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学位論文題目 **Effects of Solute Interactions on Mechanical Properties of Vanadium Alloys Developed for Fusion Reactors**

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論文内容の要旨

Fossil fuels will be depleted if people continue to burn them for energy, and an energy shortfall would appear in less than fifty years. People are looking for innovative energies to meet the demand. The most attractive but challenging one is to make nuclear fusion work on earth. If this is successful, we will have a clean energy source that is inexhaustible owing to the abundant fuel in seawater. One of the promising approaches to fusion is the magnetic confinement concept. A dozen of Tokamak devices have been built around the world. DT plasmas are confined in the torus vessels by magnetic field. When the plasmas are heated up to over 100 million degree with high density and long holding time, fusion reaction will take place. A breakeven condition for energy in and out has been almost achieved by Tokamak devices and the experiments are approaching to an ignition. ITER will be constructed with an expectation of 10 times more energy produced than used for heating the plasma.

It is a great challenge to make fusion a commercial reality. The size, the cost and the complexity of the reactor must be reduced. A safe and efficient tritium handling technique must be developed. Development of fusion reactor materials is also a great concern. The materials must be able to survive high heat flux, retain strength and ductility despite neutron irradiation and have a low activation property. In terms of the applications in a fusion reactor, major fusion reactor materials are classified into plasma facing materials (PFM) and structural materials for vacuum vessel and blanket. Many candidate structural materials have been studied with the high potentiality of ferritic/martensitic (F/M) steel, vanadium alloy and SiC/SiC composite for near, middle and long term applications. In spite of less experience in large-scale application, vanadium alloy has many advantages over F/M steel, such as lower radioactivity, higher thermal load capability and stronger resistance to neutron irradiation. V-4Cr-4Ti is referred as the leading one for fusion application because of its quite low DBTT and acceptable high temperature strength.

There remain a number of critical issues to be solved for vanadium alloys despite their good properties. One of the issues is the effect of interstitial O, C and N impurities and their precipitates on mechanical properties. Although there were studies showing their effects on recovery, recrystallization, precipitation hardening, high temperature tensile and creep strength, the influence of substitutional solutes were scarcely studied. DSA (dynamic strain aging) caused by the impurities is known to be strongly affected by Ti. But the studies on the effect of Cr were rarely reported. Precipitation is generally not welcome in high temperature service for the purpose of keeping a good thermal stability of microstructure and mechanical strength. Thus small effort has been made on the feasibility to utilize the precipitation for enhancing the strength of vanadium alloy structures. Effect of alloying elements on precipitation needs to be studied further.

The objective of the present study is to clarify the effects of interstitial and substitutional solutes on mechanical properties of low activation vanadium alloys. Emphases were placed on the mechanisms of hardening by C, N and O, effects of Ti on the role of these interstitial solutes, role of Cr on the interaction of Ti with C, N and O. The role of substitutional solute of W, which is a potential alternative to Cr, was also investigated. The study was oriented to supporting to optimize chemical compositions and processing steps of vanadium alloys and the impurity control during the use in the blanket structure.

In the present study, many sorts of V-based alloys, designed according to phase diagram and neutron induced activity, were developed in laboratory, including some new alloys with addition of W. The alloys were V-4Ti, V-4Cr-4Ti, V-4Ti-3Al, V-3Ti-1Al-Si, V-8W, V-7W-0.3Al, V-6W-(1-4)Ti and so forth. Alloys were melted in a magnetic floating furnace, forged at ~950-1150°C and hot rolled at 400-850°C in air with surface protection, and cold rolled to 0.5-1 mm thick plate finally. 50%CW (defined as thickness reduction by cold rolling) plates were used to study their recovery and recrystallization behavior by isochronal annealing at 200-1100°C for 1h. The solid solution hardening by the alloying elements was investigated from the hardness data of the 1100°C-annealed samples. Some complete recrystallized alloys were tensile-tested at

400-800°C in vacuum to study DSA and the role of alloying elements. To clarify precipitation hardening, alloy plates in solid solution state were again isochronally annealed at 200-1100°C for 1h. An aging was then conducted at 600°C for 1-393 hrs to learn the time dependence of the hardening. Following the aging, samples were further annealed at 200-1100°C for 1h to study the thermal stability of the hardening. For all cases, hardness test was performed at room temperature (RT). TEM (Transmission Electron Microscope) and SEM (Scanning Electron Microscope) were used to analyze microstructures and fracture features.

