High temperature deformation and superplasticity of titanium alloys

Zhu, Xuejun

2006

Zhu, X. J. (2006). High temperature deformation and superplasticity of titanium alloys.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/36115>

<https://doi.org/10.32657/10356/36115>

High Temperature Deformation and Superplasticity of Titanium Alloys

Zhu Xuejun

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Ph.D

2006

Abstract

ABSTRACT

Due to its high strength, high strength-to-weight ratio, excellent corrosion resistance and biocompatibility, Commercially Pure (CP) titanium alloy is one of the most important titanium alloys and widely used in many areas such as the chemical, nuclear and biomedical industries. Superplastic Forming (SPF) is a cost-effective process for manufacturing complex shaped structural components and superplastic forming of CP titanium alloy is very attractive in many areas due to the inert nature of this alloy. The project aims at enhancing the elongation-to-failure value of the alloy and investigating the superplastic behavior of the commercially pure titanium alloy.

In this work, it was found that the surface of titanium alloys at elevated temperatures produces oxidation. The thickness of the oxide film increased with increasing temperature and exposure time. This film is detrimental to the ductility of the alloy while having little influence on the ultimate tensile strength and yield strength. Studies showed that clefs generated in the oxide film, and they propagated under tensile stress. The mechanism was studied and a model was proposed for crack initiation and propagation.

In order to prevent the alloy from oxidising during SPF of this alloy at high temperature, one type of oxygen barrier coating was applied onto the surface of a titanium alloy prior to superplastic forming by the plasma spray method. The effects of the coating layer on the mechanical properties of the alloy were also studied. Studies show that Zircon coating layer greatly decreases the oxidation rate during high

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temperature tensile tests and the elongation of coated samples increase dramatically. The coating layer has little effect on the mechanical properties of the alloy and can be easily cleaned by using 5% HF.

High temperature tensile tests were conducted with an initial strain rate varied from 0.1 to 0.0001/s. The optimum superplastic deformation conditions for the CP titanium alloy under uniaxial tensile test were determined to be at 600°C with an initial rate of 0.001/s and 750°C with an initial rate of 0.01/s. The maximum elongations obtained were 188% and 186% respectively.

The alloy that was deformed at 600°C shows high cavitation ratio at fracture. In the present study, it was found that the cavity phenomenon was influenced by temperature. At high temperatures, e.g. 750°C and 800°C, no cavity was found in the deformed samples.

Both the static and dynamic grain growth of the CP titanium alloy were investigated to examine its significance towards superplastic deformation. At high temperatures (750°C and 800°C), grain sizes of this alloy grow dramatically even at a high strain rate (0.1/s). At a lower temperature (600°C), excessive grain growth can also take place if the strain rate is very low (0.0001/s). Studies also show that dynamic recrystallization (DRX) happens during high temperature deformation and this process not only decreases the average size of the alloy, but also increases the misorientation angle and strain rate sensitivity index, i.e. *m*-value, of the commercially pure titanium alloy.

Abstract

Recognizing the capability of CP titanium alloy to dynamically recrystallized, a 'Two Stage Deformation Method' was proposed to enhance superplasticity. A maximum tensile elongation of 243% can be obtained via this method. During stage-I of deformation, dynamic recrystallization takes place at 600°C and 0.001/s, hence resulting in a fine-grained microstructure ($\leq 10\mu\text{m}$). Subsequently, stage-II is performed at higher temperature (i.e. 750°C) with a faster initial strain rate (0.01/s). It was found that by combining these two deformation mechanism, a significant improvement in elongation-to-failure can be realized.

Acknowledgements

ACKNOWLEDGEMENTS

First and foremost, I would like to express my sincere appreciation to my supervisor, Dr. Tan Ming Jen, for his guidance and advice. His support and advice illuminate me throughout the research work. I am deeply impressed with his erudition and working spirit, and benefit from them throughout three years research.

I am very deeply grateful to Dr. Zhou Wei, for his good advice and kind assistance.

Thanks also to Mr. Leong Kwok Phui, Mr. Thomas Lew, Mr Sadon Ahmad, technicians of Materials Lab A and B, school of MAE, NTU. They provided training and technical assistance during my research.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

Due to its high strength, high strength-to-weight ratio, and excellent corrosion resistance and biocompatibility, Commercially Pure (CP) titanium alloy is one of the most important titanium alloys and widely used in many areas such as chemical, nuclear industry and especially biomedical area [1-4]. Superplastic forming (SPF) is a cost-effective process for manufacturing complex shaped structural components [5-7] and SPF of commercially pure titanium alloy is very attractive in many areas due to the inert nature of this alloy. To date, the number of research work and publications concerning the superplasticity of CP titanium alloys are very limited, since the majority of researches are concentrated on Ti-6Al-4V alloys. Consequently, only little basic know-how on the superplasticity of CP titanium alloy is available. The investigations of its superplasticity mechanism, related phenomena and microstructure evolution are important for achieving desired mechanical behaviors of the material.

Superplasticity is the ability of a polycrystalline material to exhibit very large tensile elongation prior to failure. The most commonly considered mechanism for superplastic flow is grain boundary sliding (GBS), which is accommodated by dislocation slip and climb, grain boundary migration, grain rotation, diffusion flow and/or recrystallization process, etc [8]. One of the basic requirements for a material to exhibit structure superplasticity is fine and stable microstructure [9]. However, some

materials with relatively large grain size can also be superplastic formed through recrystallization [10-13] and this method is worthy of investigation.

Superplastic deformation leads to large “neckfree” elongation, but most superplastic materials develop internal cavitation during deformation [14–16]. It has been recognized that for such materials, cavitation often precedes failure and excessive cavitation may impose significant limitations on the industrial use of superplastically formed components [14]. As cavitation will degrade the post deformation properties of materials, characterization of the microstructure evolution, e.g. cavitation nucleation, growth, coalescence, interlinkage and finally failure is important of cost effective methods for cavitation suppression.

Generally, superplastic forming process is achieved at relatively high temperatures. At high temperatures, oxidization of the titanium alloys causes oxide film [17, 18]. This is a serious problem for the producing of sound products. Unfortunately, little research on the effect of oxidation on the superplasticity of titanium alloy has been done, and also sufficient understanding of the effect of oxidation on the superplasticity of titanium alloys has not been well established yet. On the other hand, it has been reported that oxidation could be prevented during superplastic forming through the use of a plasma sprayed oxidation resistant coating [17]. This method is attractive and investigation on it has both theoretical and practical significance.

Microstructure plays a very important role during the superplastic forming process. Microstructural feature, such as grain boundary characteristics, have been discussed extensively in literature [19-22], which have documented the common features of many superplastic alloy systems. However, for the CP titanium alloy, studies on its microstructure characteristics during SPF are scarce. The emergence of Electron Backscatter Diffraction (EBSD) technique provides an access to characterize the evolution of microstructure both at a single grain level and at a statistical level of contiguous grains, e.g., orientation variation and deformation of a single grain, and variation of misorientation population, etc. Beyond this, the specialty of EBSD technique provides the possibility of the determination of local texture evolution of materials. This unique advantage of EBSD technique has not been fully utilized to investigate the superplastic mechanism and microstructure evolution. This is an attractive research area worthy of further exploration.

