

A Novel Thermic Process for Producing V-Based Solid Solution Type Hydrogen Storage Alloy *¹

Akio Kawabata¹, Hideo Yoshinaga¹, Makoto Tsukahara², Tetsuo Sakai³,
Seiji Sakurai¹, Yoshihisa Kamiya², Kunio Takahashi², Hiroyuki Takeshita³,
Nobuhiro Kuriyama³ and Jun Shi^{3, *2}

¹Ako Laboratory, Taiyo Koko Co., Ltd., Ako 678-0232, Japan

²IMRA Material R&D Co., Ltd., Kariya 448-0021, Japan

³Osaka National Research Institute, Ikeda 563-8577, Japan

The performance of a high hydrogen capacity alloy, V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta, is sensitively influenced by dissolved aluminum and oxygen, both of which can be removed from vanadium by a refining process, but the process currently used is too expensive. It is necessary to develop a process to remove these impurities at a reasonable cost. We propose a new method for production of the alloy. A V-15%Ni-1.8%Nb precursor with a low enough level of aluminum was produced by alumino-thermic reduction from a mixture of V₂O₅, Nb₂O₅ and nickel. Subsequently, a V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta alloy was obtained by alloying the precursor and the other constituents of titanium, cobalt and tantalum, and by adding mischmetal as a reducing agent to remove oxygen to a low enough level. It was demonstrated that, by the method described here, the vanadium-based alloy could be produced at a reasonable cost.

(Received February 23, 2001; Accepted June 29, 2001)

Keywords: vanadium, solid solution, hydrogen storage alloy, hydrogen absorption, pressure-composition-isotherm, thermic reduction, deoxidization, concentration equilibrium constant, mischmetal, oxygen, aluminum

1. Introduction

It has been proposed that vanadium-based solid solution alloys with a very large hydrogen capacity¹⁾ could have applications in hydrogen storage processes, hydrogen compressors, heat pumps²⁾ and nickel-hydrogen batteries.³⁻⁵⁾ In recent years, these alloys have attracted growing interest from the energy and environmental standpoints.⁶⁾ Though vanadium is often regarded as a rare metal, it is the 22nd most abundant element⁷⁾ and more abundant than copper and nickel in the earth's crust. It is known that Orinoco tar, which is expected to be used as an alternative to crude oil, is rich in vanadium. It is planned to start operation of a large-scale power plant using Orinoco tar as a power source in 2007. Boiler ashes would cause environmental pollution because of the vanadium present, if the ashes were thrown away without removing the vanadium. It is expected that the use of vanadium-based alloys as hydrogen storage materials will be promoted as a means of utilizing the Orinoco tar.

Vanadium metal is mostly produced by alumino-thermic reduction from V₂O₅. However, it contains sufficiently high levels of aluminum^{8,9)} and oxygen^{10,11)} to significantly decrease the hydrogen storage capacity of hydrogen storage alloys made from that vanadium. In order to remove these impurities, electron beam purification¹²⁻¹⁶⁾ is performed, which makes the cost of vanadium very high.¹⁷⁾ Therefore, it is very important to develop a new process to remove these impurities more efficiently. It is expected that the use of vanadium as a hydrogen energy source will be promoted, as well as the Orinoco tar. In this paper, a novel process to produce vanadium metal containing sufficiently low levels of oxygen and aluminum at a reasonable cost is described.

2. Experimental

Throughout this paper, the chemical composition of the specimens examined, the levels of impurities, and the purity of constituent metals are expressed as mass percent.

2.1 Preparation of the V-15%Ni-1.8%Nb precursor by alumino-thermic reduction

The V-15%Ni-1.8%Nb precursor was prepared from a mixture of powders of V₂O₅ (> 99.7%, Taiyo Koko), Nb₂O₅ (> 99.9%, Mitsuwa Chemicals) and nickel (> 99%, Mitsuwa Chemicals) using aluminum powder (> 99.9%, Mitsuwa Chemicals) as a reducing agent, by the following reaction:



The quantity of aluminum was 85%–101%, expressed as the chemical equivalent for reaction (1). For > 101% aluminum, aluminum was left in the precursor to seriously decrease the hydrogen storage capacity of the final alloy. The mixture was put in an Al₂O₃ crucible. Reaction (1) was started by ignition under air at room temperature. Sufficient reaction heat was released to melt the mixture. After cooling the mixture to room temperature, the precursor was separated from the Al₂O₃ slag.

