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1. Introduction

A vanadium alloy, V-4Cr-4Ti, is a primary candidate material for fusion reactor structural applications because of its inherently low-induced radioactivity, large thermal stress factor and high fracture toughness before high energy particle irradiation. In order to make the alloy more attractive, it is necessary to improve both the resistance to embrittlement by irradiation and the strength at high temperatures. The resistance to radiation embrittlement and high-temperature strength are structure-sensitive properties and may be improved by introducing microstructures of fine grains and finely dispersed, thermally stable particles.

It is known that vanadium has a good ductility, but is very chemically active with gaseous interstitial impurities such as nitrogen and oxygen. Once vanadium solves the impurities, it causes hardening and loses its ductility significantly. In order to minimize such ductility loss, vanadium and its alloys have been fabricated by melting techniques for purification. In melting techniques, however, the microstructures that one can control are limited; neither fine grains nor extremely finely dispersed particles are available. For this reason, no successful work on the development of vanadium and its alloys with the above microstructure and good ductility has been reported so far.

The powder metallurgy (P/M) method including mechanical alloying (MA) and hot isostatic pressing (HIP) is most useful for microstructure control. It can lead to the production of a variety of microstructures, including the above microstructure of fine grains and finely dispersed, thermally stable particles. However, in order to apply the P/M method to fabricate vanadium and its alloys with good ductility and the target microstructure, there are two issues. One is to make the effects of gaseous impurities such as solute nitrogen and oxygen contained in the starting powders and introduced through the fabrication processes negligibly small and suppress the loss of ductility. The other is to optimize the MA conditions to produce sufficient amount of mechanically alloyed powders with ultra-fine grains and negligible contamination with pots and balls used during MA. In this paper, at first, a process for microstructure control to fabricate vanadium and its alloys with good ductility and the target microstructure is proposed. It is shown that the process with optimized MA condition is very effective in solving the two issues. It is also shown that the developed alloy exhibits improved strength and good ductility at and below room temperatures even in the condition of no plastic working after consolidation by HIP.

The success of fabrication of vanadium alloys with negligible effects of impurities and good mechanical properties even in the condition of no plastic working will enable to develop newly advanced alloys that have not been fabricated because of poor workability. An example is V-Cr alloys with chromium contents higher than 25wt%. V-Cr alloys form a continuous solid solution and it is expected that as the chromium content is increased, the alloys will show more excellent corrosion and oxidation resistances and higher strength by solution hardening. Therefore, in this study V-28wt%Cr and V-52wt%Cr alloys with fine grains and finely dispersed particles of Y_2O_3 and YN are fabricated and the characteristics of the resulting microstructure and mechanical properties of developed alloys are presented.

2. Principle of Microstructure Control

In order to make the effects of solute nitrogen and oxygen in matrix negligibly small and maintain good ductility of vanadium and its alloys, it is necessary to remove solute nitrogen and oxygen from the matrix. The only solution for removal is that all of the solute oxygen and nitrogen are consumed to form finely dispersed oxide and nitride particles stable at high temperatures. For this, it is very effective to use powders of pure vanadium and yttrium as the starting powders because yttrium forms more stable oxides and nitrides than vanadium and Y_2O_3 and YN has good high-temperature stability. A microstructure with fine grains and very finely dispersed yttrium particles is first produced by MA. Then solute oxygen and nitrogen, contained in the starting powders and introduced through the fabrication processes, are consumed as yttrium compounds formed during consolidation and subsequent heat treatments and thus are removed from the matrix. These oxide and nitride particles, in turn, can work to improve the high temperature strength by impeding the movement of dislocations at high temperatures. They can also improve radiation resistance by suppressing radiation damage by providing a large number of sinks for vacancies and interstitials induced during irradiation. However, an excessive density of these particles may have the detrimental effect of decreasing ductility. Therefore, it is also necessary to control of oxygen and nitrogen to the level required to form a suitable amount of finely dispersed particles.

3. Experimental

The starting materials were pure vanadium (particle size: <150μm, oxygen: 0.08wt%, nitrogen: 0.07wt%), pure yttrium (<750μm, 1.56wt%, 0.05wt%) and pure chromium (100~200μm, 0.035wt%, 0.005wt%) powders. They were mixed and subjected to MA with planetary ball mill in a purified argon atmosphere (purity 99.9999%), where pots and balls made of WC/Co were used. In order to optimize MA conditions, effects of several parameters, including volume ratio of vessel to balls, weight ratio of balls to powder, rotational velocity of vessel and milling time, were examined. Hot isostatic pressing (HIP) was conducted at 1273K and 200MPa for 10.8ks in an argon atmosphere. In view of the result of chemical analysis of the hipped compacts the fabricated alloys were designated to as V-2Y, V-28Cr-2Y and V-52Cr-2Y.

