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# Microstructure and impact properties of ultra-fine grained tungsten alloys dispersed with TiC

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**Abstract**

In order to improve both the low temperature toughness and the resistance to embrittlement by recrystallization and irradiation in currently available tungsten and its alloys, ultra-fine grained tungsten alloys with TiC additions of 0.2 and 0.5 wt% were developed by mechanical alloying and hot isostatic pressing. It is shown that the impact toughness of the developed alloys is very sensitive to the magnitude of relative density and is greatly improved by increasing its value. An alloy with 0.2 wt% TiC, which has the highest relative density of 99.5% among the developed alloys, exhibits a much lower ductile-to-brittle transition temperature and higher strength than pure tungsten which has a relative density of 100%. For the alloy, recrystallization and grain growth occur during 1-h heating between 2273 and 2473 K, much higher than the equivalent temperature range for pure tungsten. Increasing the TiC content to 0.5 wt% makes the alloy more resistant to recrystallization and grain growth. © 1999 Published by Elsevier Science B.V. All rights reserved.

## 1. Introduction

Tungsten and its alloys are considered as probable candidate materials for plasma facing components applications because of the low sputtering yield, high thermal conductivity, high strength at elevated temperatures and low tritium inventory [1–5]. However, key issues for these metals are that the ductile-to-brittle transition temperature (DBTT) is around room temperature and significant increase in DBTT occurs by recrystallization [6–10] and neutron irradiation [11–13]. Therefore, it is necessary to develop tungsten alloys with much improved toughness before and after recrystallization and neutron irradiation.

The authors have already reported the idea of alloy design and microstructure control to solve the key issues [14–16]. The application to molybdenum demonstrated that the idea was very effective for improving the toughness before and after recrystallization and neutron irradiation [14–18]. Since molybdenum and tungsten are quite similar in physical and chemical properties, the idea is very likely to be applicable also to tungsten. However, the melting point of tungsten is 3683 K, 800 K higher than that of molybdenum. This makes the fabrication of tungsten much more difficult.

With this in mind, the authors have made efforts to improve the toughness of tungsten. As a result, some success was achieved in improving the toughness before recrystallization and irradiation, although more improvement should be required. In this paper, the current status of R & D of tungsten alloys developed in the Oarai Facility of Institute for Materials Research (IMR) at Tohoku University is presented.

## 2. Experimental

Powders of pure tungsten (average particle size 3.6 μm and purity 99.9%) and TiC (0.57 μm, 98%) were

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mixed to provide the target compositions of W–0.2 wt% TiC and W–0.5 wt% TiC. These mixed powders were put into a vessel made of WC and then subjected to a mechanical alloying (MA) treatment by ball milling with a planetary ball mill for 360–864 ks in a purified argon atmosphere (purity 99.9999%). All of these procedures were conducted in a specially designed glove box.

Hot isostatic pressing was conducted in an argon atmosphere at 200 MPa for 18 ks at two temperatures of around 1623 K and around 2223 K. All of the as-hipped samples were hot-forged and then hot-rolled. The as-hipped sample with TiC addition of 0.2 wt% was successfully hot rolled at around 1770 K to approximately 2 mm thickness. However, the as-hipped samples with increased TiC addition to 0.5 wt% were not successfully hot rolled because of cracking. Table 1 shows the designation and fabrication conditions of the alloys. The measured density in the as-hipped condition was about 97.5% of theoretical one, regardless of TiC content. The density in the as-forged condition increased to approximately 98% and that in the as-rolled condition to 99.5%. Table 2 shows the chemical compositions of these alloys and commercially available pure tungsten. It should be noted that the oxygen impurity content of the developed alloys does not exceed the level contained in the starting powders, although the content is much higher than that of pure tungsten. This indicates that a reduction of oxygen impurity content in the alloys is easily achieved as long as high purity powders are available.