The material was weighed to obtain 2 kg, 10 kg and 50 kg of the V-15%Ni-1.8%Nb precursors by reaction (1).

2.2 Selection of an oxygen reducing agent

The precursor prepared by alumino-thermic reduction contains sufficient oxygen to significantly decrease the hydrogen storage capacity of the final alloy. The oxygen content must

*¹This Paper was Originally Published in J. Japan Inst. Metals **64** (2000) 221–226 in Japanese.

*²Engineer of New Energy and Industrial Technology Development Organization. Present address: Hitachi Maxell Co., Ltd., Ibaraki 567-8567.

be reduced by adding a suitable reducing agent during the alloying process.

For use in tests to select a suitable reducing agent, vanadium preparations containing 0.93% oxygen, instead of the precursor, and other constituents, *i.e.* titanium (> 99.9%, Mitsuwa Chemicals), nickel (> 99%, Mitsuwa Chemicals), niobium (> 99.9%, Mitsuwa Chemicals), cobalt (> 99.9%, Mitsuwa Chemicals) and tantalum (> 99.9%, Mitsuwa Chemicals), were used to prepare V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta.¹⁸⁾

Each of various oxygen reducing agents such as calcium (> 99%, Kojundo Chemical Laboratory), CaNi₅ (> 99.9%, Kojundo Chemical Laboratory), Mg₂Ni (> 99.9%, Kojundo Chemical Laboratory), lanthanum (> 99.9%, Kojundo Chemical Laboratory) and mischmetal (Mm) (> 99%, Kojundo Chemical Laboratory) was added at a concentration of 5% during the alloying process by arc-melting. When CaNi₅ or Mg₂Ni was added as the reducing agent, the nickel contained became a part of the composition of the final alloy. Therefore, nickel quantity to be added was determined considering the nickel amount in the reducing agent. The alloy produced without any reducing agent contained 0.62% oxygen, which significantly decreased the hydrogen storage capacity.

Next, this process was also applied to precursors prepared by thermic reaction (1) at an aluminum ratio of 95% and 97% on a 50 kg reaction scale.

2.3 Analysis

The aluminum in the precursor prepared by thermic reduction was classified into metallic aluminum and oxidized aluminum. The oxygen was classified into dissolved oxygen and aluminated oxide. In this paper, the sum of the oxidized and metallic aluminum was defined as the total aluminum. Oxygen was analyzed by the combustion method. The sample was obtained from the central part of the V-15%Ni-1.8%Nb precursor after being crushed with a jaw crusher and from the V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta alloy after being pulverized by hydrogenation, crushing and subsequent dehydrogenation.

2.3.1 Total aluminum analysis

The sample was crushed in a mortar to obtain a particle diameter of less than 0.5 mm. A mixture of 0.200 g of the sample and 2.0 g of LiB was heated at 1123 K for 1200 s to melt the materials completely. After cooling to room temperature, the materials were dissolved in 10 mL of 12 N HCl. The solution was diluted with water to the mark in a 250-mL flask. In this solution, all of the aluminum in the precursor was dissolved, and the aluminum content *C* (t-Al) was evaluated at a wavelength of $\lambda = 396.2$ nm using an inductively coupled plasma emission spectrophotometer (ICP-AES) (SPS-1500VR Seiko Instruments Inc.).

2.3.2 Metallic aluminum analysis

The sample was crushed in a mortar to obtain a particle diameter of less than 0.5 mm. In a beaker, 0.500 g of the sample was added to a mixture of 10 mL of 18 N H₂SO₄ and 10 mL of 16 N HNO₃, followed by heating on a hotplate until the material solidified. The residue was dissolved in water and the obtained solution was diluted with water to the mark in a 250-mL flask. 25 mL of this solution was placed in a 100-mL

flask and then 2 mL of 18 N H₂SO₄ was added. The solution was diluted with water to the mark, and subsequently it was filtered using a paper filter. In this solution, only metallic aluminum in the precursor was dissolved, and the metallic aluminum content *C* (m-Al) was evaluated at a wavelength of $\lambda = 309.3$ nm using a polarized light Zeeman atomic absorption photometer (Z-6100 Instrument, Hitachi Ltd.).

