THE EFFECT OF HEAT TREATMENT AND CHROMIUM ADDITION ON
γ-TITANIUM ALUMINIDE RESISTANCE TO HYDROGEN ATTACK

KHAIRMEN SUARDI

A thesis submitted in fulfillment of the
requirements for the award of the degree of
Master of Engineering (Mechanical)

Faculty of Mechanical Engineering
Universiti Teknologi Malaysia

MAY 2005

ACKNOWLEDGEMENT

Praise to Allah, the Most Gracious and Most Merciful, Who has created the mankind with knowledge, wisdom and power. Being the best creation of Allah, one still has to depend on others for many aspects directly and indirectly. This is, however, not an exception that during the course of study the author received so much of help, co-operation and encouragement that need to duly acknowledge.

First of all the author whishes to express profound gratitude to his research supervisor Assoc. Prof. Dr. Esah Hamzah for the noble guidance and valuable advice throughout the period of study. Her-ever-dynamic approach, love and dedication for promoting research and development have paved the way to attain a smooth finishing of the present study.

The author is also thankful to his Co-supervisor Assoc. Prof. Dr Ali Ourdjini, for his guidance during accomplishment of this thesis. Acknowledgements are due to Mr. Mo Zhiqiang from PSB Corporation Singapore for his assistance on TOF-SIMS analysis and Mr Liu Rong from Surface Science laboratory NUS for his assistance on MS-SIMS. The author would also like to thank the staff of Malaysian Institute Nuclear Technology (MINT) for their assistance in Galvanostatic corrosion tests. A word of gratitude is extended to the technical staffs of the Material Science Laboratory, Faculty of Mechanical Engineering University Technology Malaysia.

Special dedication to my family especially my mother for their support and encouragement. Special gratitude is reserved to all of my best friends in UTM, Rhino, Rival, Dadan, Fikri, Roni, Mr Nazori, Mr. Hadi Nur, Mr. Endra, Mr. Didik, Mr. Gigih, Maiieligan, Ong Wei Rex, Azmah Hanim, Tan Chu Li etc that I cannot mention all of them here.

ABSTRACT

The intermetallic alloys of γ-titanium aluminide are emerging as one of the most attractive alternative structural and machinery part materials for high and low temperature applications. One critical area of application is in hydrogen storage tank in chemical, oil and gas industries or in combustion engine when entail the use of hydrogen as a fuel. It has been widely reported by researchers that these materials exhibit environmental embrittlement in the presence of hydrogen, hence the diffusivity of hydrogen and the effect of hydrogen to the mechanical properties of γ-titanium aluminide is significant and technologically important. Therefore, in the present research, an investigation had been carried out to determine what causes the hydrogen attack and dealuminification. Control microstructure and phases through heat treatment by heating to 1200^0C for 30 minutes and cooled in three different ways (i.e. water-quenched, air-cooled and furnace-cooled), and addition of a third alloying element namely chromium become the focus of this research. Samples were subjected to corrosion attack under cathodically charged with galvanostatic mode for 6, 24 and 48 hours. Hydrogen diffusion coefficient (D) was calculated based on Fick's second Law and these results were compared with that obtained from micro-Vickers hardness profiling data. The corroded and uncorroded samples were analyzed by using x-ray diffraction (XRD), scanning electron microscopy (SEM) and secondary ion mass spectroscopy (SIMS). It was found that α_2-Ti_3Al or lamellae phases are more prone to hydrogen attack than γ-TiAl phases but γ-TiAl is more susceptible to dealuminification. Slowly cooled (furnace-cooled) Ti-Al exhibited the least hydrogen attack due to its low hydrogen diffusion coefficient. However the effect of heat treatment on dealuminification is insignificant. When γ-titanium aluminides were alloyed with chromium, their resistance towards hydrogen attack and dealuminification increased.