From the as-forged or as-rolled sheets of the developed alloys together with the as-rolled sheet of pure tungsten, bend bar specimens were machined to dimensions of 1 mm by 1 mm by 20 mm with the longitudinal axis parallel to the rolling direction. Sections of the as-forged or as-rolled sheet of the alloys were subjected to heating at 2073, 2273 and 2473 K for 3.6 ks in a vacuum of $10^{-5}$ Pa. The low-temperature toughness was examined by impact 3-point bending tests at temperatures from 288 to 544 K by using a specially designed electrically controlled hydraulic machine with a span of 12.5 mm and an impact velocity of approximately 5 m/s [19]. Fracture surfaces of impact tested specimens were examined by scanning electron microscopy (SEM) to determine the fracture mode. TEM observation and Energy Dispersive X-ray (EDX) analysis were made with JEM 4000FX operating at 400 kV in the Oarai Facility of IMR.

## 3. Results and discussion

Since in the as-rolled specimens strain contrast due to a very high density of dislocations made it difficult to observe TiC particles, the as-hipped specimens were used for TEM observation (Fig. 1). As seen from the figure, there are large differences in grain size between the three alloys. The average grain size was 1.6 μm for WMTC-02-1, 0.44 μm for WMTC-05-1 and 0.05 μm for WMTC-05-2. This indicates that the grain size of the alloys can be controlled by TiC content and hipping temperature. The lower part of Fig. 1 shows fine particles mostly existing at grain boundaries and having sizes in the range of several nm to 40 nm. EDX analysis showed that the particles may be titanium carbide or titanium oxy-carbide. It is also seen that the lattice images from fine particles are connected to either of adjacent matrices, indicating that the particles have good coherency with either of the adjacent matrices.

Load-displacement curves of the alloys and pure tungsten are shown in Fig. 2. Pure tungsten fractured at a very low load without showing any ductility up to 544 K, the highest test temperature available in the present testing machine. On the other hand, all of the developed alloys exhibit improved toughness, i.e., the fracture of the alloys occurs at much higher load than that of pure tungsten. In particular, WMTC-02-1 exhibits significant ductility at a lower temperature of 452 K. In view of the fact that the test was not a static bending test but an impact bending test where the strain rate is 5 orders higher than the former, the result of WMTC-02-1 seems to be very significant. The side view of WMTC-02-1 tested at 452 K is shown in Fig. 3 as evidence of the occurrence of significant ductility.

Table 1
Designation, fabrication conditions and relative density of the developed tungsten alloys

| | WMTC-02-1 | WMTC-05-1 | WMTC-05-2 |
|---|---|---|---|
| Target composition | | | |
| TiC (wt%) | 0.2 | 0.5 | 0.5 |
| HIP condition | | | |
| Temp. (K)/Time (h) | 2223/5 | 2223/5 | 1623/5 |
| Hot forging | ○ | ○ | ○ |
| Hot rolling | ○ | | |
| Grain size (μm) | 1.6 | 0.44 | 0.05 |
| Relative density (%) | | | |
| As-hipped | 97.5 | 97.6 | 93.9 |
| As-forged or As-rolled | 99.5 | 98.2 | 97.7 |

Table 2
Chemical compositions of pure tungsten and the developed tungsten alloys (wt ppm)

| | Ti | C | N | O |
|---|---|---|---|---|
| Pure W | | <10 | <1 | 8 |
| WMTC-02-1 | 1800 | 330 | 160 | 300 |
| WMTC-05-1 | 3500 | 700 | 210 | 390 |
| WMTC-05-2 | 3200 | 1030 | 180 | 190 |

Fig. 4 shows the test temperature dependence of the total absorbed energy ($E_t$) and maximum strength. The DBTT, which is defined as the temperature where $E_t$ is one half of the value in the upper shelf region, is around 440 K for WMTC-02-1, above 484 K for WMTC-05-1, above 541 K for WMTC-05-2 and above 544 K for pure tungsten. This difference in DBTT between the developed alloys is attributable to the difference in relative density (see Table 1) because pores act as crack initiators. Since the relative density of WMTC-02-1 is 99.5%, it would be useful to increase its density to 100%, as for pure tungsten. In other words, a further improvement of low temperature toughness for the alloys may be made by increasing the density towards 100%.

Fig. 5 shows SEM micrographs of fracture surfaces of the alloys. It appears that WMTC-05-1 and WMTC-05-2 may fracture intergranularly and WMTC-02-1 intergranularly and transgranularly.