1.2 SCOPE

Due to the fact that the literature on the superplastic behavior of CP titanium alloy is scarce as most of the research works are targeted at Ti-6Al-4V alloy, it is important that the superplasticity of CP titanium be given greater attention due to its growing importance. The key objective of this research aims at improving the ductility of the CP titanium alloy. In order to achieve this goal, it is essential to elucidate its superplastic deformation behavior and the governing deformation mechanisms. The evolutions of microstructures and their effects on superplasticity are investigated and carefully analyzed in order to further enhance its deformation capability.

The scope of this work consists of:

- (1) To investigate the deformation behavior and the predominant deformation mechanisms of the commercially pure titanium alloy. To study the effect of test temperature, initial strain rate on the superplasticity of the material and to determine the optimum deformation conditions of the alloy.
- (2) To study the evolution of the microstructure of the alloy during the superplastic deformation, with a focus on the dynamic recrystallization of the alloy. This part of work also has significance on the broadening of the application of EBSD technique on superplasticity study
- (3) To characterize the cavitation behavior of the alloy during high temperature deformation.
- (4) To study the oxidation behavior of the alloy and its effect on the superplasticity of the titanium alloys at high temperature,
- (5) To employ dynamic recrystallization to refine the grain structure, and in order to attain greater elongation-to-failure.

CHAPTER 2 LITERATURE REVIEW

2.1 TITANIUM ALLOYS

2.1.1 Background

Titanium is a low-density metallic element and it ranks as the ninth most plentiful element and the fourth most abundant structural metal in the earth's crust. The existence of titanium was first recognized in 1791 by William M. Gregor, an English mineralogist, who detected the oxide of a new metal in mineral ilmenite (FeOTiO_2). In 1937, a commercially viable process for separating metallic titanium from its ores was demonstrated by Wilhelm Kroll. This opened the way to the industrial exploitation of titanium [4].

2.1.2 Characteristics of Titanium Alloys

Titanium alloys have a number of features that distinguish them from the other metals. The major advantages of choosing titanium alloys for engineering designs can be listed as follows [4, 23]:

- 1) Outstanding corrosion resistance

Titanium is a highly reactive metal but, because of the presence of a very stable, self-healing oxide film, these alloys exhibit excellent corrosion resistance in a wide variety

of environment. These alloys are immune to corrosive attack by saltwater and marine atmospheres. It also exhibits exceptional resistance to a board range of acid, alkalis, nature water, corrosive gases, etc.

2) Superior strength-to-weight ratio

The densities of Titanium-based alloy ranges between 4.43kg/l and 4.95kg/l. Yield strength range from 172 MPa for commercial pure titanium alloy to above 1400MPa for the heat-treated beta alloy. These ratios for titanium-based alloys are superior to almost all other metals.

3) Excellent biocompatibility

Titanium and titanium alloys also show an outstanding resistance to corrosion by body fluids which is superior to that of stainless steels and it is one of the few materials which will not induce formation of a fibrous tissue barrier when placed in contact with healthy born.

4) High heat transfer capability

Under “in-service” conditions, the heat transfer properties of titanium alloys are similar to those of admiralty of brass and coppernickel. There are several reasons:

--The higher strength and corrosion resistance of titanium permits the use of thinner wall equipment.

- The oxide film confers unusual characteristics which are beneficial to heat transfer.
 - The absence of corrosion leaves the surface bright and smooth for improved lamellar flow.
 - Titanium's excellent corrosion-erosion resistance permits significant higher operating velocities.
- 4) Low thermal expansion coefficient
 - 5) Non-magnetic character
 - 6) Short radioactive half-life
 - 7) High rigidity to weight ratios, good fatigue strength and toughness

Because of these characteristics and improved fabrication technology, titanium and its alloys are widely used in many industry areas.

2.1.3 Applications of Titanium Alloys

2.1.3.1 Aerospace

Although the development of titanium alloys only commenced in the late 1940s, their uniquely high strength: weight ratios led to their introduction in aircraft gas turbines as early as 1952 when they were used for compressor blades and discs in the famous Pratt

and Whitney J57 engine. Since then, air craft gas turbines have continued to provide the major application for titanium alloys which make up around 30% of the weight of most modern engines. In addition to turbines, titanium alloys are also used for most of the blades, discs and other components for aerospace applications. Nowadays, titanium plays a critical role in weight reduction of airplanes. For example the McDonnell-Douglas F15 fighter aircraft contains some 7000 kg of titanium alloys which represent 34% of the structural as compares with 48% for aluminum alloys.

2.1.3.2 Biomaterials

Titanium and titanium alloys show outstanding resistance to corrosion by body fluids which is superior to that of stainless steels. This factor, together with good stress-corrosion resistance, high mechanical properties and acceptable tissue tolerance has lead to their use for biomedical areas. Unalloyed and alloyed titanium have been used in medical engineering for many years. The applications are varied and include the following:

- joint replacement parts for hip, knee, shoulder, spine, elbow and wrist,
- bone fixation materials such as nails, screws, nuts and plates,
- dental implants and parts for orthodontic surgery and dental prosthetics,
- heart pacemaker housings and artificial heart valves,
- surgical instruments for heart and eye surgery,
- components in high-speed blood centrifuges

2.1.3.3 Chemical and General Engineering

Because titanium alloys have excellent corrosion resistance in many environments, these alloys are widely used in chemical and general engineering areas. Resistance to chlorides is perhaps its most valuable attribute and titanium is uniquely suited for equipment handling solutions, e.g. bleaching agents, hot brine, ferric chloride and chlorinated hydrocarbons.

In addition to the above mentioned areas, titanium alloys are also applied to other areas such as military, advanced sporting equipment, automotive & transport, offshore, etc.

2.1.4 Classification of Titanium Alloys

The phase diagrams of titanium alloys are often complex and many are unavailable. However, the titanium-rich sections of pseudo-binary system enables them to be classified into three simple types, as shown in Fig. 2-1. Elements that dissolve preferentially in the α -phase expand this field thereby raising the α/β transus (Fig. 2-1a) and, of the comparatively few elements that behave in this way, aluminum and oxygen are the most important [9]. Elements which depress the α/β transus and stabilize the β -phase may be classified in two groups: those which form binary systems of the β -isomorphous type (Fig. 2-1b) and those which favour formation of a β -eutectoid (Fig. 2-1c). The main elements that promote the three types of binary phase diagrams are also given in Fig. 2-1.

Fig. 2-1. Basic types of phase diagrams for titanium alloys. The dashed phase boundaries in (a) refer specifically to the Ti-Al system. The dashed lines in (b) and (c) show the martensite start (M_s) temperature. Alloying elements favoring the different types of phase diagrams are: (a) Al, O, N, Ga; (b) Mo, W, V, Ta; (c) Cu, Mn, Cr, Fe, Ni, Co, H.