Results showed that all alloying elements concerned and interstitial solutes of C, N and O are strong solid solution strengtheners. The hardening coefficient of the interstitial solutes is much higher than that of the substitutional solutes of Cr, Ti and W being about 9.55, 8.92 and 7.13Hv/%mass at room temperature, respectively. Cr contributed more to the solid solution hardening than Ti. Considering the much bigger atomic weight of W, W should be the strongest species per atom to strengthen the alloy among the substitutional atoms.

The alloys with many previously formed large precipitates showed weak or no precipitation in the following annealing. Notable precipitation occurred at 600~800°C for Ti-bearing alloys in solid solution annealing state. The annealing at 600~700°C produced high number density of fine precipitates of Ti-CON, which hardened the alloy significantly. Peak hardening occurred at 700°C for V-4Cr-4Ti but 600°C for V-6W-4Ti in the isochronally annealing for 1 hr. The hardening of V-4Cr-4Ti was more prominent than V-6W-4Ti alloy by aging at 600°C, indicating Cr contributes also to precipitation hardening. For Ti in the range of 1-4% in mass, it hardly showed any effect on the hardening behavior of the alloys without Cr. The growth of the precipitates is controlled by Ti diffusion, thus Cr is presumed to slow down Ti diffusion due to the strong interaction of Cr and Ti. The precipitation hardening is stable at <500°C, since Ti is relatively immobile below the temperature. The aging hardening showed a slight effect on ductility of V-4Cr-4Ti and at certain aging condition even increased its static fracture toughness, defined as the absorbed energy during tensile test. So the precipitation hardening may be used to attain high strength vanadium alloys.

Alloying elements studied in the present study showed little effect on the annealing temperature for complete recrystallization. However, the starting temperature for notable hardness recovery of the 50%CW cold-rolled alloys was increased by ~100°C by alloying V with Ti. Besides, unlike V-8W and unalloyed V, the Ti-bearing alloys showed no additional hardening at ~300°C. Interstitial C, N and O impurities in matrix also showed a certain effect on the recovery behavior. More C, N and O in matrix led to less hardness recovery and even additional hardening around 600°C for the alloys with 4%Ti in mass. All these behaviors seem to be resulted from both the resistance of the interstitials to dislocation motion and the role of Ti reducing the mobility of the interstitials.

During the tensile tests at 400-700°C in certain strain rate range, interstitial impurities moved to interact with dislocations and caused DSA for V-Ti alloys. As a result, load-displacement serrations occurred and the strength of the alloy increased. The strongest serrations appeared at ~300°C for unalloyed V. Due to the role of Ti decreasing the mobility of interstitial impurities, the temperature for the strongest serrations shifted to ~600°C for both V-6W-4Ti and V-4Cr-4Ti. Tensile strength started to increase at ~400°C with increasing temperature for both alloys, but the V-4Cr-4Ti alloy showed better mechanical performance than V-6W-4Ti at higher than 600°C. The tensile strength of V-6W-4Ti began to decrease above 600°C while that of the V-4Cr-4Ti continued to increase till 700°C. Their different precipitation-hardening behaviors give evidence that Ti and interstitial impurities in V-4Cr-4Ti are less mobile than those in V-6W-4Ti, probably caused by the interaction of Cr and Ti. This should account for the difference in high temperature mechanical performance of V-4Cr-4Ti and V-6W-4Ti.

The conclusions of the present study are as follows.

- (1) The effect of solutes and solute interactions on mechanical properties of vanadium alloys was significant.

All of the solutes concerned were solid solution strengtheners. The hardening coefficient of the

interstitial solutes was much higher than that of the substitutional solutes.

