refractory Superalloys*

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The microstructure stability and creep properties of Ir-base refractory superalloys (Ir-Nb and Ir-Zr) with an fcc and $L1_2$ two-phase structure were investigated. An orderly arrayed structure composed of cuboidal coherent $L1_2$ precipitates was observed in the Ir-Nb alloys. By a different heat treatment, a maze structure and a discontinuous coarsened lamellar structure were obtained in the Ir-Zr alloys. Creep behavior was investigated for samples with these three kinds of microstructure between 1500 and 1800°C. The creep behavior was explained according to microstructural changes before and after creep.

Key Words: Precipitation Hardening, Cuboidal Precipitates, Maze Structure, Lamellar Structure

1. Introduction

We have investigated the compression strength behavior and deformation mechanism of Ir-base alloys⁽¹⁾⁻⁽⁴⁾. The study was undertaken following our suggestion that "refractory superalloys"⁽¹⁾ are based on Ir or Rh with fcc and $L1_2$ two-phase coherent structures and are potentially useful at ultra-high temperatures at which Ni-based superalloys cannot be used.

Among Ir-base alloys, the Ir-Nb and the Ir-Zr alloys have been investigated mainly to determine their precipitate morphology dependence of strength⁽⁵⁾⁻⁽⁷⁾. The structure, in which cuboidal $L1_2$ precipitates are orderly arrayed, and the maze structure composed of plate or rod $L1_2$ precipitates were observed in the Ir-Nb and Ir-Zr alloys. These precipitates had a coherent interface with the fcc matrix. A semi-coherent structure with misfit dislocations at the interface also exists in addition to the coherent structure in the Ir-Zr alloy. The precipitation hardening of the Ir-Zr alloy was higher than that of the Ir-Nb

alloy⁽⁵⁾. The deformation mode was also investigated and showed that the deformation of the Ir-Zr alloy progresses as a result of shearing precipitates⁽⁶⁾. The deformation mode of the Ir-Nb alloy was suggested to be a bypass mechanism⁽⁷⁾.

Creep properties and microstructure stability are important factors for use as high-temperature materials. We observed a semi-coherent structure in the Ir-Zr alloy. A semi-coherent structure is formed to reduce interfacial energy. Thus, misfit dislocations are introduced at the interface. This suggests that the microstructure of the Ir-Zr alloy is unstable, although precipitation hardening is high among Ir-base alloys. If the microstructure stability is low, the creep property will be poor because, in the creep condition, materials must stand high temperature for a long time. In this study, we investigated the microstructure stability of the Ir-Nb and Ir-Zr alloys by heat treatment at high temperature. We then investigated creep behavior. The microstructural dependence of the creep behavior and the potential of Ir-Nb and Ir-Zr alloys as high-temperature materials were discussed.

2. Materials and Methods

The Ir-17 at% Nb and Ir-12 and 15 at% Zr alloys were prepared as 30 g button ingots by arc melting in

* Received 11th June, 2001

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an argon atmosphere. According to the phase diagram, these compositions are located in the fcc and $L1_2$ two-phase region⁽⁸⁾.

Cylindrical samples 3 mm in diameter and 6 mm high were cut from these ingots to investigate microstructural stability and creep behavior. These samples were heated between 1 200 and 1 900°C for up to 24 hours.

To understand creep behavior, the Ir-17 at% Nb and Ir-12 at% Zr were chosen because they include 50% $L1_2$ precipitates in a volume fraction. Before a creep test, a heat treatment at 1 800°C for 24 hours was carried out so that the Ir-Nb alloys could form $L1_2$ precipitates. Heat treatments at 1 200°C for 10 hours and 1 900°C for 4 hours were carried out for the Ir-12 at% Zr alloys. Heating at 1 200°C was carried out with these samples encapsulated in quartz tubes filled with argon gas, followed by water quenching. For heat treatments above 1 200°C, the whole sequence of heating and cooling was carried out within a vacuum furnace with a tungsten mesh heater to prevent damage to the heater by introduction of air above 100°C. The microstructures of the samples before and after the creep test were observed by scanning electron microscopy (SEM) (Philips model XL 30) after the samples had been electrolytically etched in an ethyl alcohol solution of 5% HCl.

Compression creep tests were carried out for the heat-treated samples between 1 500 and 1 800°C in a vacuum atmosphere for 300 hours under 137 MPa using an Instron 8560 testing machine.