Among the α -stabilizers, aluminum is by far the most important alloying element of titanium. The interstitial elements oxygen, nitrogen, and carbon also belong to this category. In addition to extending the α phase field to higher temperatures, the α -stabilizers develop a two-phase $\alpha+\beta$ field. α -stabilizing elements are subdivided into β -isomorphous and β -eutectic elements. Of these, the β -isomorphous elements, e.g. Mo, V, and Ta, are by far more important due to their much higher solubility in titanium. On the other hand, even very low volume fractions of β -eutectic element, e.g. Fe, Mn, Cr, Co, Ni, Cu, Si and H, can lead to the formation of intermetallic compounds. Sn and Zr are considered neutral elements since they have no influence on

the α/β phase boundary. As far as strength is concerned, they are not neutral since they primary strengthen the α phase.

According to the predominant phases present in the microstructure at near room temperature. Titanium and their alloys are usually classified into three main categories:

Alpha Alloys, Alpha+Beta and Alloys Beta Alloys.

The essential difference between the three alloy classes α , $\alpha+\beta$ and β are outline on the basis of physical, mechanical and technological properties in Table 2-1.

Table 2-1. Properties of different titanium alloys.

	α	$\alpha+\beta$	β
Density	+	+	-
Strength	-	+	++
Ductility	-/+	+	+/-
Fracture toughness	+	-/+	+/-
Creep strength	+	+/-	-
Corrosion behavior	++	+	+/-
Oxidation behavior	++	+/-	-
Weldability	+	+/-	-
Cold formability	--	-	-/+

2.1.4.1 Alpha Alloys

These alloys consist predominantly of a close packed hexagonal crystal structure at room temperature. These alloys offer high strength as well as good creep and oxidation resistance at elevated temperatures. They are also weldable, non-heat treatment and maintain their strength even at cryogenic temperature. The down side is that these alloys are relatively difficult to be formed. The commonly used alloy in this group is commercially pure (CP) titanium alloy.

Compared with β , α is characterized by the following properties:

- higher resistance to plastic deformation
- reduced ductility
- anisotropic mechanical and physical properties
- a diffusion rate which is at least two orders of magnitude lower
- higher creep resistance.

2.1.4.2 Alpha+Beta Alloys

This class contains the largest numbers of commercial alloys. These alloys are formulated so that both the hexagonal alpha phase and bcc beta phase coexist at room temperature. They are treatable, stable at elevated temperatures, relatively strong and more formable than alpha alloys. The most commonly used alloy of this class is Ti-6Al-4V.

2.1.4.3 Beta Alloys

Titanium requires the addition of beta stabilizers before it is able to exist entirely in the beta phase at room temperature. Beta titanium alloys are the most versatile class of titanium alloys. They offer the highest strength to weight ratios and very attractive combinations of strength, toughness and fatigue resistance at large cross sections. These alloys can be readily formed at room temperatures and possess better weldability than alpha-beta alloys. They can also be solution heat-treated, have relatively high strength and exhibit good creep resistance. Some of the disadvantages compared to $\alpha+\beta$ alloys are increased density, a rather small processing window, and higher cost. An example of alloy in this group is Ti-13V-11Cr-3Al.

2.1.5 Commercially Pure Titanium Alloy and Its Applications [24]

Commercially Pure (CP) titanium alloy is an α alloy and at room temperature its microstructure consists only α phase. The various CP titanium alloy grades differ primarily in oxygen content. As an interstitial alloying element, oxygen drastically increases strength with a simultaneous reduction in ductility. To reach the required strength levels of CP titanium grades, only oxygen is intentionally alloyed; while elements like carbon and iron are considered impurities brought into the alloy via the manufacturing process.

The chemical composition of four type of CP titanium alloy, i.e. Grades 1 to 4, is shown in Table 2-2. Of these, Grade 1 has the lowest strength level and excellent cold

formability. Therefore, it is used for deep drawing application, as cladding alloy for parts which require excellent corrosion resistance but only low strength. Grade 2, with tensile strength levels between 390 and 540 MPa, is the most popular CP titanium grade. Higher strength Grade 3 is nearly exclusively used for pressure vessel applications. This still moderately cold-formable higher strength grade allows for designs with reduced wall thickness and is therefore used where weight is a concern. Grade 4 has the highest strength of up to 740 MPa and is preferentially used for mountings and fitting. However, complex parts have to be shaped at temperature around 300°C.

Table 2-2. Chemical composition of different commercially pure titanium.

Alloy	Chemical composition [wt %]
Grade 1	0.08 C; 0.20Fe; 0.03N; 0.18O; 0.015H
Grade 2	0.10 C; 0.30Fe; 0.03N; 0.25O; 0.015H
Grade 3	0.10 C; 0.30Fe; 0.05N; 0.35O; 0.015H
Grade 4	0.10 C; 0.50Fe; 0.05N; 0.40O; 0.015H

Like other titanium alloy, CP titanium alloy is strong, light, and corrosion resistant. This alloy has been widely used in many areas such as chemical and nuclear industry and especially in the biomedical industry. Another type of titanium alloy, Ti-6Al-4V alloy has been used as implant material for many years. However, recent studies have shown that the release of aluminum and particularly vanadium ions from the alloy might cause such long-term health problem as peripheral neuropathy osteomalacia and

Alzheimer diseases. For CP titanium alloy, because this alloy does not have any alloying element, this alloy has prosperous future in this area.

2.1.6 Oxidation of Titanium Alloys

Oxygen is the most important interstitial solute in titanium alloys because it strongly influences its microstructures and mechanical properties of the alloy [23]. It is always present in significant concentration in commercial products. Most commercial titanium alloys contain concentrations between 0.1% and 0.2 % oxygen which significantly affect the mechanical properties [25].

However, when titanium alloys are exposed to elevated temperature in atmosphere, oxidation will occur on the surface of titanium alloys. Du [17] studied the process of oxidation behavior of Ti-6Al-4V between 650 and 850°C and found that the oxide scale developed on the alloy consisted of alternating layers of Al_2O_3 and TiO_2 . The number of oxide scale increased with increasing exposure time and temperature and the oxidation kinetics for the titanium alloy can be represented by the relationship:

$$y^n = K_n t \quad (2-1)$$

where y =weight gain per unit area, n =reaction index, K_n =reaction constant, t =exposure time.

Exposing titanium alloy in air at high temperature results not only in oxidation but also in solid solution hardening of the surface as a result of inward diffusion of oxygen

leading to the formation of surface hardened zone known as “alpha case”. A few researchers [18, 26] have investigated the effect of alpha case on the mechanical properties of titanium alloys. Hall *et al.* [26] reported that alpha case formed on the surface of titanium alloy can cause solid solution strengthening and restricts slip thus increasing the creep resistance. Evans *et al.* [27] pointed out that transgranular cracks generated in brittle alpha case during creep test propagate beyond the alpha case region leading to the premature failure of the titanium alloy. Patankar *et al.* [18] found that alpha case is detrimental to the ductility of titanium alloy during superplastic deformation while has little influence on the ultimate tensile strength and yield strength. Because the alpha case is hard and brittle, it must be removed before components are put into service. Normal methods of removal the alpha case include shot blasting and picking, hot salt bath descaling and machining, grinding and the like.

