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論文内容要旨

Tungsten (W) has many favorable properties for use as high heat flux components and high-density power structural materials for fusion reactors, including a high melting point, low thermal expansion coefficients, low sputtering yield and excellent compatibility with liquid metals. However, it exhibits serious embrittlement, i.e., low temperature embrittlement, recrystallization embrittlement and radiation embrittlement. Therefore, it is necessary to achieve simultaneous improvements in the resistance to these types of embrittlement. Such embrittlement is microstructure sensitive, and thus the author has been making efforts to establish a process for overcoming the problem by introducing fine grains and finely dispersed carbide-particles in the microstructure using powder metallurgical methods, particularly mechanical alloying (MA), followed by sintering and hot working. In this thesis, the efforts are presented with emphasis on the low temperature embrittlement and recrystallization embrittlement.

Chapter 1 is the introduction and presents the research background and the purpose of the study. The outline of this chapter is as follows; the necessity of fusion energy, the significance of the development of advanced materials that can be safely used under severe conditions of high heat loads and high energy particle irradiation, the advantages and disadvantages of the application of tungsten materials to high heat flux components, introduction of commercially available tungsten alloys developed so far, and the purpose of this study.

Chapter 2 reviews two studies that are very useful to propose an improved fabrication method to achieve the purpose of this study. When tungsten alloys with fine grains and finely dispersed particles of transition metal carbide (TMC) were prepared by MA, hot isostatic pressing (HIP) and hot forging and rolling, some of the alloys, in particular W-0.2wt%TiC alloy, exhibited much better low temperature toughness and much higher recrystallization temperature than commercially available pure W. On the other hand, there remain three problems that may limit the improvement in the resistance. One is the frequent occurrence of insufficiently densified bodies, with relative density of 92.5 ~ 97% at the as-HIPed condition. The second is the occurrence of coarse W_2C precipitates that are very brittle and promote embrittlement by acting as crack initiators. The third is difficulty in plastic working, i.e., hot forging and hot rolling to the required level for ductility improvement. The causes of each problem are discussed.

Chapter 3 presents the methods to solve the above three problems. To produce consolidated bodies with higher relative density than 98%, the MA atmosphere was changed from purified argon to purified H_2 and the sintering process from HIP to vacuum hot pressing (VHP) with additional HIP. To suppress the precipitation of coarse, brittle W_2C, the determination of added amounts of TMC was made based on the W-M(= Ti, Ta)-C ternary phase diagram. For successful plastic working to the required level, the sintered consolidates were placed in a crucible made of pure Mo to alleviate relatively rapid decrease in specimen temperature during hot working. As a result, the author has obtained densified consolidates with higher relative density than 98 % by VHP-HIP at temperatures from 2123 to 2323 K for 1hr without W_2C precipitates detectectable by X-ray diffraction and has been able to conduct hot forging and rolling at around 1770 K to approximately 1 mm thick for W-Ti, W-Ti-C, W-TiC, W-TiC-Ti and W-Ta-C alloys.

Chapter 4 presents the low temperature toughness, recrystallization properties and microstructures for the TMC dispersed alloys shown in Chapter 3. Evaluation of the ductile-to-brittle transition temperature (DBTT) was performed by 3-point impact bending tests at 5 m/s for miniaturized flat sheet specimens (1 x 1 x 20 mm). As a result, the as-rolled specimens of the developed alloys showed appreciable plastic deformation at lower temperature than previously developed W-0.2%TiC and commercially available pure W. In particular, TI025-C05 showed plastic deformation even at a temperature as low as 237 K. This occurrence of ductility in impact testing below room temperature is the first to observe for tungsten and its alloys. The DBTT, defined as the temperature at the absorbed energy corresponding to 1/2 of the upper shelf energy (USE), was 260K for TI025-C05, 330K for TIC015-TI018-1 and 350 K for TIC03-2 and TIC015-TI018-2, whereas the DBTTs for W-0.2%TiC and pure W were 440 K and 560 K, respectively. Therefore, the developed alloys have excellent low temperature toughness compared with W-0.2%TiC and pure W. Since these alloys showed good low-temperature ductility, static tensile tests were performed at temperatures from 173 to 473 K at the initial strain rate of 10^{-3} s^{-1} for sheet specimens (1.2 x 0.5 x 5 mm). The result showed that TI025-C05 exhibits appreciable plastic deformation at 263 K. However, the other developed alloys showed plastic deformation at higher temperatures than pure W, in spite of fabricating by almost the same processes as TI025-C05.