3. Results

3.1 Typical microstructure

In our previous paper, $L1_2$ cuboidal precipitates 100 nm in size with a coherent interface were observed and aligned along $\langle 100 \rangle$ in the fcc matrix in the Ir-Nb alloy by heat treatment at 1 200°C for 168 hours similar to Ni-base superalloys⁽⁷⁾. We call this microstructure an orderly arrayed structure. To investigate microstructure stability, heat treatments at 1 800 and 1 900°C were performed in this study. Figure 1 shows the microstructure of Ir-Nb alloys heat-treated at 1 800°C for 24 hours and 1 900°C for four hours. Cuboidal precipitates (dark contrast) still formed after these heat treatments and aligned as orderly as those in the sample heated at 1 200°C (Fig. 1(a) and (b)). The sizes of the precipitates were about 100–200 nm, and there was no clear difference among the samples heated at 1 800 and 1 900°C. However, when the alloy was heat-treated at 1 800°C for 168 hours, $L1_2$ precipitates coarsened and became 500 nm in size⁽⁷⁾.

In the Ir-Zr alloys, a three-dimensional maze

Fig. 1 Secondary electron images of the Ir-17 at% Nb alloys heat-treated at (a) 1 800°C for 24 hours and (b) 1 900°C for 4 hours, and of the Ir-15 at% Zr alloys heat-treated at (c) 1 200°C for 10 hours and (d) 1 900°C for 4 hours

structure composed of plate or rod-like precipitates was formed in grains⁽⁵⁾. They were coherent precipitates. A semi-coherent structure, namely, misfit dislocation formed at the interface of the fcc matrix and $L1_2$ precipitates, was also observed because the lattice misfit between the matrix and precipitates was large in this alloy⁽⁶⁾. Furthermore, a discontinuous coarsened lamellar structure (DCLS) was also formed at grain boundaries and grew into grain during heat treatment at 1 200°C for 10 hours (Fig. 1(c)). We call this microstructure a maze structure, although a semi-coherent structure and a DCLS also formed to a small extent. The growth rate of the DCLS was slow at 1 200°C, and the DCLS grew about 10 μm from the grain boundary after heat treatment for 168 hours⁽⁵⁾. On the other hand, the DCLS growth was very fast at 1 900°C, and the DCLS covered the entire sample after four hours. As shown in Fig. 1(d), the lamellar spacing of the DCLS was about 2–5 μm, and each phase was not strictly plate. However, the orientation relationship between the fcc and $L1_2$ phases was the same as that of the coherent structure; that is, $\{111\}_{fcc} // \{111\}_{L1_2}$, $[100]_{fcc} // [100]_{L1_2}$. Thus, the interface of the fcc and $L1_2$ phases in the DCLS is coherent or semi-coherent in the atomic scale. We distinguish among the DCLS, the coherent maze structure, and the semi-coherent structure because the DCLS is formed later and replaces the coherent structure.

3.2 Creep curves

The creep strain curves of the Ir-Nb with an orderly arrayed structure, the Ir-Zr alloys with a maze structure, and the DCLS at 1 500°C as a function of time are shown in Fig. 2(a). To obtain these structures, the Ir-17 at% Nb alloy was heated at

Fig. 2 Creep strain-time curves of the Ir-17 at% Nb and Ir-12 at% Zr alloys. The creep condition is under 137 MPa at (a) 1500°C and (b) 1650 and 1800°C.

1800°C for 24 hours, and the Ir-12 at% Zr alloys were heated at 1200°C for 10 hours and at 1900°C for four hours, respectively. Here, the volume fraction of $L1_2$ precipitates in the Ir-17 at% Nb and Ir-12 at% Zr alloys is 50%, according to the phase diagram⁽⁸⁾. The alloys with the orderly arrayed structure and the maze structure showed a primary creep. Strain then increased gradually at a constant rate. However, the slope of the creep curve in the Ir-Zr alloy with the maze structure increased after 170 hours. On the other hand, the Ir-Zr alloy with the DCLS did not show a primary creep clearly, and the strain increased gradually with time from the beginning of the test. For the 300-hour duration of the test, we did not observe a tertiary creep in the samples. When the creep test was stopped after 300 hours, the strain of the Ir-Nb was about 1.2%. This was the smallest strain among the three samples. In the Ir-Zr alloys, the strain of the sample with a maze structure was about 1.7%, i.e., smaller than that of the sample with the DCLS, 3.2%.

For the Ir-Nb alloys, the temperature dependence of creep behavior was also investigated. The creep curves at 1650 and 1800°C are shown in Fig. 2(b). At these temperatures, creep deformation was very fast.