2.3.3 Oxygen analysis

The sample was crushed in a mortar to obtain a particle diameter in the range of 1–2.8 mm. After the sample had been washed with dilute HCl solution, it was rinsed with running water. Subsequently, it was washed with acetone. The oxygen content *C* (O) was measured using an oxygen and nitrogen simultaneous analyzer (TC-436 LECO), where 0.05 g of the sample in a 0.5-g nickel capsule as a combustion aid was analyzed.

Under these conditions, the aluminum oxide formed was not measured. Therefore, the dissolved oxygen content of the metallic phase was obtained.

2.3.4 Pressure-composition isotherms (PCT curves)

The V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta alloy sample was pulverized to obtain a particle diameter in the range of 0.04–0.1 mm by hydrogenation at high temperature under a high-pressure hydrogen atmosphere. 0.5–1.0 g of the sample was analyzed using a Sieverts-type apparatus as described previously.^{3,19)}

For activation of the sample, the reactor was heated at 673 K for 1800 s under vacuum, followed by introduction of hydrogen (purity > 99.9999%) into the reactor at a pressure of 3.3 MPa and subsequent cooling to room temperature. Just before each run of PCT measurement, the reactor was evacuated at 673 K for 14000 s in order to obtain the hydrogen zero point.

3. Results and Discussion

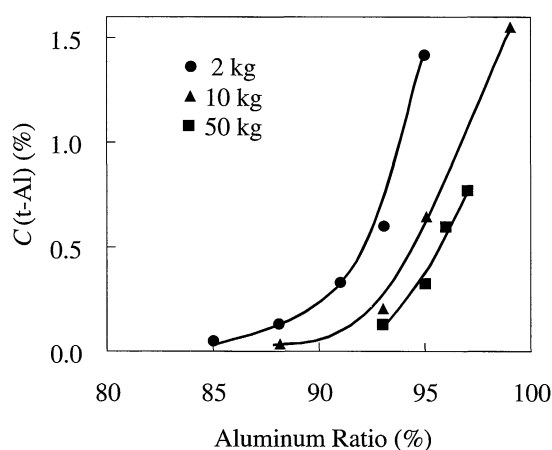
3.1 The V-15%Ni-1.8%Nb precursor prepared by aluminothermic reduction

Table 1 shows the results of analysis of the oxygen, total aluminum and metallic aluminum content of the V-15%Ni-1.8%Nb precursor prepared by thermic reduction. In Fig. 1, the total aluminum content of the precursor is plotted against the ratio of aluminum to the chemical equivalent of thermic reduction (1) for various reaction scales. The total aluminum content was found to increase with increase in the aluminum ratio, especially for an aluminum ratio of > 91% at the 2 kg scale and for an aluminum ratio of > 93% at the 5 kg or 10 kg scale. The total aluminum content was found to decrease with the increase in the reaction scale, and this was attributable to decreased heat loss because of decreasing surface area to alloy volume. As the result of being kept at a high temperature for a long time, the Al₂O₃ slag generated in reaction (1) was effectively separated from the molten precursor.

In Fig. 2, the metallic aluminum content of the precursor is plotted against the ratio of aluminum to the chemical equivalent for thermic reduction (1) for various reaction scales. As shown in Fig. 2, the metallic aluminum content significantly depends on the aluminum ratio but it does not depend on the scale. Therefore, reaction (1) is considered to reach an equilibrium state. The relation of the metallic aluminum, oxygen

Table 1 Oxygen, total aluminum and metallic aluminum content of the precursor prepared by thermic reduction.