The obtained recrystallization property showed that the developed alloys have lower recrystallization temperatures than W-0.2%TiC. In particular, TI025-C05 and TIC015-TI018 started recrystallization at a temperature as low as approximately 1500 K. This is attributable to remarkable loss of carbon, which is a constituent of transition metal carbides to prevent grain growth. However, TIC03-2 containing 380-wppm carbon, which is larger than those of TI025-C05 and TIC015-TI018 alloys, showed a recrystallization temperature of 1800 K, which is still lower than that of W-0.2%TiC. SEM observation of etched microstructures of fully recrystallized TIC03-2 showed that there is significant heterogeneity in grain size and particle distributions.

The above results show that there are considerable differences in ductility and recrystallization temperatures among the developed alloys. It is pointed out that the differences are attributable mainly to three microstructural factors; (1) precipitation of very fine brittle W_2C that is undetectable by XRD, (2) heterogeneity in grain size and particle distributions and (3) loss of carbon which is a constituent of transition metal carbides.

Chapter 5 presents a fabrication process to eliminate the detrimental effects of the three microstructural factors shown in Chapter 4.

W_2C was found to form during sintering by the reaction of W with WC impurity contaminated from the pots and balls made of WC/Co used for MA. The contamination of WC/Co was inevitable even by the optimization of MA conditions. In addition, Co is a highly radioactive element after neutron irradiation and must be eliminated. Therefore, the author decided to develop new pots and balls made of Mo and its alloys. Because Mo and in belongs to the same group VIa, in the periodic table, and Mo_2C, may be less harmful and has a lower free energy for formation than W_2C. The effects of Mo addition on the microstructural evolution, relative density and Vickers microhardness for W-0.3wt%TiC were studied. Finally, a Mo alloy, TZN (Mo-0.5%TiC-0.1%Zr) was chosen as the material of new pots and balls for MA.

Heterogeneities in grain and particle size distributions come from a MA process with use of a planetary ball mill. The MA process often resulted in a mixture of powders having less, different degrees of MA, leading to sintered compacts with heterogeneity in grain and particle size distributions. To obtain MA powders without such heterogeneity, a 3MPDA (three mutually perpendicular directions agitative) ball mill was newly developed. In the MA process using this equipment, the optimization was made so as to meet three requirements: (1) to reach the final stage of MA, (2) to collect a sufficient amount of mechanically alloyed powder, and (3) to suppress contamination with TZM coming from the milling pots and balls during MA. For the optimization of the milling parameters, the weight ratio of balls to powder, pot agitation speed and milling time were examined.

Significant loss of carbon was confirmed as the result of decarburization during VHP. Since the MA treated powder contained an appreciable amount of oxygen as an impurity, 1000~2000 wppm, carbon reacted with the impurity oxygen during VHP above 1723K for 3.6 ks and was lost as CO gas, of which free energy for formation decreases significantly with increasing temperature. In order to suppress decarburization, HIP should be conducted with metal capsulation of the MA powder. First, Ta was selected as the capsulation metal. However, HIP using a Ta capsule often led to insufficient densification of the compacts with a relative density between 92 and 97 %, which stems from insufficient outgassing from the MA powder and cracking of the capsule. The sealing of the MA powder within a Ta capsule requires electron beam welding, which is conducted at room temperature in a vacuum and is not suitable for outgassing. Nitrogen or oxygen during the welding causes significant hardening and embrittlement of Ta, resulting in no further densification. Therefore, the author has proposed the following process in order to achieve nearly full densification by HIP: At first HIP with a mild steel capsule that allows sufficient outgassing from the MA treated powder is performed at 1623K ($0.44T_m$, where T_m is the melting point of W). Then, the sintered compact taken from the metal capsule and covered with Ta foil is subjected to a further HIP process at 2223K (0.60Tm) in an Ar atmosphere.

Chapter 6 presents the low temperature toughness and recrystallization properties of the TiC dispersed W alloys developed in Chapter 5.