Fig. 3 Creep strain-rate-time curves of the Ir-17 at% Nb and Ir-12 at% Zr alloys. The creep condition is under 137 MPa at (a) 1500°C and (b) 1650 and 1800°C.

Thus, the length of the creep test was one order shorter than that at 1500°C. The tertiary creep clearly appeared in addition to the primary and the secondary creep above 1650°C. The samples were crashed after three hours with 5% strain at 1800°C.

3.3 Minimum creep rate

Figure 3 shows the strain rate as a function of time of these alloys. The Ir-Zr alloy with the DCLS showed the highest minimum creep rate among the alloys at 1500°C. The strain rate of the other two alloys decreased gradually, reached a minimum value, and then retained the constant value for a long time. This shows that the creep stage is in the secondary creep and not in the tertiary creep. The minimum creep rate of the Ir-Nb alloy was the lowest among the alloys tested. The alloy with a smaller minimum creep rate reached the minimum creep rate later. The strain rate of the Ir-Zr alloy with the maze structure increased at 170 hours and the higher value was retained for a while.

The strain rates of the Ir-17 at% Nb alloys at 1650 and 1800°C are shown in Fig. 3(b). Here, it is very clear that the strain rate increased at a more rapid pace after the strain rate reached the minimum value. This shows that the tertiary creep was very clear at these temperatures. The secondary creep

Fig. 4 Secondary electron images of the Ir-17 at% Nb alloys after a creep test at (a, b) 1500°C and (c, d) 1650°C under 137 MPa for 300 hours. (a, c) normal and (b, d) parallel directions for applied stress. The arrows show the compressive direction. These alloys were heat-treated at 1800°C for 24 hours before a creep test.

continued longer at 1650°C than at 1800°C. The acceleration of the strain rate in the tertiary stage at 1800°C was larger than at 1650°C. The minimum creep rate was about 10^{-7} s^{-1} at 1500°C and two orders smaller than those at 1650 and 1800°C.

3.4 Microstructure after creep

The microstructure of the Ir-Nb alloys, which were crept at 1500 and 1650°C, are shown in Fig. 4. The two sections parallel and normal to the compression direction were observed. The microstructures crept at 1800°C were not observed because of the crash of the sample. Cuboidal precipitates still remained and aligned orderly after the creep at 1500°C (Fig. 4(a) and (b)). There was no difference in microstructure between the two sections parallel and normal to the compression direction. After the creep at 1650°C, in spite of the creep being in a tertiary stage, cuboidal precipitates still remained and aligned orderly although coarsening of the L1_2 and fcc phase at the grain boundary was observed (Fig. 4(c) and (d)). In the Ir-Zr alloy with the maze structure, the DCLS was formed in a wide area. In the normal orientation for the compression axis, the whole area was covered by the DCLS (Fig. 5(a)). However, in the parallel orientation for the compression axis, only the edge of the sample was covered by the DCLS (Fig. 5(b)). This is because the DCLS preferred to grow from the grain boundaries and sample surface. Inside the sample, we observed fine plate-like precipitates. The volume fraction of the DCLS was about 90% after the creep test. This shows that coarsening progressed during the creep test, and

Fig. 5 Secondary electron images of the Ir-12 at% Zr alloys after a creep test at 1500°C under 137 MPa for 300 hours. (a) normal and (b) parallel direction for applied stress. The arrows show a compressive direction. The alloys were heat-treated at 1200°C for 10 hours before a creep test.

the DCLS replaced the maze structure. On the other hand, for the Ir-Zr alloy with the DCLS before the creep, no change was observed after the creep in SEM.

4. Discussion

4.1 Microstructure stability

We investigated three kinds of microstructure in the samples with the same volume fraction of L1_2 precipitates, that is, the orderly arrayed structure, the maze structure, and the discontinuous coarsened lamellar structure. After the creep, cuboidal precipitates in the orderly arrayed structure did not coarsen and retain their shape. On the other hand, the maze structure was replaced by the DCLS. This shows that the maze structure is not stable at 1500°C because of a large lattice misfit. As shown in the previous paper, the lattice misfit of the Ir-Zr alloy is larger (2%) than that of the Ir-Nb alloy. When the lattice misfit is large and there is no misfit dislocation at the interface, the coherency strain energy is high. Thus, a semi-coherent structure in which misfit dislocations formed at the interface was also formed. Furthermore, discontinuous coarsening occurs to accommodate high strain energy at the interface. Similar behavior was observed in a Ti-Al alloy, in which a fine fully lamellar structure is formed first, then discontinuous coarsening occurs at grain boundaries to reduce interfacial energy, and finally the discontinuous coarsened lamellar structure covers the whole sample⁽⁹⁾. Generally, the migration of an incoherent interface is faster than that of a coherent or semi-coherent interface because the migration is governed by the rate at which lattice diffusion can remove the excess atoms from ahead of the interface, and the lattice diffusion is slow at the coherent or semi-coherent interface⁽¹⁰⁾. Thus, an increase in the thickness of plate-like precipitates or the fine lamellar structure is difficult, and, in this case, a discontinuous coarsening, which is accompanied by a migration of grain boundaries, often occurs⁽¹¹⁾. In our study, the discontinuous coarsening was observed in only one sample with the maze structure composed