Aluminum ratio (%)	Scale	C (O) (%)	C (t-Al) (%)	C (m-Al) (%)
85	2 kg	6.1	0.049	0.017
88		3.8	0.15	0.057
91		2.9	0.33	0.045
93		2.0	0.59	0.014
95		0.96	1.4	0.12
88	10 kg	4.4	0.043	0.025
93		2.2	0.20	0.030
95		1.5	0.67	0.054
99		0.33	1.6	1.0
101		0.18	3.2	2.2
93	50 kg	2.0	0.13	0.052
95		1.0	0.33	0.088
96		0.80	0.60	0.092
97		0.61	0.77	0.26

Fig. 1 Relation between the ratio of aluminum to the chemical equivalent for the thermic reduction at various reaction scales and the total aluminum content $C(t-Al)$.

and Al_2O_3 content is expressed as follows:

$$K = C(m-Al)^2 C(O)^3 / C(Al_2O_3) \quad (2)$$

where K is constant.

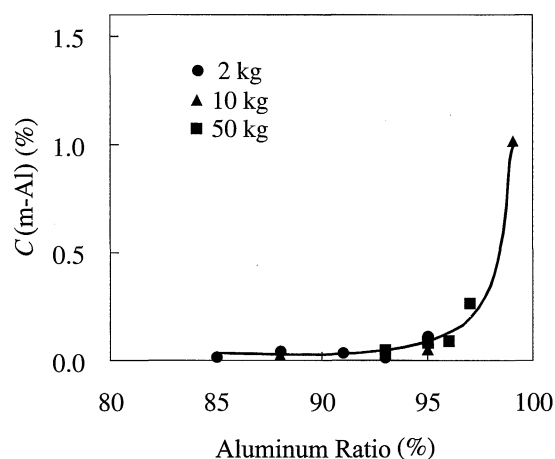
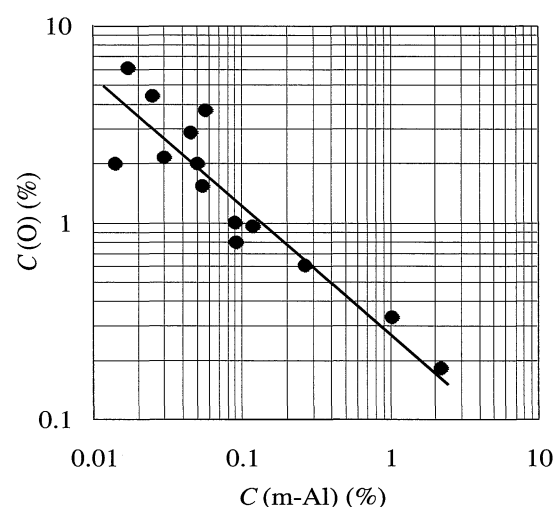
The Al_2O_3 slag was almost separated from the precursor during reaction (1) because of the difference in density between the Al_2O_3 slag and the precursor. However, as listed in Table 1, a small amount of slag remains in the alloy. Because of the low solubility of the Al_2O_3 slag in the precursor, it hardly dissolves in the precursor in the temperature range of the present experiment. Therefore, the apparent equilibrium was described by the metallic aluminum and oxygen content as follows:

$$K' = C(m-Al)^2 C(O)^3 \quad (3)$$

where K' is defined as a deoxidization force constant. Therefore,

$$\log C(O) = -2/3 \log C(m-Al) + 1/3 \log K' \quad (4)$$

Figure 3 shows the relation between $\log C(m-Al)$ and $\log C(O)$. A straight line was obtained for the experimen-

Fig. 2 Relation between the aluminum ratio of aluminum to the chemical equivalent for the thermic reduction and the metallic aluminum content $C(m-Al)$, in the case of thermic reduction at various reaction scales.Fig. 3 Logarithmic plot of the metallic aluminum content $C(m-Al)$ and the oxygen content $C(O)$ of the V-Ni-Nb precursor obtained by the thermic reduction process.

tal data by the least-square method. The slope is very close to $-(2/3)$ of eq. (4). Then, K' was estimated to be 0.026 from the fitting line.

An alloy containing more than 0.5% metallic aluminum shows lower hydrogen storage capacity than an alloy containing less metallic aluminum.