The as-hipped compacts were cut into sheets and cold rolled by 50 and 80% for V-2Y and 70% for V-28Cr-2Y to 0.6 mm thick. From the sheets with and without cold rolling, miniaturized tensile specimens with the gauge section of 1.2 x 0.5 x 5 mm were punched out and then reduced to 0.5 mm thick by mechanically polishing with emery paper up to # 2000. The specimens were wrapped with Zr foil and annealed at temperatures from 1273 to 1673K for 3.6ks in a vacuum of better than 5×10^{-5} Pa. The impurity content of tungsten coming from the milling pots and balls used during MA is suppressed to be 0.026 ~ 0.27wt%. Assuming that all of oxygen and nitrogen determined by chemical analysis are consumed to form yttrium compounds, the volume fractions of Y_2O_3 and YN are 1.0 and 0.7 % for V-2Y, 0.7 and 0.5% for V-28Cr-2Y and 0.7 and 0.3% for V-52Cr-2Y, respectively.

Vickers microhardness measurements were conducted at room temperature with loads of 1.96 N for 20 s. Tensile tests were performed at 77 K to room temperature at an initial strain rates from 1×10^{-3} s^{-1} to 10 s^{-1} and at 873 to 1273K at initial strain rates from 1×10^{-5} to 1×10^{-2} s^{-1}. The fracture surfaces of tensile-tested specimens were examined by scanning electron microscopy (SEM). Microstructure examinations were made by optical microscopy (OM) and transmission electron microscopy (TEM) with JEM-2000FX operating at 200 kV in the Oarai Branch of IMR at Tohoku University. X-ray diffraction analysis was made to identify the dispersed compound particles with a voltage of 30 kV and an amperage of 250mA.

4. Results and Discussion

4.1 Removal of solute oxygen and nitrogen from the matrix

Since oxygen and nitrogen in vanadium cause a significant solution hardening, the degree of removal of solute oxygen and nitrogen from the matrix is estimated by the hardness of matrix regions free from dispersed particles and grain boundaries. For this estimate, a V-2Y-A alloy having scattered coarse grains surrounded by fine-grained regions was specially prepared because such coarse grains contained only a few particles and are large enough to measure Vickers

microhardness. The result of the hardness test for coarse grains showed that the hardness is slightly lower than that for pure vanadium containing only 24wppm oxygen and 1 wppm nitrogen. This result may indicate that solute oxygen and nitrogen were effectively removed from the matrix. As a result, the developed alloys showed a good ductility even at room temperature as shown in section 4.3.

4.2 Microstructure of the developed alloys

From X-ray diffraction analyses, it was found that in the as-hipped condition V-2Y, V-28Cr-2Y and V-52Cr-2Y alloys surely include Y_2O_3 and YN as dispersed particles.

TEM observation revealed that the developed alloys have very fine grains of approximately 330nm in size for V-2Y and 270nm for V-28Cr-2Y alloys and extremely fine particles of 7nm in diameter for V-2Y and V-28Cr-2Y alloys. These results indicate that the target microstructure of fine-grained and finely dispersed, thermally stable particles were achieved in the developed alloys.

As the annealing temperature increased, the grain size and particle size increased for all the developed alloys, but their increase was not very significant. No significant difference in particle growth between the alloys was observed, whereas the grain growth was dependent of the alloys and increased in the order of V-52Cr-2Y, V-28Cr-2Y and V-2Y, which corresponds to the increasing order of volume fraction of dispersed particles. For V-2Y having the largest volume fraction of Y_2O_3 and YN the increase in grain size stayed in the small range from 330 to 750nm. This indicates that the dispersed particles of Y_2O_3 and YN have a large effect of pinning grain boundaries and determine the grain size of the alloys.

4.3 Tensile properties at and below room temperature

It should be noted that all of the developed alloys, without plastic working after HIP, exhibit very high strength and good ductility and the strength and ductility are widely controlled only by the post HIP annealing. For example, for V-28Cr-2Y the annealing from 1273 to 1673K varied the yield stress from 860 to 400MPa, the total elongation from 14 to 26 % and the uniform elongation from 6 to 16%. The success in the development of vanadium alloys with such good room-temperature tensile properties and the above microstructure is the first time.

It was found that among the observed wide tensile properties, the optimum combination of strength, ductility and work hardening capability of the alloys was obtained by the annealing at 1373K for V-2Y, 1473K for V-28Cr-2Y and 1673K for V-52Cr-2Y. The effect of cold rolling on the tensile properties was not very significant for all of the developed alloys although the cold rolling had the effect of slightly increasing the reduction of area (RA) to fracture. The room temperature tensile properties of the developed alloys are listed in table 1 together with the data on V-4Cr-Ti fabricated by NIFS (NIFS-Heat 1).