by plate or rod precipitates in the Ir-Zr alloy.

4.2 Microstructure dependence of the creep behavior

The smallest minimum creep rate was shown in the Ir-Nb alloy. The second and third smallest minimum creep rates were shown in the Ir-Zr alloys with the maze structure and the DCLS, respectively. Generally, fine microstructure, that is, small precipitates or fine lamellae etc, is effective to obtain large creep resistance because interfaces prevent the movement of dislocation. For example, in Ti-Al, the finer lamellar structure showed a smaller minimum creep rate under low stress⁽¹²⁾. From this point, the largest minimum creep rate in the sample with DCLS can be explained because the DCLS had a coarser microstructure with a width of 2–3 μm than the other structure. However, the maze structure seemed to be finer than the orderly arrayed structure because the precipitate width in the maze structure was about 20–30 nm. On the other hand, the width of precipitates in the orderly arrayed structure was about 100 nm. For these structures, the minimum creep rate was insensitive to microstructure fineness. To understand the behavior of the minimum creep rate, the dislocation structure during creep is under investigation. During creep, the maze structure coarsened by discontinuous manner. Thus, after the creep rate reached the minimum value, the creep rate increased and was closed to the creep rate of the DCLS. However, the creep rate was constant for a while because the creep was not in a tertiary stage.

4.3 Temperature dependence of creep

We found that the creep deformation above 1650°C was very fast, and the tertiary creep was clearly observed within 24 hours. In spite of this, cuboidal precipitates did not coarsen or deform during a creep test by observation in SEM. The microstructure after a creep at 1650°C was not different from that after a creep at 1500°C (Fig. 4). The only difference was the existence of a coarsened phase at the grain boundaries after a creep test at 1650°C. This coarsened phase made creep resistance low at 1650°C. For another reason, a dislocation structure may be different. Their dislocation structures are now under investigation.

4.4 Possibility as ultra-high-temperature materials

The creep resistance depended on the microstructure. The total strain after a creep for 300 hours was about 3.2% in the most deformed sample at 1500°C. For reference, we tested Ni-base superalloy, TMS 75, which has a rupture life of 196 hours under 98 MPa in a tensile condition at 1150°C⁽¹³⁾. However, under compression stress at 1200°C, the sample was

buckled, and we could not accurately measure the strain. This shows that our alloys have superior creep properties than Ni-base superalloys. Another comparison test indicated that the compressive creep strain rates of an IrAl single phase with a B2 structure at 1100°C were between 10^{-6} and 10^{-5} s^{-1} under between 100 and 220 MPa⁽¹⁴⁾. The strain rate of IrAl at 1100°C was one or two orders larger than that of our alloys at 1500°C. This shows that our alloys with fcc and L1₂ two phase are more promising materials because they have a high creep resistance. The tensile creep property of pure Ir was also shown⁽¹⁵⁾. The rupture life of pure Ir at 1600°C is less than 10 hours under 5 MPa. We cannot compare our data and pure Ir data simply because the creep temperature and creep conditions are very difficult; however, we expect that our alloy will have a higher creep resistance than pure Ir because of the two-phase coherent structure.

From the above results, we believe that Ir-base alloys can be used at least at 1500°C under compression stress. However, the maze structure in the Ir-Zr alloy is not stable, and it coarsened at high temperature. In this case, the Ir-Nb alloy is more stable to use at high temperature. The microstructural stability gives the Ir-Nb alloy higher resistance for creep deformation than the Ir-Zr alloy, even the maze structure attributes have strong precipitation hardening in the Ir-Zr alloy⁽⁶⁾. A coherent structure with a suitable lattice misfit is desirable to obtain both high precipitation hardening and strong resistance to creep deformation. On the other hand, above 1650°C, the creep deformation was very fast, and the sample fractured during a creep at 1800°C after only three hours. Thus, it is very difficult to use the Ir-base binary alloys above 1650°C although we did not investigate the Ir-Zr alloys at high temperature.