In view of the K' value of 0.026 and eq. (3), it is evident that the oxygen content would be more than 0.5% in order to obtain a precursor containing less than 0.5% metallic aluminum. As a result, the alumino-thermic reduction was found not to reduce simultaneously oxygen and aluminum contents to a sufficient low level. When a precursor with a sufficiently low metallic aluminum content is produced, the precursor contains a high level of oxygen, and it must be deoxidized during the subsequent alloying process.

As shown in Fig. 4, the total aluminum content of the precursor seemed to be inversely proportional to the oxygen content. The total aluminum content and the oxygen content decreased with the increase in the reaction scale. As described in the following subsection, the total aluminum content should be decreased, because a reducing agent added during the sub-

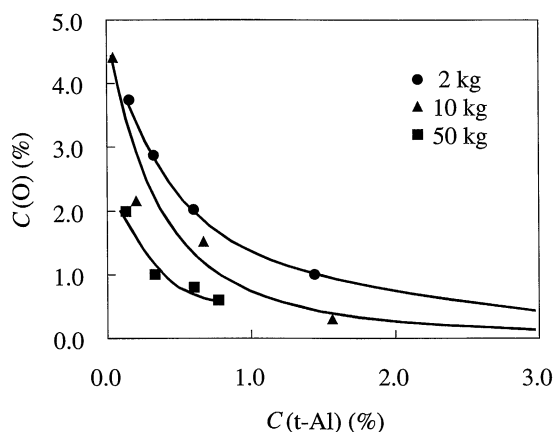


Fig. 4 Relation between the total aluminum content $C(t\text{-Al})$ and the oxygen content $C(O)$ of the V-Ni-Nb precursor obtained by thermic reduction.

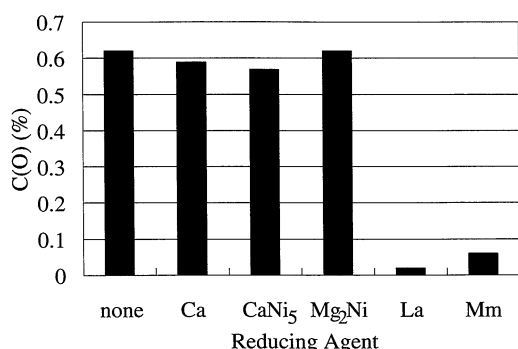


Fig. 5 Change in the oxygen content $C(O)$ observed using various oxygen reducing agents.

sequent process would also reduce Al_2O_3 .

3.2 Selection of an oxygen reducing agent

The V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta alloy was prepared by alloying vanadium containing 0.93% oxygen and other constituent elements by arc-melting. Each reducing agent was added at a concentration of 5% to the alloy during the alloying process. Figure 5 shows the oxygen content of the alloy after the deoxidization step. The oxygen content of the alloy prepared without any reducing agent was 0.62%, which was less than that of the precursor, because of the weight increase by being alloyed with other constituents. By adding calcium, CaNi_5 and Mg_2Ni to the alloy, the oxygen content was not changed as compared to that of the alloy prepared without adding any reducing agent. Calcium, CaNi_5 and Mg_2Ni were considered to evaporate without deoxidization of the alloy, because the boiling points of these compounds are lower than the melting point of the alloy. By adding lanthanum and Mm, the oxygen content was markedly decreased. Mm was chosen in this study as a suitable oxygen reducing agent, because it is less expensive than lanthanum.

The V-15%Ni-1.8%Nb precursor (V Alloy (Lo)) (0.61% oxygen, 0.77% total aluminum, 0.26% metallic aluminum) prepared by thermic reduction at an aluminum ratio of 97% on a 50 kg reaction scale was used to obtain the V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta alloy by alloying the precursor with other constituent el-

Table 2 Oxygen, total aluminum and metallic aluminum content of alloy specimens prepared from the alloy precursor (V Alloy (Lo)) and other constituents, with Mm added as a reducing agent.