2.1.6.1 Plasma Spray and Ceramic Coating

Oxidation on the surface of Titanium alloy can cause oxide film and degrades the ductility of the alloy. In order to prevent oxidation, in most cases, superplastic deformation of these alloys is carried under Ar protection. Though this method can protect titanium alloys from oxidation during SPF processes, it greatly increases the cost of the processing and needs complicated equipment. It is well accepted that coating method is a good method to protect substrate from oxidation during high temperature deformation. Plasma spray is one of the coating methods and widely used in many industry areas.

2.1.6.1.1 Plasma Spray

Plasma spraying is a process that grew out of the oxyacetylene flame. It is a fast growing technology that has diffused progressively from aeronautical and nuclear industries to other industries. Plasma spraying is primarily used for coating application processes, usually for the purpose of extending the service life of critical parts exposed to adverse environmental conditions [28].

The plasma spraying process involves the use of an inert plasma stream of high velocity to melt and propel the coating material onto a substrate (Fig. 2-3). The process consists of the generation of a gas plasma which is usually comprised of an inert gas plus some additions of He or hydrogen to increase the enthalpy. The plasma is formed by passing the arc gases between two concentric electrodes where an rf triggered plasma is sustained by a DC arc with current levels ranging from 200 to 1500 amperes. The material to be deposited is injected into the high temperature plasma some distance downstream from the arc chamber by means of a special feeder and a carrier gas. Upon entering the stream, the powder is melted and accelerated towards the substrate where it impinges, rapidly solidifies and forms a coating as the plasma generator is moved over the substrate surface.

Fig. 2-2. Schematic diagram of the plasma spray process.

There are several critical factors that determine the adhesion and cohesion quality of the sprayed coatings as well as their thermo-mechanical properties. The velocity, size and density of the molten particles upon impact on the substrate play by far the most significant role. This can be controlled by adjusting the heat and momentum transfers between the plasma jet and the particles. Coating properties are also affected by the chemical reaction of their particles with the surrounding atmosphere as well as their possible decomposition upon entry the plasma jet. These variations also control the residual and cracking within the coating.

2.1.6.1.2 Ceramic Coating

Due to their excellent mechanical properties at high temperatures, ceramic materials are widely used as coating materials [28].

Ceramics are compounds that contain a mixture of both ionic and covalent bonds. As such they possess both completely filled valence bands as well as completely empty

bands. Depending on the ceramic used and the additives introduced, the optical and electrical properties of the ceramic used and the additives introduced, the optical and electrical properties of the ceramic can be altered to suit the needs. Ceramics are also very hard and stiff due to the high bond strength between their atoms and possess high resistance to both corrosion and oxidation.

There are four major categories of ceramics film production techniques. They include atomic deposition process, particulate deposition process, bulk coating and surface modifications [79]. The various techniques under these four broad categories are merely extensions from the basic processes developed many years ago; and with advances in modern technologies coupled with the development of numerous new techniques over the years, revolutionary changes have occurred in the types and quality of coating that can be produced. There are two important aspects to take note of when processing ceramic coating of films. One is the interaction of the depositing ions with the substrate surface as the kinetic energy of these ions can actually affect the coating process [80]. The other aspect is the energy of the deposited ion once it has reached and equilibrium state with the surface temperature. This affects not only the stability of the coating but also its texture and crystal structure.

Zircon, or zirconium silica, is a commonly used ceramic for coatings and can be formulated as ZrSiO_4 or as $\text{ZrO}_2 \cdot \text{SiO}_2$ and can be often found in igneous rocks and crystalline schists. Chemically, zircon is a very stable substance, especially at low temperature. Zircon is also very resistant to acids, except for concentrated hydrofluoric acid, which violently attacks it. It is also widely used as a refractory material due to its

excellent mechanical and chemical properties. It is also reported that zircon possesses excellent thermal shock resistance.

2.1.6.1.3 Properties of Plasma Sprayed Ceramic Coatings

The usefulness of ceramics as a form of protective coatings has been widely established in the industrial world. One of the most common methods of coating application through the means of plasma spraying due to its ease of use and uniformity of coating achievable. The microstructure of a plasma sprayed ceramic is generally lamellar in nature, formed by the flattened platelet of individual particles. However, depending on the rate of quenching and hence rate of solidification of the coating, different crystallographic modifications can exist within the ceramic coating. For instance, some metastable high temperature crystallographic polymorph may be frozen in the coatings. Defects such as microcracks and different kind of process may also be present due to temperature gradients occurring within the substrate and coating. These defects can affect the properties of the coating and hence their applications.

Physical and mechanical properties of ceramic coatings are usually determined by several methods: porosity, bulk density and bond strength. Thermal diffusivity is another factor that has to be considered when the ceramic is used as an oxide coating. Of all the ceramic coatings available, zirconia exhibits the lowest diffusivity even at elevated temperatures [81], making it very suitable as a thermal barrier on metals. However, zircon thermal barrier coatings are also relatively prone to failure due to a loss of adherence. This can occur due to several mechanisms: oxidation or corrosion of

the bond coat over which the zirconia coating is sprayed, thermal expansion mismatch and destabilization of the zirconia. New coating compositions and deposition techniques have been developed to overcome these problems.

2.2 SUPERPLASTICITY MECHANISM AND RELATED PHENOMENA

2.2.1 Superplasticity

Superplasticity is the ability of a polycrystalline material to undergo very large tensile elongation prior to failure. In general, a material exhibiting elongation-to-failure in excess of 200% when uniaxially loaded can be classified as superplastic [28]. However, there is no fixed criterion. One reason is that elongation value of a material depends on geometry of specimen. Another reason, which is most important, is that different materials have different intrinsic ductility. If the elongation obtained is apparently much higher than that under normal conditions, the material may be considered superplastic. At 1991 International Conference on superplasticity in Advanced Materials (ICSAM'91) held in Osaka, Japan, a new definition of superplasticity was suggested and accepted:

“Superplasticity is the ability of a polycrystalline material to exhibit, in a generally isotropic manner, very high tensile elongations prior to failure [29].”

To date, many materials have been shown to be superplastic, this ranges from metallic, ceramic, intermetallic to composite materials with uniform or uniform, relatively coarse (20 μ m) to ultrafine (30nm) grain sizes that have isotropic or anisotropic grain (phase), size or orientation [30].

Superplasticity has drawn much attention from researchers all around the world because its potential to form materials to great extent beyond achievable by conventional forming techniques. The advantages of this method are obvious [31]:

- (1) By using this method, complicated and intricate shapes can be formed from a single piece of material using a single processing step, thereby contributing to cost saving.
- (2) The high forming temperature effectively relieves the stress formed during processing. As such, there is little or no residual stress present when the part is removed from the press. Therefore, there is excellent repeatability between pressings.
- (3) During sheet parts forming, this fabrication process leads to inexpensive tooling due to it requiring only a single die, as compared to conventional methods that usually require matched pairs of tooling.

