

Development of Heat Resistant Titanium Alloy for Exhaust Valves Applicable for Motorcycles

Shinji Kasatori and Yuji Marui
Honda R&D Co., Ltd.

Hideto Oyama and Kosuke Ono
Kobe Steel, Ltd.

ABSTRACT

Amidst of the recent concerns on depletion of natural resources, a new heat resistant titanium alloy has been developed using the minimum amount of rare metals. Using Ti-811 as a basis and modifying the alloy composition to Ti-7Al-2Mo-0.2Si-0.15C-0.2Nb, the mechanical property, the creep resistance and the oxidation resistance at high temperatures are improved. At the same time, with the β transformation point shifted to a higher temperature, the hot formability is also improved. The newly developed alloy has made it possible to expand the application of titanium material to exhaust valves in reciprocating engines.

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INTRODUCTION

The key to engine performance improvement is reduction of weight of component parts. The titanium alloy having a high specific strength has been used since long ago in the parts of reciprocating system and valve system in internal combustion engines. Among the parts in the valve system, it is important to reduce the weight of engine valves which have the highest share of the equivalent system weight. Accordingly, titanium alloys have been used positively in intake valves, which are used in a lower temperature environment than that of exhaust valves. In an attempt to increase applications of titanium in intake valves in the past, low-cost titanium valves for motorcycles were developed using recycled scrap materials and/or the off-grade spongy titanium material [1]. Meanwhile the application of titanium to exhaust valves, which are subjected to high temperatures, was limited. One of the reasons is a loss of strength resulting from accelerated oxidation of surfaces when the titanium is subjected to a high temperature. A heat resistant titanium alloy contains various kinds of expensive rare metals (such as molybdenum, zirconium, vanadium) to maintain strength at high temperatures. Accordingly, the near- α structure heat resistant titanium alloy such as Ti-6242S (Ti-6Al-2Sn-4Zr-2Mo-0.1Si) has been employed for exhaust valves.

Furthermore, an application of titanium valves made of titanium-aluminum intermetallic compound is reported as an example of material excelling in the heat resistance and the specific rigidity [2,3]. However, as such a material is very expensive, applications to mass-production vehicles are limited. To extend applications to mass-production vehicles, a low-cost alloy using as less rare metal as

possible is called for. Drawing attention as a general trend is how to make use of titanium "ubiquitous" using inexpensive, abundant elements instead of rare metals [4]. Some examples of alloy development using large Clarke number elements such as Si (Silicon), Al (Aluminum), Fe (Ferrous) or interstitial type elements such as O (Oxygen), H (Hydrogen), N (Nitrogen), C (Carbon) have been introduced [5]. There are causes of high material manufacturing cost other than the addition of rare metal elements. An issue is that scratch and/or cracks tend to occur at the time of hot forging because the strength of near- α structure heat resistant titanium alloy is high at high temperatures.

Developed in this study is the alloy having a hot formability in addition to a high strength, high creep resistance and oxidation resistance at high temperatures necessary for exhaust valves with a minimum use of expensive additives. The low-cost heat resistant titanium alloy having characteristics comparative to Ti-6242S, which is widely applied to racing machines, has thus been developed and applied to mass production. Reported hereafter is the overview of development of the new heat resistant titanium alloy for exhaust valves.

PRINCIPLES OF ALLOY DESIGN

Goals

While the working temperature of intake valve is approx 400°C, that of exhaust valves is approx 700°C or higher. As oxidation of titanium generally accelerates when the temperature exceeds 600°C, it is important to improve oxidation resistance in the temperature zone above 600°C.

Meanwhile in titanium alloys, a hot forming such as the blooming forging, the rolling and the bar rolling is conducted at a temperature below the β -transus temperature when the material is hot to obtain necessary mechanical property. However, as the near- α structure alloy has high strength with superior deformation resistance at high temperatures, scratch and/or cracks tend to occur. Accordingly, the addition of grinding to remove scratch and/or cracks causes loss of material yield rate, resulting in an increase of cost.