ABSTRAK

Aloi antara logam γ-titanium aluminida adalah salah satu bahan alternatif menarik yang membangun dengan pesat sebagai bahan struktur dan mesin pada suhu tinggi dan rendah. Aplikasi yang kritikal adalah pada tangki stor hidrogen bagi industri kimia, petrokimia dan sumber asli atau pada enjin pembakaran ketika penggunaan hidrogen sebagai sumber bahan api telah menyebabkan aloi titanium aluminida mengalami kerapuhan hidrogen. Oleh itu, keresapan hidrogen dan kesan hidrogen terhadap sifat mekanik γ-titanium aluminida adalah amat penting. Maka dalam penyelidikan ini, kajian telah dilakukan untuk menentukan kesan serangan hidrogen dan penyahaluminum. Kawalan mikrostruktur dan fasa melalui rawatan haba dengan memanaskan sehingga 1200^{o}C selama 30 minit dan didinginkan dengan 3 kaedah yg berbeza (iaitu lindap kejut menggunakan air, pendinginan pada suhu udara dan pendinginan dalam relau), dan penambahan unsur aloian ketiga iatu kromium adalah menjadi tumpuan penyelidikan ini. Sampel dikakiskan dengan mencas katodik menggunakan mod Galvanostatik selama 6, 24 dan 48 jam. Pekali resapan hidrogen (D) dihitung melalui Hukum Kedua Fick's dan hasilnya dibandingkan dengan pekali resapan yang diperolehi daripada profil kekerasan mikro Vickers. Sampel sebelum dan selepas kakisan telah dianalisis menggunakan pembelauan sinar-x (XRD), mikroskop elektron (SEM) dan spektroskopi jisim ion sekunder (SIMS). Hasil daripada kajian ini, didapati fasa lamela atau α_2-Ti_3Al lebih cenderung untuk mengalami serangan hidrogen jika dibandingkan dengan fasa γ-TiAl. Manakala fasa γ-TiAl lebih cenderung mengalami penyahaluminum. Sampel titanium aluminida yang dirawat haba secara pendinginan perlahan (pendinginan dalam relau) menunjukkan paling sedikit serangan hidrogen disebabkan pekali resapan hidrogen yang rendah. Walau bagaimanapun rawatan haba tidak menunjukkan kesan ketara terhadap penyahaluminum. Apabila γ-titanium aluminida dialoikan dengan kromium, ketahanannya terhadap serangan hidrogen dan penyahaluminum meningkat.

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NOTATIONS

γ	-	Gamma Phase/ tetragonal atomic structure
α	-	Alpha phase/ hexagonal atomic structure
α_2	-	Alpha two phase/ hexagonal closed packed atomic structure
β	-	Betha phase/ cubic atomic structure
at.%	-	Atomic percentage
Γ	-	Average jump frequencies
C	-	Concentration of diffusing species (hydrogen)
Z	-	Charge number of electro-active diffusing species
F	-	Faraday constant
S	-	Sectional area common to both electrode and electrolyte
D	-	Kinetic diffusion coefficient
I	-	Constant current
L	-	Sample half thickness
Vm	-	Volume molar
E	-	Potential
$dE/d\delta$	-	Potential variation of the electrode (γ-TiAl) with the change in hydrogen composition
Hv	-	Microhardness vickers
erf	-	Error function
λ	-	wave length
d	-	interplanar spacing
hkl	-	miller indices
θ	-	diffraction angle
a, b, c	-	lattice constant
Å	-	Amstrong constant

SEM	-	Scanning Electron Microscope
XRD	-	X-ray Diffraction
NA	-	Number of grain
f	-	Jeffries’s constant
SIMS	-	Secondary ion mass spectroscopy
TOF-SIMS	-	Time of flight-secondary ion mass spectroscopy
KeV	-	Kilo electron volt

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CHAPTER I

INTRODUCTION

1.1. Background of The Research

Since titanium was first discovered in 1790 and was mass-produced in the early 1950's [Mangonon, 1999], the development and research on titanium and its alloys have been well developed. Until now, scientists and engineers had discovered new advanced material: gamma titanium-aluminide, well known as "γ-TiAl". γ-TiAl based alloys with compositions ranging from 45 to 50 at.%Al, is an intermetallic compound consist of Ti_3Al (α_2-phase) and Ti-Al (γ-phase) with low density, high Young's Moduli, good creep and oxidation resistance up to 900^{o}C (creep limit) [ASM, 1994]. Due to their high properties, this γ-TiAl extent the capabilities of titanium-based alloys beyond that of conventional α-β titanium alloys and potentially viable to replace nickel-based super alloys in some application with a material having one-half the density [Zheng *et al*., 1995; Cheng *et al*., 1999; Nombela *et al*., 2000]. This γ-TiAl have been considered attractive candidates for applications in advanced fields such as in aerospace: blades, body frames, compressor cases, discs; in marine applications: turbocharger rotors, flywheel, turbine engine compressor component, and turbine engine exhaust system components; in automotive engine components and in chemicals and other applications: hydrogen storage tank, chemical storage tank and medical profession. [Mangonon, 1999; ASM, 1994; Seagle and Wood, 1993; Huang and Chessnut, 1994; Kim and Dimiduk, 1991 and Maeland *et al*., 1999] .