There are two well-established types of superplastic behavior in polycrystalline solid: fine-structure superplasticity (FSS) and inter-stress superplasticity (ISS). In recent years, high strain rate superplasticity (HSRS) received increasing attention. In fact, HSRS is an extension of FSS. The strain rates for high strain rate superplasticity, typically 10^{-2} s^{-1} to 10^{-1} s^{-1} , are considerably higher than typical forming rate used for conventional materials, rather close to the commercial hot working rates of 10^{-1} s^{-1} to 10^{-2} s^{-1} .

2.2.2 Structure Prerequisites for Superplasticity

For superplastic behavior, there are three most basic requirements [9]:

- (1) A fine and stable microstructure.
- (2) In the presence of a suitable microstructure, superplasticity occurs at temperatures generally above $0.5 T_m$ where T_m is the absolute melting point in Kelvin
- (3) A specific range of strain rates, usually varying from 10^{-4} s^{-1} to 10^{-1} s^{-1} .

There are other prerequisites that need to be satisfied, among them are as follows:

Grain Size

Grain size is the most important factor affecting superplasticity. In general, superplastic materials must exhibit an average grain size of 10-15 μm before

deformation by grain boundary sliding (GBS) mechanism can occur. The grain size can affect the strain rate as well as the magnitude of flow stress. When GBS is the dominant rate-controlling process, reducing the grain size can increase the strain rate for superplasticity. It has been reported [32] that the strain rate is inversely proportional to the grain size raised to the power of two or three

$$\dot{\epsilon} \propto d^{-p} \quad (2-2)$$

where $p=2$ or 3 . The flow stress also decreases when the grain size becomes finer, hence reducing the force required for deformation. It is important to note that superplasticity is not necessarily confined to fine-grained materials. For example, in some Fe-Al-based alloys, however, it is shown recently that superplasticity also occurs when grain size is much large, around $700\text{-}800\mu\text{m}$ [33].

Second Phase

Second phase and particles at grain boundaries play an important role in inhibiting excessive grain growth in fine-grained materials during high temperature superplastic deformation. With the presence of second phases, the fine grain size can maintain during deformation which enables the occurrence of grain boundary sliding.

The effectiveness of second phases in constraining grain growth greatly relies on their size, morphology, distribution and strength. Fine and uniformly distributed particles are more effective in inhibiting grain growth. Superplastic flow can also be improved

by minimizing the difference of strength between the matrix phase and second phase, therefore reducing stress concentration and nucleation cavitation.

Grain Boundary Structure

Grain boundary orientation also plays an important role in determining the extent of deformation in FSS. High energy grain boundaries, i.e. high angle and disordered, at adjacent matrix grains are preferred over low energy, i.e. low angle, boundary. This is because high angle grain boundaries are more prone to sliding when shear stresses are exerted.

To experience GBS, the grain boundaries should be mobile to avoid the development of stress concentration at the triple points and other obstacles found along the boundary. By grain boundary migration (GBM), stress concentration can be reduced and hence avoid the nucleation of cracks and failure. GBM can contribute towards the presentation of equiaxed grains even after extensive superplastic deformation. Besides that, grain boundaries should also possess good resistance towards tensile separation to attain high elongation-to-failure.

Texture and Shape of Grains

The effect of texture on the properties of alloys is attributed to the development of preferred grain orientation in a polycrystalline material. Due to the existence of texture, polycrystalline superplastic materials exhibit anisotropy of relative elongation but flow stress remains isotropic. According to Kaibyshev *et al.* [36], the anisotropy of flow stress was only observed for the case of an alloy having grains elongated in the rolling direction. Relative elongation varies with texture since strain accommodation at triple points is relatively difficult compared to another nontextured material. Equiaxed grains are important to allow the sliding of grain boundaries when shear stress is applied. Thus, elongated cylindrical grains can only experience limited boundary sliding when longitudinally tested.

2.2.3 Superplasticity Mechanisms

Elevated temperature deformation of fine-grained materials can be represented in Fig 2-3. A logarithmic plot of stress vs. strain rate for a typical superplastic material is shown in this figure [28]. It can be divided into four regions, i.e. Region 0, I, II and III. The slope of the plot is the strain rate sensitivity, m , where

$$m = \frac{d \log \sigma}{d \log \dot{\epsilon}} = \frac{1}{n} \quad (2-4)$$

Fig. 2-3. Strain rate dependence of flow stress in a superplastic material.

Region 0 is where true diffusion creep dominates [37]. In this region, the strain rate sensitivity initially decreases with the reduction of strain rate but further reduction of strain rate will lead to a slope of unity. This phenomenon has been observed, for example in Zn-Al eutectoid and has cited as evidence for diffusion controlled flow with the activation energy for flow Q equals to that of grain boundary diffusion Q_{gb} [35].

Region I represents deformation at low strain rates. Dislocation activity is normally not observed due to the low strain rates. The m value measured within region I is low (i.e. ≈ 0.2) and has been suggested to indicate the existence of threshold stress, σ_0 . Although it is known that σ_0 is a function of temperature and grain size, its actual meaning is still unclear [8].

Region II is the region where a material can deform superplastically when loading is carried out at intermediate strain rates. The strain rate sensitivity is high ($m \geq 0.5$) and grain boundary sliding is the predominant deformation mechanism. Flow stress is grain size dependent, i.e. $p=2 \sim 3$ and the activation energy Q is similar to the activation energy for grain boundary diffusion, Q_{gb} . Strain is accommodated by the motion of individual grains or clusters of grains relative to each other by sliding and rolling. In this region, the grains remain equiaxed throughout deformation and crystallographic texture may reduce during deformation.

At high strain rates, i.e. Region III, the strain rate sensitivity, m , is low, varying from 0.2 to 0.3. In this region, the deformation is dominated by recovery controlled dislocation creep. Activation energy for flow is close to the activation energy for lattice diffusion Q_L and the strain rate exhibits grain size insensitivity. Strain is accumulated by the glide of dislocations within grains.

2.2.4 Grain Boundary Sliding (GBS) and Accommodation Processes

Up to now, the exact governing mechanisms of superplastic flows are still not understood or thoroughly developed. Several plausible hypotheses for the origin of superplasticity in fine grain materials have been suggested, yet none has been found to be capable of accurately describing both the mechanical and microstructural features of superplastic deformation.

Three principal modes of deformation have been considered in explaining the creep behavior of structural superplastic material [8].

- 1) Diffusion flow
- 2) Grain boundary sliding (GBS) accommodated by diffusional flow
- 3) GBS accommodated by dislocation gliding

Among these three modes, GBS accommodated by slip [36] shows the best fit with the experimental data. The mechanism of this mode can be represented by the following equation:

$$\dot{\epsilon} = A \cdot \left(\frac{b}{d}\right)^2 \left(\frac{D_L}{b^2}\right) \left(\frac{\sigma}{E}\right)^2 \quad (2-5)$$

where $\dot{\epsilon}$ is the strain rate, b is Burgers vector, d is the grain size, D_L is the lattice diffusivity, σ is the stress, E is the dynamic unrelaxed Young's modulus and $A=2 \times 10^9$, an empirical constant. This correlation is in agreement with the 'core and mantle theory' proposed by Gifkins [38], which suggests that GBS accommodated by slip occurs in the mantle region while slip occurs within the core of each grain. Consequently, superplasticity takes place when the former process dominates deformation and when the latter is dominant, normal ductility can be observed. Table 2-2 lists the various quantitative models that have been proposed to describe superplastic flow.