This study has started to develop a heat resistant titanium alloy that lasts at a working temperature of 700°C and excels in the hot formability. The following are the goals:

1. Shall have the equivalent mechanical properties and oxidation resistance as Ti-6242S, which is a heat resistant titanium alloy, from the room temperature up to 700°C.
2. The alloy should be designed to maintain hot formability and compatible with the mass production line.

Regarding (1), it was decided to determine the direction of material development using the Ti-8Al-1Mo-1V (hereafter as Ti-811) containing less rare metal among many heat resistant titanium alloys and producible at a low cost as a base alloy. Note that Ti-811 is a heat resistant titanium alloy developed sometime around 1960, and widely used in the compressor blades of aircraft engines, etc. [6].

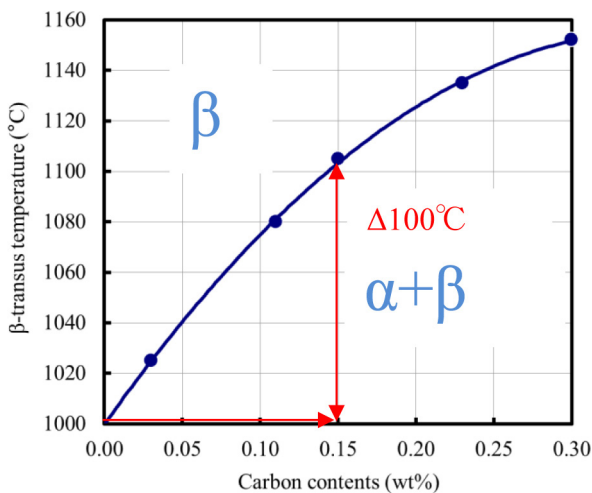


Figure 1. Carbon content vs. β -transus temperature

Regarding (2), attempts were made to ensure producibility by increasing the temperature at the time of hot forming. When the temperature exceeds β -transus temperature in a hot forming, as the crystal grains grow very large, deterioration of mechanical property tends to occur. Therefore, forming should be performed below the β -transus temperature. We have therefore aimed at improvement of hot formability by raising the β -transus temperature using carbon, which is an interstitial type element originally treated as an impurity element. The relationship between the β -transus temperature and the carbon content calculated by thermodynamics analysis is shown in Figure 1. In this calculation, formulation of TiC is not assumed.

Along with an increase of carbon content, the β -transus temperature goes up. However, when the carbon content exceeds 0.2%, the ductility may lower because TiC reduces [7]. Therefore, it was decided to first add carbon by 0.15% to the Ti-811 and analyze oxidation resistance in the working temperatures of exhaust valves. This titanium alloy is hereafter referred to as Ti-811C.

Oxidation Resistance of Ti-811C

To assess oxidation resistance, changes of tensile properties before and after the high temperature exposure were measured. The high temperature exposure conditions were set at 700°C x 20 h for both Ti-811C and Ti-6242S. The measured data are compared in Figure 2. In Ti-6242S, although the elongation and the reduction of area decline after the high temperature exposure, no decrease of tensile strength or lowering of proof stress is obtained. Meanwhile in Ti-811C, lowering is confirmed in tensile strength, elongation and reduction of area. With respect to the proof stress, it was impossible to take measurement after the high temperature exposure because the test piece showed fracture from brittleness. That phenomenon can be considered due to the composition in that the oxygen diffusion advances easier than in Ti-6242S. Accordingly, as another method to assess oxidation resistance, changes of surface hardness relative to the exposure time period were compared. It is because the hardness increases from the material surface to the inside when the oxygen diffusion advances in the base material. We consider that the less changes of surface hardness occur when the oxidation resistance is high and the diffusion of oxygen in the material surface is restricted. Measured changes of surface hardness at each exposure time at 700°C are shown in Figure 3. The surface hardness increases proportionally to the exposure time period. The rate of change of surface hardness of Ti-811C is approximately twice more than those of Ti-6242S, which is an indication of deterioration of oxidation resistance. As the Ti-811C as it was did not show adequate oxidation resistance at 700°C, it was decided to deal with it by changing the alloy composition.