Composition	$C(O)$ (%)	$C(t\text{-Al})$ (%)	$C(m\text{-Al})$ (%)
V Alloy (Lo)-16%Ti-0.96%Co-2.8%Ta	0.61	0.77	0.26
V Alloy (Lo)-16%Ti-0.96%Co-2.8%Ta + 11%Mm	0.23	0.73	0.70

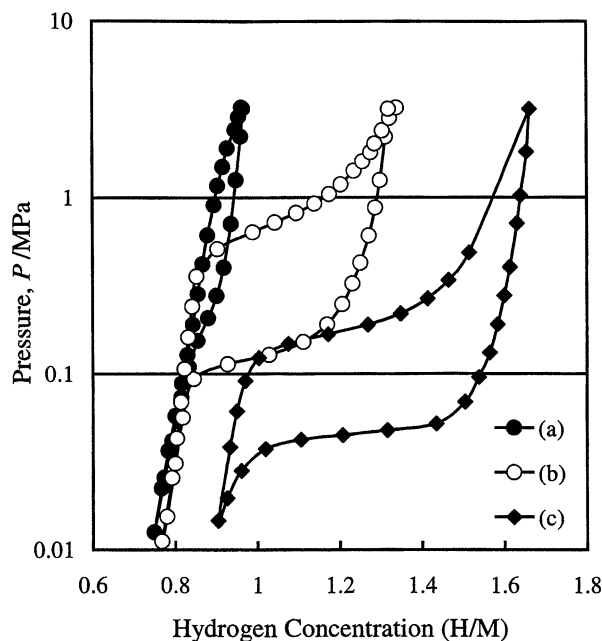


Fig. 6 PCT curves for V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta prepared from V Alloy (Lo) and other constituent metals (a) without and (b) with the Mm reducing agent, as compared with (c) the alloy prepared from high purity metals.

ements and 11% Mm by arc-melting. Table 2 shows the results of analysis of the oxygen, total aluminum and metallic aluminum content of the V Alloy (Lo) and the V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta alloy with/without Mm added. The oxygen content was markedly decreased from 0.61 to 0.23% as a result of adding Mm. The total aluminum content of the alloy obtained was also decreased from 0.77 to 0.73%, because metallic aluminum was partially evaporated during the alloying process. On the other hand, the metallic aluminum content was increased from 0.26 to 0.70% by adding Mm, because Mm reduced the Al_2O_3 slag to metallic aluminum.

Figure 6 shows PCT curves for these alloys. The PCT curve for alloy (a) prepared without adding any reducing agent showed no plateau. The PCT curve for alloy (b) prepared with the Mm reducing agent showed improved features compared with that for alloy (a), because of the decreased oxygen content. However, the PCT curve for alloy (b) showed a significantly narrower plateau than that for alloy (c) (0.23% oxygen) which was prepared from only high purity constituent metals. This is considered to be due to the metallic aluminum in the alloy. Therefore, it was considered to be necessary to decrease the total aluminum in the precursor.

The V-15%Ni-1.8%Nb precursor (V Alloy (Ho)) (1.0%

Table 3 Oxygen, total aluminum and metallic aluminum content of alloy specimens prepared from the alloy precursor (V Alloy(Ho)) and other constituents, with Mm added as a reducing agent.

Composition	C (O) (%)	C (t-Al) (%)	C (m-Al) (%)
V Alloy (Ho)-16%Ti-0.96%Co-2.8%Ta	1.0	0.33	0.088
V Alloy (Ho)-16%Ti-0.96%Co-2.8%Ta + 11%Mm	0.06	0.31	0.25

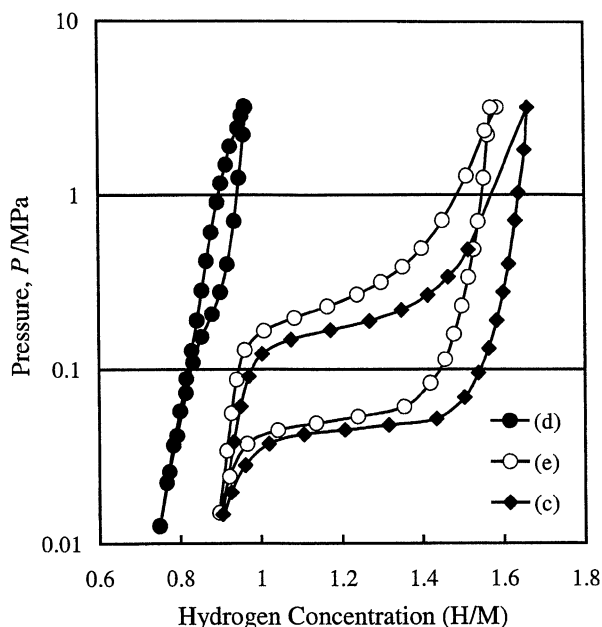


Fig. 7 PCT curves for V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta prepared from V Alloy (Ho) and other constituent metals (d) without and (e) with the Mm reducing agent, as compared with (c) the alloy prepared from high purity metals.