5. Conclusions

The compression creep behavior of Ir-Nb with an orderly arrayed structure, the Ir-Zr alloy with the maze structure, and the Ir-Zr alloy with a discontinuous coarsening lamellae (DCLS) was investigated between 1500 and 1800°C under 137 MPa.

(1) At 1500°C, the microstructure dependence on creep behavior was investigated. Only the primary and secondary stages were observed. The creep strain was below 3.2%. Maximum strain was shown in the sample with the DCLS in the Ir-Zr alloy. The second largest strain was shown in the maze structure in the Ir-Zr alloys. The Ir-Nb alloy with an orderly arrayed structure was the most stable during creep.

(2) Above 1650°C, the tertiary creep stage was also observed. The strain rate was two orders higher

than at 1500°C. At 1800°C, the sample crashed after three hours.

(3) After creep, the microstructure of the Ir-Nb alloy was stable. On the other hand, discontinuous coarsening of the maze structure was observed in the I-Zr alloy. The creep property of the Ir-Zr alloy was worse than that of the Ir-Nb alloy because of the coarsening of the coherent structure.

Acknowledgments

We are grateful to Mr. S. Nishikawa of Furuya Metal Co., Ltd. for preparing the Ir alloy ingots.

References

- (1) Yamabe, Y., Koizumi, Y., Murakami, H., Ro, Y., Maruko, T. and Harada, H., *Scripta Materialia*, Vol. 35, No. 2 (1996), pp. 211-216.
- (2) Yamabe-Mitarai, Y., Koizumi, Y., Murakami, H., Ro, Y., Maruko, T. and Harada, H., *Scripta Materialia*, Vol. 36, No. 4 (1997), pp. 393-398.
- (3) Yamabe-Mitarai, Y., Ro, Y., Maruko, T., Yokokawa, T. and Harada, H., *Structural Intermetallics 1997*, in *The Second International Symposium of Structural Intermetallics/1997*, ed. by Nathal, M.V., Darolia, R., Liu, C.T., Martin, P.L., Miracle, D.B., Wagner, R. and Yamaguchi, M., TMS, Warrendale, PA, (1997), pp. 805-814.
- (4) Yamabe-Mitarai, Y., Ro, Y., Maruko, T. and Harada, H., *Met. Trans. A*, Vol. 29 A (1998), pp. 537-549.
- (5) Yamabe-Mitarai, Y., Ro, Y., Maruko, T. and Harada, H., *Intermetallics*, Vol. 7 (1999), pp. 49-58.
- (6) Yamabe-Mitarai, Y., Ro, Y., Maruko, T. and Harada, H., *Scripta Materialia*, Vol. 40, No. 1 (1999), pp. 109-115.
- (7) Yamabe-Mitarai, Y., Gu, Y., Ro, Y., Nakazawa, S., Maruko, T. and Harada, H., *Scripta Materialia*, Vol. 41, No. 3 (1999), pp. 305-310.
- (8) *Binary Alloy Phase Diagrams*, ed. by Massalski, T.B., ASM International, Materials Park, OH (1992), p. 2330, p. 2473.
- (9) Yamabe, Y., Honjo, N. and Kikuchi, M., *JIMIS6, Proc. of Intel. Symp. on Intermetallic Compounds*, ed. by Izumi, O., JIM, (1991), pp. 821-826.
- (10) Porter, D.A. and Easterling, K.E., *Phase Transformations in Metals and Alloys*, second edition, (1992), pp. 279-287, Chapman & Hall.
- (11) Livingston, J.D. and Cahn, J.W., *Acta Metall.*, Vol. 22 (1974), pp. 495-503.
- (12) Yamamoto, R., Mizoguchi, K., Wegmann, G. and Maruyama, K., *Intermetallics*, Vol. 6 (1998), pp. 699-702.
- (13) Koizumi, Y., Kobayashi, T., Kimura, T., Osawa, M. and Harada, H., *Materials for Advanced Power Engineering 1998*, ed. by Lecomte-Beckers, J., Schubert, F. and Ennis, P.J., (1998), pp. 1089-1098.
- (14) Chiba, A., Ono, T., Li, X.G. and Takahashi, S., *Intermetallics*, Vol. 6 (1998), pp. 35-42.
- (15) Fischer, B., Behrends, A., Freund, D., Lupton, D.F. and Merker, J., *Intermetallics*, Vol. 43, No. 1 (1999), pp. 18-28.