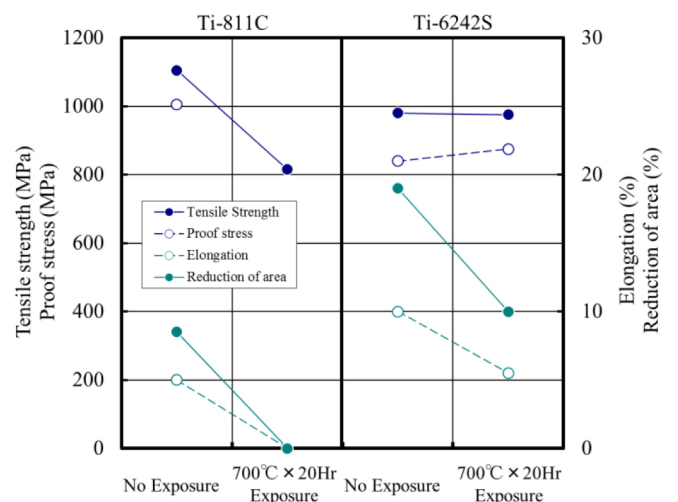


Figure 2. Tensile properties of Ti-811C and Ti-6242S

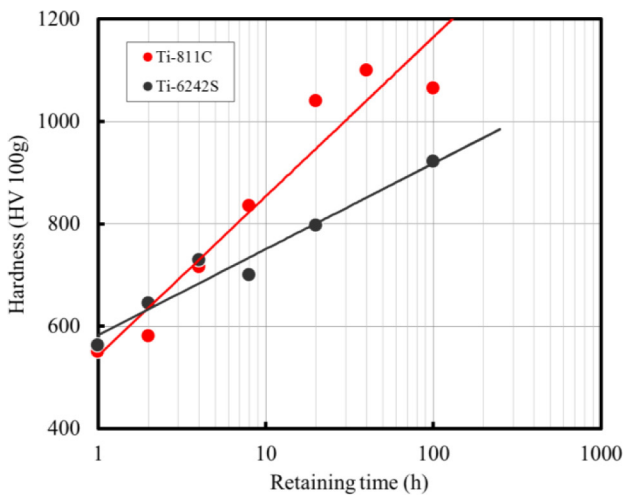


Figure 3. Hardness at 700°C measured at each retaining time

Selection of Additional Elements

Influence of Al Equivalent on Thermal Stability of Titanium Alloy

Aluminum, which is an α -stabilizing element, tin and zirconium which are a neutral element to improve solubility, are generally added in a heat resistant titanium alloy. As these elements form Ti_3Al in high temperatures when large amounts are added, and make the alloy brittle, the additions are limited to the degree indicated by the following equation from experiences [8].

$$[Al]_{eq} = [Al] + 1/3[Sn] + 1/6[Zr] + 10[O] \leq 9 \text{ mass\%}$$

As oxygen is contained in a titanium alloy at a rate of approximately 0.1%, the Al equivalent of Ti-811C is approximately 9%. The brittleness of Ti-811C after the high temperature exposure in Figure 2 may be attributable to the formation of Ti_3Al . Therefore, the amount of aluminum was restricted at 7%.