As was reported elsewhere [14–16,18], the resistance to recrystallization and grain growth is increased as the amount of TiC addition increases. However, WMTC-02-1 which has the highest low temperature toughness, contains only 0.2 wt% TiC. In order to examine the effect of vacuum heating on the microstructure and low temperature toughness for WMTC-02-1, 1-h heating at 2073, 2273 and 2473 K was conducted. Fig. 6 shows the microstructures of WMTC-02-1 as a function of heating temperature. It appears that the heating at 2073 K causes no appreciable changes in microstructure; a high density of dislocations are still observed. After heating at 2273 K, in some grains dislocations disappeared and grain growth occurred. After heating at 2473 K, dislocations were scarce in most grains and pores were often observed at grain boundaries. Fairly large particles were observed together with fine particles and recrystallized texture. These results indicate that the recrystallization of WMTC-02-1 started between 2273 and 2473 K. This

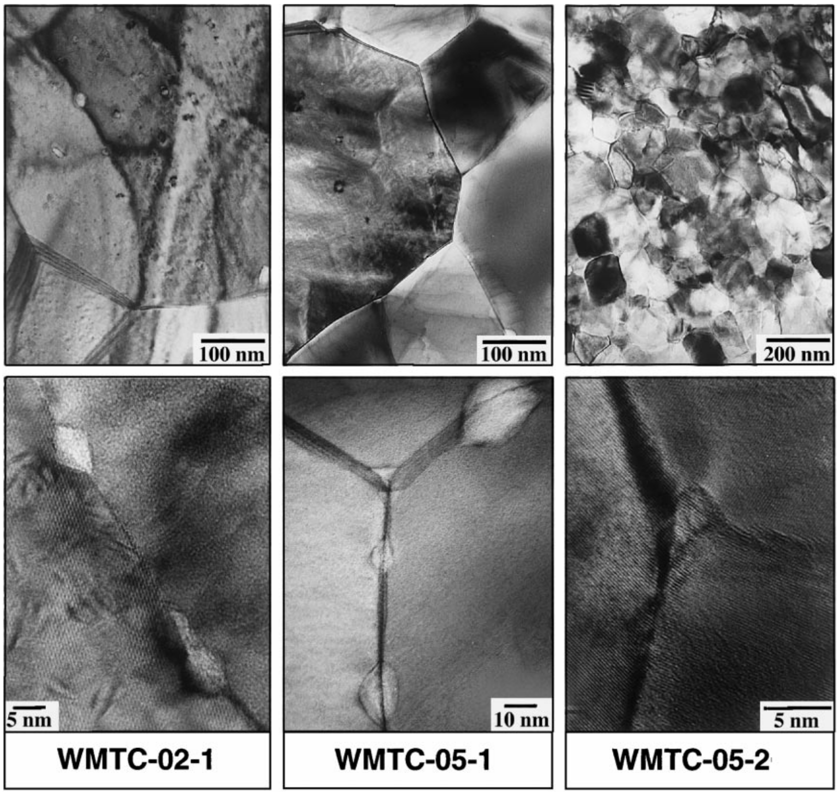

Fig. 1. TEM micrographs showing the grain appearance (the upper part) and fine particles mostly existing at grain boundaries (the lower part) in the as-hipped WMTC-02-1, WMTC-05-1 and WMTC-05-2.