The future of titanium aluminide intermetallics is bright and well developed deformation mechanisms theory can explain the relationship between mechanical properties and microstructure. The fundamental understanding of phase stabilities is enabling the optimization of microstructure and properties.

In normal air condition, γ-Titanium aluminide intermetallics are known to be highly resistant to atmospheric corrosion at room temperature. However, their tendency to oxidize to form Al_2O_3 preferentially to TiO_2 exits only up to 850^{o}C, which is known as high temperature corrosion [Kim and Dimiduk, 1991]. However, at room temperature γ-titanium aluminide is often subjected to hydrogen-damage mechanisms, although the surface oxide film forms barrier to hydrogen atom entry to metal lattice. It is already known that titanium alloys are susceptible to hydrogen to form hydride on the surface. Hydrogen causes embrittlement leading to the deterioration of the properties of the alloys [Sha and Mckinven, 2002]. Much effort has been made to quantify the hydrogen susceptibility and its effect to properties of titanium alloys. Takasi *et al*. [1994] noted that for Gamma TiAl alloy, the yield strength increased with increasing amount of hydride but the ultimate tensile strength, ductility and fracture toughness decreased [Takasi *et al*., 1994]. Therefore the amount of hydrogen that a titanium alloy can absorb during service is a major measure of the ability of the alloy to retain good properties [Sha and Mckinven, 2002]. Also, some researchers found that hydride formed on the surface and the possibility that some hydrogen may occupy the interstitial sites in the alloy [Takasaki *et al*., 1994; Gao *et al*., 1993 and Sundaram *et al*., 2000].

It was found that hydrogen attack is more likely to occur in α_2 or lamellae phases rather than γ-TiAl phases. Control of microstructure and phases could be the answer to this problem. Appropriate γ-titanium aluminide which is more resistant to environment embrittlement and has useful properties need to be investigated. The focus of this research is to investigate the influence of microstructure and an alloying element content in γ-titanium aluminide namely chromium to corrosion attack in the form of hydrogen attack or hydrogen embrittlement.

1. 2. Objectives of the Research.

The objective of this research is to study the effect of microstructure variation by heat treatment process and chromium addition on γ-titanium aluminide resistance to hydrogen attack and dealuminification.

1. 3. Scope of the Research.

The scope of the research include:

1. Investigation of the effect of microstructure of γ- titanium aluminide generated by heat treatment on corrosion attack in the form of hydrogen attack.
2. Investigation of the influence of an alloying element, namely chromium, added to γ-titanium aluminide on corrosion in the form of hydrogen attack.
3. Investigating the effect of microstructure and chromium content on corrosion kinetics; namely coefficient of diffusivity of hydrogen in γ-titanium aluminide
4. Investigating the hydride formed on the surface of titanium aluminides.

6.2 Recommendations for Future Work

Further research can be carried out to enhance the current research and the following are areas which are recommended for further investigation;

1. In-depth investigation on the mechanical properties namely; tensile, fatigue and creep strength of γ-titanium aluminide after it is subjected to hydrogen attack and dealuminification.
2. Metallurgical and microstructural study in other ternary titanium aluminides such as, Ti-48%Al-X%(Nb, V, Mo, Mn), and in-depth investigation on the effect of heat treatment to corrosion behavior of the ternary titanium aluminide. Understanding microstructural control through combination of heat treatment and addition of third alloying element which may produce better microstructures that more resistant to hydrogen attack and dealuminification.
3. Study on the heat treated alloyed γ-titanium aluminide and its effect on corrosion

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