- (2) Ti and the interstitial C, N and O were necessary and were responsible for higher high-temperature strength and keeping the cold-rolling hardening at elevated temperature. Additionally they were the cause of precipitation, and the resulting hardening could be utilized for enhancing strength of the vanadium alloy for relatively low temperature application. For these properties, Cr also provided large positive contribution by its effect to reduce the mobility of Ti due to their interactions.
- (3) All these results showed interactive role of interstitial and substitutional solutes on mechanical properties of vanadium alloys through solid solution hardening, mutual binding or trapping, interaction with dislocations, precipitation and precipitate resolution.

論文の審査結果の要旨

Jiming CHEN 氏の論文は、核融合炉候補バナジウム合金 (V-4Cr-4Ti) の強度特性の一層の向上を目標とし、強度特性に及ぼす格子間不純物 C, N, O の役割、候補材の合金元素である Ti, Cr の役割、及びこれらの相互作用の効果を明らかにする研究を行ったものである。系統的な実験によって得られた一連の成果に基づき、新しい知見と将来の開発指針がまとめられており、博士論文として価値のあるものと判断した。

本研究では、まず、合金元素である Ti, Cr の濃度を変えた一連のバナジウムモデル合金を製作した。製作に当たっては、浮遊溶解法における合金化、成型加工、熱処理の各段階での酸素不純物の混入過程を明らかにし、熱間圧延時に酸化防止被覆を施すことにより、低酸素濃度の合金作製を可能とした。これらの合金について、加工熱処理条件をパラメータとして硬度測定、引張り試験、破壊試験、組織観察等を行った。その結果、C, N, O は固溶により強度を著しく向上させること、高温では C, N, O は Ti と反応し Ti-CON 析出を形成することにより強度を保つこと、Cr の存在環境では Ti の移動度が下がり、その結果 Ti-CON 析出がより高温まで微細かつ高密度に保たれ、強度を維持すること、Ti の移動度の低下は、高温における加工組織の回復と結晶粒の粗大化を抑制する効果もあること、などが明らかになった。Cr の代わりに固溶硬化がさらに大きい W を添加した合金においては、Ti の移動度を下げる効果が小さく、高温では Ti の析出の粗大化により強度低下が起こることが分かった。また、引張り変形挙動の解析から、固溶 C, N, O と移動転位との動的相互作用 (DSA) の強度、温度範囲、およびそれらに及ぼす合金元素、熱処理条件の効果を明らかにした。

本研究ではさらに、適切な量の析出硬化を起こさせることにより、延性や靱性を損ねることなく V-4Cr-4Ti の高温強度を向上させることができることを示した。適切な密度とサイズの析出は、破壊を促進することなく、移動転位をピン止めすることにより強度を高めることができる。この条件は、不純物の挙動、析出の形成・成長、および析出と転位の相互作用の基礎的な知見により得られたものである。この方法は、広範に利用できるバナジウム合金の強化法として有望である。

本研究以前にもバナジウム合金の C, N, O の効果、および Ti 添加効果の研究は行われていたが、Cr まで含めた溶質元素全体の相互関係を明らかにしたのは今までに無い新しい研究成果である。現在の候補材 V-4Cr-4Ti の特性発現の機構を説明するとともに、さらなる特性向上に向けた指針を与えた点は高く評価される。また、論文にはエネルギー問題、核融合炉の役割と開発課題、核融合炉材料の開発戦略などについて分かりやすく説明しており、研究の背景に関して深い理解を有していることが分かった。

以上の通り本論文では、核融合炉候補バナジウム合金 (V-4Cr-4Ti) の強度特性を支配する因子として、C, N, O 不純物と Ti の相互作用、および Ti と Cr の相互作用の重要性を明らかにするとともに、新しい知見に基づいて、微細析出分散による強度特性の向上指針を明らかにしたもので、核融合炉材料の研究開発に大きく寄与するものである。以上より、本論文は博士論文として充分価値があるとの結論に達した。