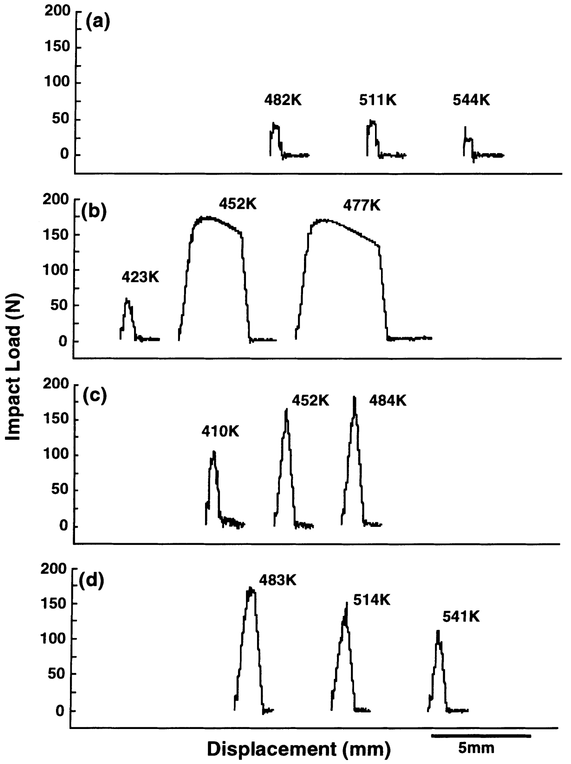

Fig. 2. Load-displacement curves of pure tungsten (a), WMTC-02-1 (b), WMTC-05-1 (c) and WMTC-05-2 (d). The test temperature is indicated in the figure.

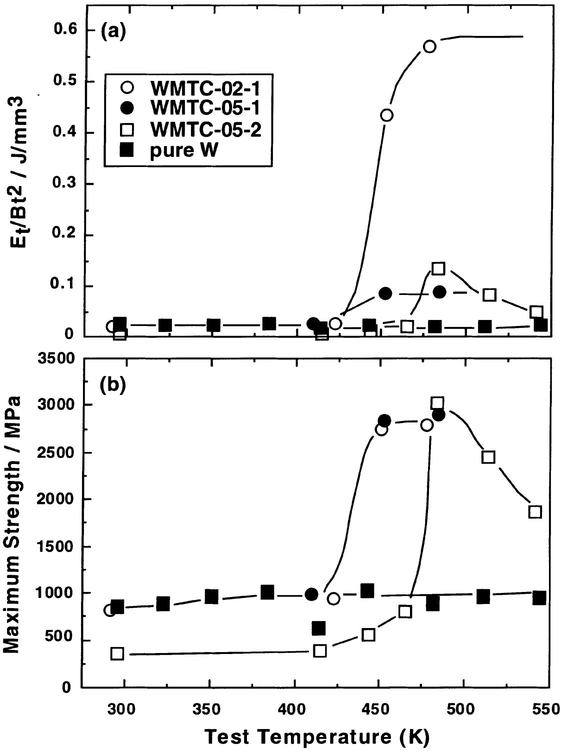

Fig. 4. Test temperature dependence of total absorbed energy normalized by $Bt^2$ ($B$ is the specimen width and $t$ is the specimen thickness) (a) and maximum strength (b) for WMTC-02-1, WMTC-05-1, WMTC-05-2 and pure tungsten.

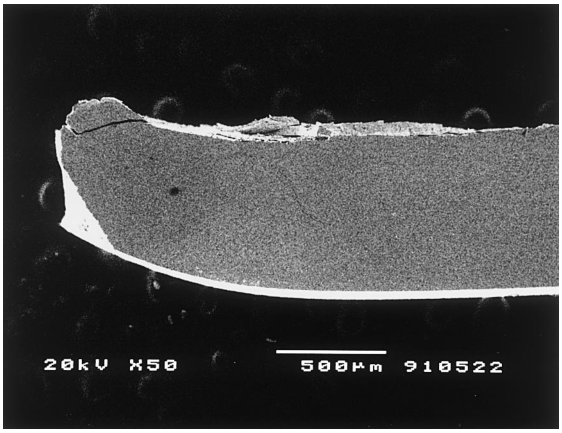

Fig. 3. The side view of WMTC-02-1 specimen impact tested at 452 K.

recrystallization temperature is much higher than that of pure tungsten, around 1600 K.

Impact 3-point bending test results on the heated specimens of WMTC-02-1 showed that the absorbed energy decreased to the level of pure tungsten mentioned above, regardless of heating condition. Density measurements showed that the heating at 2273 and 2473 K decreased the relative density to 98.2% and 97.5%, respectively. The density decrease and the above microstructure changes may be responsible for the embrittlement. However, in 2073 K-heated specimens, no appreciable changes in microstructure, fracture mode and relative density were seen. Therefore, the fracture surfaces were examined in detail to study the cause of the embrittlement in 2073 K-heated specimens. It was found that a significant grain growth occurred in the region where the maximum fiber stress is applied and that the fracture initiated from this region. Since TiC particles in the developed alloys are considered not to be distributed uniformly, the reduction of TiC content as in WMTC-02-1 may produce regions where TiC particles are very few or absent. Since TiC particles can suppress grain boundary migration at high temperatures, recrystallization and grain growth may preferentially occur in TiC-poor regions. On the other hand, WMTC-05-2 with TiC addition to 0.5 wt% was found to show no indication of recrystallization and grain growth even after 1-h heating at 2473 K. Therefore, for further improvement of low temperature toughness and resistance to