Table 1 Room temperature tensile properties for the developed alloys and V-4Cr-4Ti.

Alloy	V-2Y	V-28Cr-2Y	V-52Cr-2Y	V-4Cr-4Ti
Yield Stress (MPa)	610	590	610	300
Ultimate Tensile Stress (MPa)	680	720	800	410
Total Elongation (%)	19	25	19	32
Uniform Elongation (%)	9	14	16	20

Examination of the cause of such high room-temperature strengths showed that grain boundary strengthening and solution hardening by Cr are responsible for the high strength.

In the case of V-2Y, such good tensile properties were maintained up to 173K and 10 s^{-1}.

4.4 Tensile properties at high temperatures

It was found that below 1073K the developed alloys show considerably higher strength than V-4Cr-4Ti. However, above 1073K the test temperature and strain rate dependence of yield stress of the developed alloys became more significant than that of V-4Cr-4Ti. From the results of activation energy for the deformation and stress exponent of plastic strain rate, the mechanism controlling the deformation of each alloy was identified.

In addition, the decrease of ductility occurred around 973K and 1173K, respectively. The ductility loss was attributable to the effect of yttrium particles. Since the yttrium particles resulted from yttrium uncombined with oxygen and nitrogen, the observed ductility decrease can be suppressed by decreasing the content of yttrium addition.

5. Conclusions

1. The proposed fabrication process was very effective in removing solute oxygen and nitrogen from the matrix and thus suppressing the loss of ductility.
2. By applying the process, alloys of V-2Y, V-28Cr-2Y and V-52Cr-2Y with the target microstructure of fine grains and finely dispersed, thermally stable particles of Y_2O_3 and YN and good room-temperature ductility were successfully developed.
3. The developed alloys, without plastic working after HIP, exhibited very high strength and good ductility at room temperature and the strength and ductility were widely controlled only by the post HIP annealing. For V-2Y such good tensile properties were maintained up to 173K at the strain rate of 10 s^{-1}.
4. Grain boundary strengthening and solution hardening by Cr are responsible for the high strength.
5. Below 1073K the developed alloys showed considerably higher strength than V-4Cr-4Ti, however above 1073K the developed alloys showed more significant dependence of yield stress on test temperature and strain rate than V-4Cr-4Ti.
6. For V-28Cr-2Y and V-52Cr-2Y the decrease of ductility occurred around 973K and 1173K, respectively. The ductility loss was attributable to the effect of yttrium particles and can be suppressed by decreasing the content of yttrium addition.

論文審査結果の要旨

核融合炉材料としてのバナジウム（V）合金の課題は、高速中性子照射により生ずる照射脆化の改善と高温強度の向上である。これらの改善・向上のためには、メカニカルアロイング（MA）法を中心とする粉末冶金法により、微細結晶粒・粒子分散組織を導入することが最も有効である。しかしながらVではその極めて化学的に活性な性質により、製造工程時に侵入型ガス不純物が混入・固溶し、それにより著しく脆化するという難点があることから、粉末冶金法による組織制御に成功した例は報告されていない。本論文は、このような不純物による脆化の問題を解決して、微細結晶粒・粒子分散組織をもつVおよびV－Cr合金を試作し、その機械的性質を明らかにしたものであり、全編5章よりなる。

第1章は序論であり、本研究の背景および目的を述べている。

第2章では、目標組織として微細結晶粒・粒子分散組織とともに高純度化された母相を設定し、そのための組織制御の方法と得られた組織が目標通りのものであることを示している。

第3章では、純Vを母相にもつ試作材（イットリウム添加材：V－2Y）の構造材料の最も基本的な引張特性について述べている。試作材は十分な延性をもち、また世界共通試料として広く特性評価が行われているV－4Cr－4Ti合金材に比べて　973K以下では、より高い強度をもつなど優れた性質を有することを示すとともに、その発現機構を明らかにしている。

第4章では、難加工性のために、これまで製造されたことのないV－28Cr、V－52Cr合金に本方法を適用して、試作材を作製した結果を述べている。試作合金の組成と引っ張り特性を調べ、試作合金が室温でV－2Y以上の優れた強度と伸びをもつことを示すとともに、高温での変形挙動とその発現機構を明らかにしている。

第5章は結論である。

以上要するに、本論文は、化学的に極めて活性なVに対して侵入型ガス元素による脆化の問題を解決することにより、核融合炉構造材料としての特性改善に不可欠な微細結晶粒・粒子分散組織の導入に成功するとともに、そのような組織をもつV、V－28CrおよびV－52Cr合金を初めて試作し、その機械的性質と発現機構を明らかにしたものであり、核融合炉材料工学の発展に寄与するところは少なくない。

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。