Effects of Additional Element on Oxidation Resistance

With respect to the lowering of ductility from the high temperature exposure, while the earlier-mentioned formation of Ti_3Al is a concern, the deterioration of material from oxidation can be considered another major cause. For example, compared to Ti-6Al-4V, the increase of weight after the high temperature exposure is less in Ti-5Al-2.5Sn, Ti-7Al-4Mo [9]. The degree of deterioration after the high temperature exposure in Ti-8Al-1Mo-1V-C and Ti-6Al-2Sn-4Zr-2Mo-0.1Si are compared in Figure 2. While the degree of deterioration is higher in Ti-811C, it is supposed that V (vanadium) lowers oxidation resistance because the aluminum content of 5%-8% does not affect significantly to the oxidation resistance taking into account the above-mentioned difference of oxidation between the alloys. Accordingly considering that Mo (molybdenum) was more effective for improvement of oxidation resistance than V, the 1% V in Ti-811C was substituted by Mo to increase Mo, and formulated the basic composition as Ti-7Al-2Mo-C.

As added Nb (niobium) dissolves in TiO_2 as an element having a larger valence (more than 5) than Ti, it is known that the addition of Nb reduces oxygen vacancy, restricts oxygen diffusion, and improves oxidation resistance. It is also reported that addition of a small amount (0.2%) of Nb to the Ti-Al-Si alloy lowers the surface hardness after the high temperature exposure. That is considered due to the formation of dense oxidized scale which restricts penetration of oxygen [10]. Accordingly, Nb was added to Ti-Al-Mo-C alloy and the tensile properties at high temperature were investigated while varying the content of Nb. The effects of added Nb to the tensile properties at 760°C are shown in Figure 4. It has been clarified that the small changes of Nb content do not affect significantly to the strength or elongation at high temperatures.

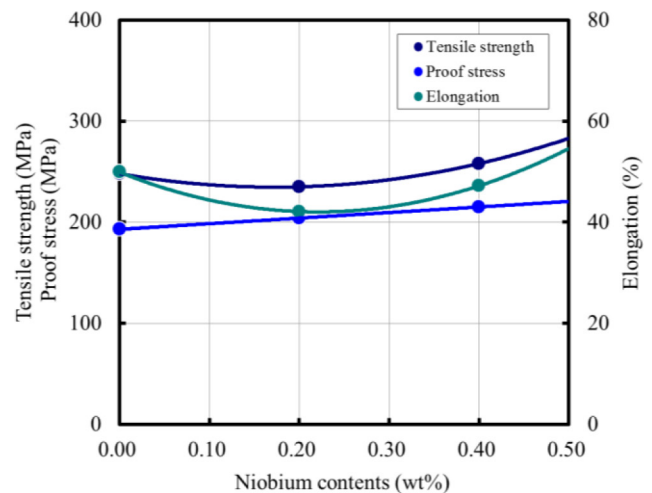


Figure 4. Tensile properties at various Nb contents

The surface hardness with (0.2%) and without Nb after exposure at 700°C is compared in Figure 5. With Nb added, the effect of lowering Vickers hardness by approximately 100-200 points is verified across the entire retaining time period of 1 h-100 h. It can be considered from the said findings that even a small amount of Nb is effective to restrict oxygen diffusion on the base material surface.

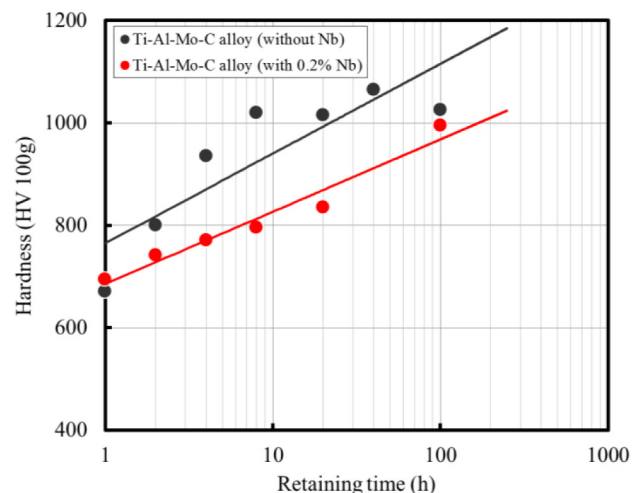


Figure 5. Hardness at 700°C measured at each retaining time