Table 2-2 Summary of proposed models of GBS

Reference	Equation	Remarks
Slip accommodation (rate controlling)		
Ball and Hutchison [39]	$\dot{\epsilon} = K_3 \left(\frac{b}{d}\right)^2 D_{gb} \left(\frac{\sigma}{E}\right)^2$	Sliding of group of grains
Langdon [40]	$\dot{\epsilon} = K_5 \left(\frac{b}{d}\right) D_L \left(\frac{\sigma}{E}\right)^2$	Movement of dislocations adjacent to grain boundary
Mukherjee [41]	$\dot{\epsilon} = K_3 \left(\frac{b}{d}\right)^2 D_{gb} \left(\frac{\sigma}{E}\right)^2$	Grains slide individually
Hayden <i>et al.</i> [42]	$\dot{\epsilon} = K_7 \left(\frac{b}{d}\right)^3 D_p \left(\frac{\sigma}{E}\right)^2$	$T < T_c$, GBS is rate controlled by slip
Gifkins [38]	$\dot{\epsilon} = K_4 \left(\frac{b}{d}\right)^2 D_{gb} \left(\frac{\sigma}{E}\right)^2$	Pile-up at trip points (core-mantle)
Gittus [43]	$\dot{\epsilon} = K_6 \left(\frac{b}{d}\right)^2 D_{IPB} \left(\frac{\sigma - \sigma_0}{E}\right)^2$	Pile-up at interphase boundary $T > T_c$, creep in the grains
Arieli and Mukherjee [44]	$\dot{\epsilon} = K_8 \left(\frac{b}{d}\right)^2 D_{gb} \left(\frac{\sigma}{E}\right)^2$	Climb of individual dislocations near grain boundary
Sherby and Wadsworth [45]	$\dot{\epsilon} = 2 \times 10^9 \left(\frac{b}{d}\right)^2 \frac{D_L}{b^2} \left(\frac{\sigma}{E}\right)^2$ $\dot{\epsilon} = 6 \times 10^8 \left(\frac{b}{d}\right)^3 \frac{D_{gb}}{b^2} \left(\frac{\sigma}{E}\right)^2$	Phenomenological $T = 0.4 - 0.6 T_m$ Phenomenological $T > 0.6 T_m$
Kaibyshev [46]	$\dot{\epsilon} = \frac{A}{kT} \left(\frac{b}{d}\right)^2 \left(\frac{\sigma - \sigma_0}{G}\right)^2$	Hardening and recovery of dislocation at GBS
Fukuyo [47]	$\dot{\epsilon} = K_{10} \left(\frac{b}{d}\right)^2 \left(\frac{D_{chem}}{b^2}\right) \left(\frac{\sigma}{E}\right)^2$	GBS accommodated by dislocation climb
Diffusion accommodation (rate controlling)		
Ashby-verrall [48]	$\dot{\epsilon} = K_1 \left(\frac{b}{d}\right)^2 D_{eff} \left(\frac{\sigma - \sigma_0}{E}\right)^2$	$D_{eff} = D_L \left[1 + \left(\frac{3.3w}{d}\right) \left(\frac{D_{gb}}{D_L}\right)^2 \right]$
Diffusional accommodation (not rate controlling)		
Padmanabhan [49]	$\dot{\epsilon} = K_9 \left(\frac{b}{d}\right)^2 D \left(\frac{\sigma}{E}\right)^2$	D may differ from D_L and D_{gb}

where:

w = Grain boundary width.

T_c = Critical temperature.

$K_I - K_{I0}$ = Materials constant.

σ_0 = Threshold stress.

D_{gb} , D_p and D_{IPB} stand for diffusivities along grain boundary, dislocation pipe and interfacial phase boundary, respectively; D_L and D_{chem} are lattice and chemical diffusivities, respectively.

2.2.5 Recrystallization and Superplasticity

Fine grain size is considered as requirement for superplastic alloys. There are many methods for achieving fine-grained microstructure such as phase transformation, recrystallization, working of duplex alloys and phase separation in duplex alloys [50]. Recrystallization has been extensively studied in many alloys. Now, it is well accepted that this method is a useful method for getting fine grain microstructure. Unfortunately, very limited literatures can be found on the effects of recrystallized microstructure have on the superplasticity of titanium alloys.

2.2.5.1 Nucleation during Recrystallization

During plastic deformation, energy is stored within the material mainly in the form of dislocations. The stored energy can be released through three major processes, i.e. recrystallization, recovery and grain coarsening. The usual definition of

recrystallization is the formation and migration of high angle boundaries (i.e. those with greater than $10\text{-}15^\circ$ misorientation) driven by the stored energy of deformation. Recovery consists of all processes releasing stored energy without involving the movement of high angle grain boundary, for example by the formation of low angle subgrain boundaries through dislocations rearrangement. Grain coarsening can, in turn, be defined as processes involving the migration of grain boundaries driven solely by the reduction in the grain boundary area [51]. It is now universally accepted [52] that the new grains that formed during recrystallization do not nucleated by ‘atom by atom’ construction. On the contrary, the nuclei grow from the recovered subgrains or cells which are already present within the deformed material. As a consequence of this idea, the orientation of new grain arises from the same orientation present in the deformed state [52]. This, in fact has been confirmed to be true by experimental evidences. Nonetheless, the question arose over why only a minority of subgrains can successfully evolve into recrystallization nucleus. The reason lies in the fact that most of the subgrains possess small misorientation with the neighboring grains, hence are lack of mobility to evolve.

Accordingly, the typical nucleation sites comprise of locations with high local misorientations and mobility, which include [53]:

- i. pre-existing high angle grain boundaries;
- ii. misoriented ‘transition’ bands inside grains;
- iii. at highly misoriented deformation zones around large particles;
- iv. within highly misoriented regions within shear bands;
- v. within a very heavily deformed material, i.e. strain $>3\text{-}5$.

As has been reported by Humphreys and Hatherly [52], very large mobility differences between 100-1000 times, were found between low angle ($2-5^\circ$) and high angle ($>15^\circ$) grain boundaries. Another direct evidence was produced by Ferry and Humphreys [54], demonstrating the increase of the mobility in Al-0.05% Si subgrain boundaries of about 14 times when the misorientation increased from 2 to 5° , and 2500 times from 2° to high angle recrystallization boundaries on annealing at 300°C .

In achieving fine grain superplasticity, the importance of having high angle boundaries and large misorientation angles can never be overemphasized. Fine grains with high angle boundaries are capable of GBS during straining at optimum conditions. Wadsworth *et al.* have demonstrated that Al-Li based and tool steels [55, 56] that are initially non-superplastic attributed to their low angle boundaries due to hot working, can be made superplastic through appropriate thermal or thermomechanical treatment because of the transformation of low angle boundaries into high angle ones. Monzen *et al.* [57] also reported that boundaries with higher degree of atomic arrangement disorder have lower resistance towards boundary sliding.