oxygen, 0.33% total aluminum, 0.088% metallic aluminum) prepared by thermic reduction at an aluminum ratio of 95% on a 50 kg reaction scale was used to optimize the process. The V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta alloy was prepared by alloying V Alloy(Ho) and other constituent elements, with/without adding 11% Mm, by arc-melting. Table 3 shows the results of analysis of the oxygen, total aluminum and metallic aluminum content of the V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta alloy. The oxygen content was markedly decreased from 1.0 to 0.06% as a result of adding Mm. The metallic aluminum content was increased from 0.088 to 0.25%. Figure 7 shows PCT curves for these alloys. The PCT curve for alloy (d) prepared without adding any reducing agent showed no plateau. Alloy (e) (0.06% oxygen) prepared with the reducing agent added had a markedly increased hydrogen storage capacity. The hydrogen storage capacity of alloy (e) was similar to that of alloy (c) prepared from high purity constituent metals.

As shown in Fig. 8(a), a high capacity hydrogen storage alloy is conventionally produced by alloying highly purified vanadium, obtained by electron beam melting, and other constituent elements. As shown in Fig. 8(b), an alloy containing sufficiently low levels of aluminum and oxygen can be produced without electron-beam purification. A V-15%Ni-1.8%Nb precursor with a suffi-

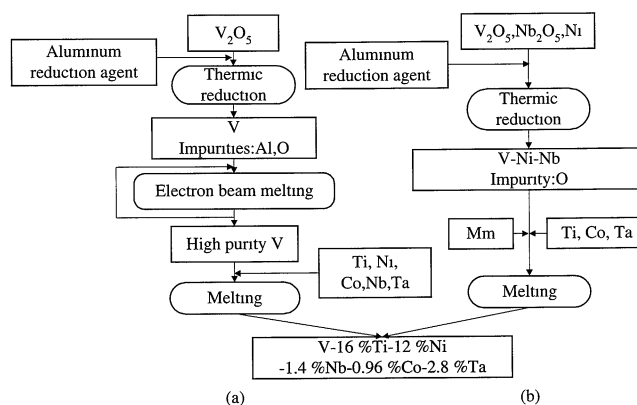


Fig. 8 Flow charts for preparation of V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta by (a) the conventional process and (b) the proposed process.

ciently low level of aluminum was successfully produced by aluminothermic reduction of a mixture of V_2O_5 , Nb_2O_5 and nickel. The V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta alloy obtained by alloying the precursor and the other constituents, *i.e.* titanium, cobalt and tantalum, was deoxidized to a sufficiently low level by adding Mm as a reducing agent. The cost of the alloy produced by the proposed process is estimated to be less than 1/10 of that of the alloy produced by the conventional electron beam purification process.

4. Conclusion

In this paper, an inexpensive process for production of vanadium-based alloys containing sufficiently low levels of aluminum and oxygen is described. First, a V-15%Ni-1.8%Nb precursor with a sufficiently low level of total aluminum (0.33% total aluminum) was produced by aluminothermic reduction of a mixture of V_2O_5 , Nb_2O_5 and nickel. Subsequently, the V-16%Ti-12%Ni-1.4%Nb-0.96%Co-2.8%Ta alloy was obtained by alloying the precursor with the other constituents, *i.e.* titanium, cobalt and tantalum, and the product was deoxidized to attain a sufficiently low level (0.06%) of oxygen by adding Mm as a reducing agent. The hydrogen storage capacity of the alloy prepared by this novel process was similar to that of the alloy prepared from high purity constituent metals.

Acknowledgments

This study was performed as a part of the Original Industrial Technology R&D promotion program of the New Energy and Industrial Technology Development Organization.

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