For the as-HIPed, as-forged and as-rolled specimens of TIC03-3 ~ TIC03-6, static 3-point bending tests were performed respectively at room temperature. The as-HIPed specimen showed the fracture strength of 1~1.3 GPa. The fracture strength significantly increased by hot forging and hot rolling and exceeded its yield stress. The fracture strength and ductility of the as-rolled specimens increased to higher than those of the-forged specimens. The fracture strength of the as-rolled TIC03-5 was 3 GPa and the total plastic strain to fracture was 1.3%. On the other hand, the fracture strength of TIC03-6 with larger grain size than TIC03-4 and TIC03-5 did not exceed its yield stress. This result shows that increase in fracture strength by plastic working after sintering depends on the grain size.

Recrystallization temperatures of most of the developed alloys were around 2073K, while that of TIC03-5 was almost the same as that of W-0.2%TiC, around 2273K.

Chapter 7 describes that the problems and the fabrication processes stated above are applicable not only to tungsten but also to other materials. The solutions of the problems shown in the previous chapters are achieved by controlling the dispersed particle, i.e., controlling nature, distribution, density and size of the particles, which is essential to the microstructural control for material development. The proposed fabrication process enables such control of the dispersed particles. Chapter 8 is the conclusion.

In this work, the author has found the following problems that must be overcome to develop TMC dispersed W alloys with improved resistances to low temperature embrittlement and recrystallization embrittlement. The problems are (1) frequent occurrence of insufficiently densified bodies with relative density of 92.5 ~ 99.2% in the as-HIPed condition, (2) precipitation of a coarse, brittle W_2C phase that may act as crack initiators, (3) difficulty in plastic working, i.e., hot forging and hot rolling to the required level, (4) loss of carbon which is a constituent of transition metal carbides, during sintering of VHP, and (5) heterogeneity in grain size and particle distributions. The author has shown a process to overcome all of the problems. The W alloys developed by applying the process exhibited good low temperature toughness and higher recrystallization temperatures.

論文審査結果の要旨

タングステン（W）は熱的特性や低トリチウム吸蔵特性を初めとして優れた多くの特性をもつことから核融合炉高熱流束機器用材料としての使用が検討されているが、脆いという大きな問題（低温脆化、再結晶脆化、照射脆化）がありその改善が必要である。これらの改善のためには、メカニカルアロイング法を中心とする粉末冶金法により、微細結晶粒・遷移金属炭化物（ＴＭＣ）ナノ粒子分散組織を導入することが最も有効であると考えられる。しかしながら、そのような組織の導入によるＷの高靭性化に関する研究は極めて少なく、Ｗの脆さはあまり改善されていない。そこで、論文提出者は、脆さの中の低温脆化と再結晶脆化の改善に的を絞り、それらの改善を可能とする組織制御法の確立を目的として研究を行っている。

主論文の第1章では、本研究の背景と目的について述べている。第2章では、微細結晶粒・TMC粒子分散組織導入によるＷの高靭性化に関する研究をレビューし、脆さの改善のためには解決すべき3つの課題があることをことを指摘している。第3章では、それらの3つの課題を検討してそれぞれの解決方法を述べ、実験によりそれらの方法が有効であることを示している。第4章では、その方法により試作したＷ合金について低温靭性と再結晶特性を評価し、263Ｋでの衝撃試験により延性を示すような極めて低温靭性に優れる合金が得られたこと、しかし試作合金間における低温靭性や再結晶特性のばらつきが少なくないことを示すとともに、それらを解決するための新たな課題を述べている。第5章では、新たな課題を解決するための製造プロセスを提案し、実際にその製造プロセスにより微細結晶粒・ＴｉＣナノ粒子分散Ｗ合金を試作して提案した製造プロセスの有効性を実証している。第6章では、試作した微細結晶粒・ＴｉＣナノ粒子分散Ｗ合金について低温靭性と再結晶特性を評価し、合金間のばらつきが少なく、低温靭性と再結晶特性に優れるＷ合金が得られたことを述べている。第7章では、第5章までに示された課題とこの製造プロセスの学理的側面に触れ、本方法がＷのみならず多くの材料の開発にとって有効であると考えられることを示すとともに、本方法の材料開発における一般的なことを総括している。第8章は結論である。

以上要するに、本論文は、Ｗの最大の課題である脆さを改善するための組織制御法を確立することを目的として、微細結晶粒・遷移金属炭化物ナノ粒子分散組織導入によるＷ高靭性化のための製造プロセスを示すとともに、その製造プロセスが多くの材料開発にとって有効であると考えられることを示したものであり、その意義は少なくない。

よって、本論文は、博士（工学）の学位論文として合格と認める。