2.2.5.2 Conventional Dynamic Recrystallization (DRX)

Dynamic recrystallization (DRX) refers to the occurrence of recrystallization during deformation. DRX involves both nucleation and grain growth (grain boundary migration) which takes place concurrently while the strain is being applied. It is now well established that the flow curves associated with DRX can be classified into either

cyclic or 'single peak'. Subsequently, it was shown that cyclic deformation indicates grain coarsening, whereas single peak flow curve indicates grain refinement [58].

To date, the mechanism surrounding the nucleation of DRX has yet to be fully identified. A question that always arises is 'low stored energy' versus 'high stored energy' nucleation. Research works that have been carried out so far for both FCC [59] and BCC [60] metals strongly suggest that low stored energy nucleation be involved. This is the case since at the high temperatures required for DRX, the highly stored energies developed during cold working cannot readily be harnessed. Accordingly, the subgrain coalescence mechanism associated with high stored energy nucleation is not active. On the contrary, strain induced boundary migration or other low energy mechanisms are expected to be playing a major role in DRX nucleation.

Furthermore, it has been reported [61] that the nucleation of DRX can be induced in the presence of sufficient quantities of hard second phase. This nucleation mechanism is known as 'particle stimulated nucleation' (PSN). The presence of sufficient hard second phase helps in raising the local dislocation densities and lattice curvatures above the critical levels needed for the initiation as well as propagation of DRX.

2.2.5.3 Continuous Recrystallization

In continuous recrystallization, refined grain structures may evolve homogeneously and gradually during the annealing of deformed metals, either with or without concurrent straining, even when the heterogeneous nucleation and growth stages of

primary recrystallization do not occur. The word ‘continuous’ refers to the homogeneous nature of the transformation of grain boundaries to high angle character. Continuous recrystallization has been observed most frequently in alloys rather than pure metals, often at relatively lower temperature than those associated with discontinuous or primary recrystallization. This is owing to the fact that discontinuous recrystallization is strongly hindered with decreasing temperatures [62].

To date, the underlying mechanisms of continuous recrystallization still remain elusive. A few mechanisms have been proposed to explain the role of recovery in high angle boundary formation during continuous recrystallization. These include subgrain growth via dislocation motion, the development of higher angle boundaries by the merging of lower angle boundaries during subgrain coalescence and the increase of boundary misorientation through accumulation of dislocations into the subgrain boundaries [63]. The above-mentioned processes have been projected to result in a gradual transition of boundary character and formation of high angle grain boundaries.

2.2.6 Fracture Modes of Superplastic Materials

The failure of superplastic materials during elevated temperature deformation can be caused either one of the two factors, namely macroscopic necking, and cavitations.

2.2.6.1 Macroscopic Necking due to Unstable Plastic Flow

Fracture by unstable flow or macroscopic necking results in materials pulling out to a fine point prior to fracture. During a uniaxial tensile test, any inhomogeneities present within the cross sectional area will generate strain localization, leading to more severe decrease in cross-sectional area as the test progresses. The growth rate of discontinuity at the cross-sectional area is governed by the rate of strain hardening and strain rate sensitivity index, m .

It is well recognized that for the metallic alloys, tensile ductility increases with an increase in strain rate sensitivity index [8]. A high m -value indicates a diffuse neck development and hence a delay on the onset of tensile failure, giving greater elongation-to-failure. This is because when m is high, neck forms gradually since the strain rate increases slowly due to the increase in stress within the neck region. In contrast, when m is low, the increase at the neck will result in a large increase in the strain rate within the region. Subsequently, the neck will grow sharply, leading to a sudden failure and lower elongation-to-failure.

Various researchers have derived a number of mathematical models that can be used to describe reasonably well the elongation-to-failure of superplastic metals which fail by necking [32]. These models are listed in Table 2-4.

Table 2-4. Various models to predict the necking phenomenon [32].

Reference	Equation	year	Remarks
Morrison	$\epsilon_f = bm^2 \frac{d_o}{L_o}$	1968	<ul style="list-style-type: none">• The dimensions of the specimen can influence the total elongation observed.• b is a material constant, d_o and L_o are the initial diameter and initial gauge length of specimen, respectively.
Avery and Stuart	$\epsilon_f = \left(\frac{1 - \beta^{1-m}}{1 - \alpha^{1-m}} \right)$	1968	<ul style="list-style-type: none">• The possible tapered shape of the specimen is taken into account.• α is ratio of the minimum to maximum area at the start of the test while β is the same ratio at some arbitrary stage of the test at which the elongation is measured.
Burke and Nix	$\epsilon_f = \left[\exp\left(\frac{2m}{1-m}\right) - 1 \right]$	1975	<ul style="list-style-type: none">• The influence of m on the neck growth in analyzed using finite element method.
Ghosh and Ayres	$\epsilon_f = \pm m \times \ln[1 \pm (f_o)^{1/m}]$	1976	<ul style="list-style-type: none">• The fracture strain can be expressed as a strong function of m.• f_o is the ratio of the initial effective load-bearing cross-sectional area of neck region to that of unnecked region.

where ϵ_f is elongation-to-failure and m is strain rate sensitivity

2.2.6.2 Cavitations

Superplastic deformation leads to large neck-free elongation, but many superplastic materials develop internal cavitation during deformation. Cavitations have been studied on many materials after superplastic deformation, such as aluminum, lead,

copper, titanium, zinc-aluminum eutectic alloys, stainless steel and MMCs [64-69]. Cavities usually nucleate at triple junctions of grain boundaries, grain boundaries, particles and even ledges on grain boundaries. Their subsequent growth, coalescence and interlinkage inevitably lead to the degradation of post-deformation properties and even the premature failure.

2.2.6.2.1 Cavity nucleation

During SPF forming, GBS is the dominative of mechanism. In order to maintain the structural integrity, GBS should be accommodated by the matter redistribution through diffusion or dislocation movement. If the accommodation process is not fast enough to accompany the boundary sliding, the stress concentration on boundaries may cause the nucleation of cavities. According to Raj and Ashby [70], under the stress σ , the stable cavity radius is, $r_c = 2\gamma/\sigma$, where γ is the surface energy. If the stress is similar to the applied stress, i.e., $\sigma \sim 10\text{MNm}^{-2}$, and $\gamma \sim 0.5\text{Jm}^{-2}$, then $r_c \sim 0.1 \mu\text{m}$. r_c could be less if cavity nucleates under stress concentration.

Supposing the condition of grain boundary diffusion stress relaxation, Stowell [71] proposed the critical strain rate:

$$\dot{\epsilon} = \frac{2.9\sigma\Omega\delta D_b}{kT\alpha dr_p^2} \quad (2-6)$$

where r_p is particle radius, d is the grain size, δD_b is the product of grain boundary width and diffusivity, α is the fraction of the total strain attributable to grain boundary sliding, Ω is the atomic volume, and k , T are the Boltzmann's constant and

temperature, respectively. This relationship predicts both microstructural and deformation parameter aspects to minimize cavitation. Supposing the stress relaxation is related to dislocation slip process, Perevezentsv [72] predicted that, starting with the largest particle when the threshold strain is exceeded, continuous nucleation during straining is expected.