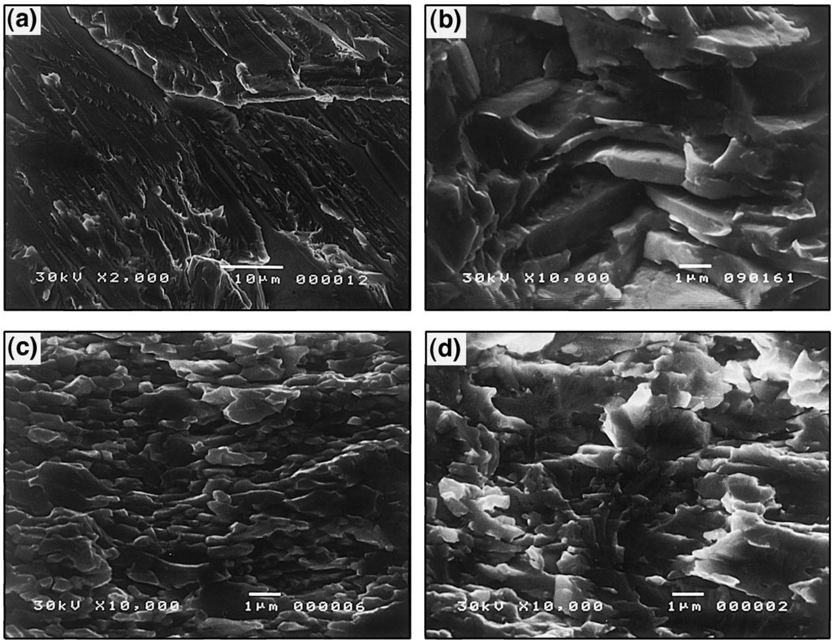

Fig. 5. SEM micrographs of fracture surfaces of pure tungsten (a), WMTC-02-1 (b), WMTC-05-1 (c) and WMTC-05-2 (d).

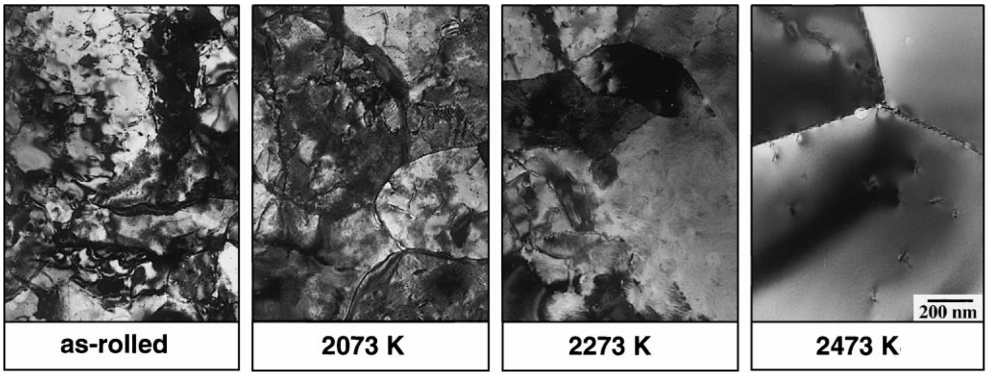

Fig. 6. Microstructures of WMTC-02-1 before and after 1-h heating at 2073, 2273 and 2473 K.

recrystallization, it is necessary to develop tungsten alloys that have 100% relative density and sufficiently high TiC content. Since the increase in TiC content caused hardening and made it difficult to increase the density by hot rolling, the optimum TiC content will be a maximum content at which hot rolling can be made.

