THE EFFECT OF HEAT TREATMENT AND CHROMIUM ADDITION ON
\( \gamma \)-TITANIUM ALUMINIDE RESISTANCE TO HYDROGEN ATTACK

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ABSTRACT

The intermetallic alloys of $\gamma$-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 $\gamma$-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 dealumination. Control microstructure and phases through heat treatment by heating to 1200°C 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 $\alpha_2$-Ti$_3$Al or lamellae phases are more prone to hydrogen attack than $\gamma$-TiAl phases but $\gamma$-TiAl is more susceptible to dealumination. 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 dealumination is insignificant. When $\gamma$-titanium aluminides were alloyed with chromium, their resistance towards hydrogen attack and dealumination increased.
ABSTRAK

Aloi antara logam $\gamma$-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 $\gamma$-titanium aluminida adalah amat penting. Maka dalam penyelidikan ini, kajian telah dilakukan untuk menentukan kesan serangan hidrogen dan penyahalumin. Kawalan mikrostruktur dan fasa melalui rawatan haba dengan memanaskan sehingga 1200$^\circ$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 $\alpha_2$-Ti$_3$Al lebih cenderung untuk mengalami serangan hidrogen jika dibandingkan dengan fasa $\gamma$-TiAl. Manakala fasa $\gamma$-TiAl lebih cenderung mengalami penyahalumin. 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 penyahalumin. Apabila $\gamma$-titanium aluminida dialoikan dengan kromium, ketahanannya terhadap serangan hidrogen dan penyahalumin meningkat.
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5.36 Secondary ion mass spectroscopy (SIMS) on water-quenched Ti-45%Al after hydrogen attack
NOTATIONS

γ - Gamma Phase/ tetragonal atomic structure
α - Alpha phase/ hexagonal atomic structure
α₂ - 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/dδ - 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
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<thead>
<tr>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>NA</td>
<td>Number of grain</td>
</tr>
<tr>
<td>$f$</td>
<td>Jeffries’s constant</td>
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<td>SIMS</td>
<td>Secondary ion mass spectroscopy</td>
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<td>KeV</td>
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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 Ti₃Al (α₂-phase) and Ti-Al (γ-phase) with low density, high Young’s Moduli, good creep and oxidation resistance up to 900°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,

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, $\gamma$-Titanium aluminide intermetallics are known to be highly resistant to atmospheric corrosion at room temperature. However, their tendency to oxidize to form $\text{Al}_2\text{O}_3$ preferentially to $\text{TiO}_2$ exits only up to $850^\circ\text{C}$, which is known as high temperature corrosion [Kim and Dimiduk, 1991]. However, at room temperature $\gamma$-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 $\alpha_2$ or lamellae phases rather than $\gamma$-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 $\gamma$-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 $\gamma$-titanium aluminide and its effect on corrosion
REFERENCES


Web 1: [http://www.aerospaceweb.org/design/waverider/examples.shtml](http://www.aerospaceweb.org/design/waverider/examples.shtml)