## 4. Conclusion

Ultra-fine grained tungsten alloys with very fine TiC particles mostly existing at grain boundaries allowed a great improvement in the impact toughness at low temperatures. The most important factor in this improvement was the increase in the density of the alloys. The increase in relative density to 99.5% was obtained for the alloy with reduced TiC content, 0.2 wt%, by hot forging and hot rolling. The alloy, designated as WMTC-02-1, was found to show a significant ductility and high strength at and above 452 K, whereas the commercially available pure tungsten with 100% relative density fractured in a completely brittle manner at low stresses even at 544 K: the DBTT for the alloy was lower by more than 100 K than that for pure tungsten. More improvement in low temperature toughness can be made by increasing the relative density of the alloy to 100%.

The effect of vacuum heating on the microstructure of WMTC-02-1 was significant at and above 2273 K. After the heating the low temperature toughness of the alloy lowered to the level of pure tungsten. For the improvement of such recrystallization embrittlement, it is necessary to increase TiC content. The optimum TiC content will be the maximum content at which hot rolling can be made to increase the density.

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## References

[1] J. Roth, Impurity generation process in particle–surface interaction: data status and needs, in: R.K. Janev, H.W. Drawin (Eds.), Atomic and Plasma-Material Interaction Processes in Controlled Thermonuclear Fusion, Elsevier, Amsterdam, 1993, p. 381.
[2] C. Garcia-Rosales, J. Nucl. Mater. 211 (1994) 202.
[3] D.A. Petti, K.A. McCarthy, W. Gulden, S.J. Piet, Y. Seki, B. Kolbasov, J. Nucl. Mater. 233–237 (1996) 37.
[4] T. Tanabe, N. Noda, H. Nakamura, J. Nucl. Mater. 196–198 (1992) 11.
[5] V.A. Chuyanov, J. Nucl. Mater. 233–237 (1996) 4.
[6] R. Matera, G. Federici, The ITER Joint Central Team, J. Nucl. Mater. 233–237 (1996) 17.
[7] M. Akiba, H. Madarame, J. Nucl. Mater. 212–215 (1994) 90.
[8] N. Nakamura, S. Suzuki, K. Satoh, M. Araki, K. Yokoyama, M. Dairaku, M. Akiba, J. Nucl. Mater. 212–215 (1994) 1201.
[9] M. Fujitsuka, I. Mutoh, T. Tanabe, T. Shikama, J. Nucl. Mater. 233–237 (1996) 638.
[10] J. Linke, V.R. Barabash, H. Bolt, A. Gervash, I. Mazul, I. Ovchinnikov, M. Rodig, J. Nucl. Mater. 233–237 (1996) 1195.
[11] J.M. Steichen, J. Nucl. Mater. 60 (1976) 13.
[12] R.K. Williams, F.W. Wiffen, J. Bentley, J.O. Steigler, Metall. Trans. 14A (1983) 655.
[13] I.V. Gorynin, V.A. Ignatov, V.V. Rybin, S.A. Fabritsiev, V.A. Kazakov, V.P. Chakin, V.A. Tsykanov, V.R. Barabash, Y.G. Prokofyef, J. Nucl. Mater. 191–194 (1992) 421.
[14] H. Kurishita, Y. Kitsunai, H. Kayano, Y. Hiraoka, K. Takebe, JCSTEA 7 Series Symp., Materials for advanced energy systems & fission and fusion engineering, in: A. Kohyama, H. Matsui, S. Tanaka, H. Takahashi, (Eds.), The Japanese Society of Materials for Advanced Energy Systems, 1994, p. 199.
[15] H. Kurishita, Y. Kitsunai, Y. Hiraoka, T. Shibayama, H. Kayano, Mater. Trans. JIM. 37 (1996) 90.
[16] H. Kurishita, Y. Kitsunai, T. Shibayama, H. Kayano, Y. Hiraoka, J. Nucl. Mater. 233–237 (1996) 557.
[17] Y. Kitsunai, H. Kurishita, M. Narui, H. Kayano, Y. Hiraoka, J. Nucl. Mater. 239 (1996) 253.
[18] Y. Kitsunai, H. Kurishita, M. Narui, H. Kayano, Y. Hiraoka, T. Takida, T. Igarashi, Sci. Rep. RITU A45 (1997) 115.
[19] H. Kayano, H. Kurishita, M. Narui, M. Yamazaki, Ann. Chem. Fr. 16 (1991) 309.