Cavity nucleation relates to the microstructure such as grain size, type, volume fraction, interfacial energy and distribution of second phase particles, proportions and properties of the matrix phase and deformation parameters such as strain, strain rate, stress state and temperature. There is strong interaction between microstructure and deformation parameters [71, 72]. It is reported that the higher flow stress associated with larger grain sizes reduce the stable cavity size, making nucleation easier and the grain growth of Al alloys during superplastic deformation result in the continuous cavity nucleation [73].

2.2.6.2.2 Cavity growth

Cavities may grow during superplastic deformation through the stress-directed diffusion and plastic deformation of the surrounding matrix. When materials are deformed under the conditions where the optimum superplasticity is observed, the individual small void growth tends to be dominated by diffusion. Diffusion controlled growth is driven by the difference in chemical potential between an atom on the stressed grain boundary and on the free surface of the void, usually located along boundaries. The growth of small spherical cavities which are equi-sized and equi-

spaced is $dr/d\varepsilon \propto \sigma_l/r^2$, where σ_l is the maximum principal stress. It can be seen that the rate of growth will slow down rapidly as the cavity grows. If the new nucleation of cavities is limited during deformation, the cavity volume fraction is in proportion to the strain, i.e. $C_v \propto \varepsilon$. When the cavity grows to the size comparable to the grain size, d , additional mass transfer along grain boundaries will enhance the growth rate. This mechanism has been termed superplastic diffusion growth. It was reported that $dr/d\varepsilon$ is independent of cavity radius, and there is $C_v^{1/3} \propto \varepsilon$. [74].

Once the void attains a radius between 0.5 to 1.5 μm , contribution of diffusional flow to the cavity growth decreases dramatically and strain controlled growth dominates. For plasticity controlled growth, Hancock [75] reported that the rate of cavity radius increases linearly with cavity size and is independent of strain rate, i.e., $dr/d\varepsilon \propto r$.

hence, there is $C_v \propto \exp(\varepsilon)$ or

$$C_v \propto C_0 \exp(\eta \varepsilon)$$

where η is the cavity growth rate parameter and C_0 is a constant.

Following the analysis of Cock and Ashby [76], η can be expressed as:

$$\eta = \frac{3}{2} \frac{m+1}{m} \sinh \left[2 \left(\frac{2-m}{2+m} \right) \left(\frac{K}{3} - \frac{P}{\sigma_e} \right) \right] \quad (2-7)$$

where η is the cavity growth rate parameter, m , is the strain rate sensitivity, σ_e is equal to uniaxial flow stress, K is a constant, the value of which is dependent on test geometry and the extent of GBS, P is the imposed pressure. It has been shown that if

50% of the strain is attributable to GBS, then $K=1.5$ and 2.25 for the uniaxial and biaxial straining, respectively.

Wilkinson and Caceres [77] reviewed the models for the calculation of η recently, the growth rate parameter depends on the shape of the void as it grows, and different assumptions used in each model resulted in different relationships for this parameter. According to Cocks and Ashby [76], it predicts $\eta = 1.85$ when $m = 0.5$, $P=0$ and under uniaxial straining and shows that η increase as m decrease. Needleman and Rice [78] applied finite element analysis to calculate η , which led to $\eta \sim 1.22$. Wilkinson and Caceres [77] re-evaluated the model of Cocks and Ashby using a more realistic assumption of void shape, and led to the relation ship,

$$m = \frac{(1/f)[(1-f)^{-n} - 1]}{1 + (2a/h)[(1-f)^{-n} - 1]} \quad (2-8)$$

where f is the cavity fraction, $2a$ and h are the height of a cavity and cylinder height containing this cavity, respectively, and n is the stress exponent index. At small volume fraction, this result simplifies considerably to $\eta = n/m$.

The total cavity growth is the combination of diffusion control and plasticity control cavity growth. When the cavity is small the diffusion flow is the dominant contributor and once the cavity exceeds above $1\mu m$, plasticity controlled growth dominates. Combine mechanisms therefore exist between these two ranges, as shown in Fig. 2-3 [35].

Fig. 2-3. Schematic illustration of the variation in cavity growth rate with cavity radius for the relevant cavity growth mechanism [35].

2.2.6.2.3 Cavity coalescence and interlinkage

The experimental observations showed that the cavity size is usually significantly larger than the size that predicted by plasticity-controlled growth models. Though some of growth models [77, 79] predicted large growth rate parameter, it is suggested that the cavity coalescence plays a significant role in the cavity development, leading to the large η [80]. Pilling [80] proposed a model based on constitutive relationships for diffusive and plastic growth of void and considered the cavity coalescence effect,

$$\frac{\Delta r}{\Delta \varepsilon} = \frac{8V_f \phi(\Delta \varepsilon)(0.13r - 0.37(dr/d\varepsilon)\Delta \varepsilon) + (dr/d\varepsilon)}{1 - 4V_f \phi(\Delta \varepsilon)\eta\Delta \varepsilon} \quad (2-9)$$

where V_f is the instantaneous volume fraction of voids, η is the cavity growth rate parameter predicted by Cocks and Ashby model [76], $\delta\epsilon$ is a small increment of strain, $dr/d\epsilon$ is the rate of void growth per unit strain of an isolated void, and $\phi(\Delta\epsilon)$ is given by,

$$\phi(\Delta\epsilon) = (1 + \eta\Delta\epsilon/3 + (\Delta\epsilon/3)^2/27). \quad (2-10)$$

This model gives a good prediction of the cavity growth rate parameter for the AA 7475, while it gives an overestimate for Supral 220 [80]. This discrepancy can be explained in terms of the actual distribution of void size and their variation with strain in each material. The continuous nucleation of new cavities in the latter material reduces the average void radius. It is recognized that, at low volume fraction of voids, void coalescence has a negligible effect on the mean void growth rate. It becomes much more significant at volume fractions greater than ~ 0.05 [80]. After diffusive and plastic growth, coalescence is increasingly important once the void size reaches the grain size of the material.

2.2.6.2.4 Control of cavitation

In order to reduce the extent of cavitation at a given strain, decreasing the cavity growth rate parameter is a practical way, which is dependent on m and the imposed pressure. There is strong evidence [73, 81] that the increase of pressure reduces the rate at which the overall volume fraction of cavities increase with strain, decreases the level of cavitation for a given strain, displaces to a higher value of the strain at which

cavitation is first detected, and increases the strain to failure. According to Cocks and Ashby model [76], the imposed pressure required to prevent cavity growth during superplastic forming is $P \geq 0.5\sigma_e$ for uniaxial deformation and $P \geq 0.75\sigma_e$ for equibiaxial bulging. These predictions are broadly in agreement with experimental results.

The other way to minimize cavitation is to lower the pre-existing cavity ratio, C_o . It can be improved by the modification of material process such as the homogenization of the materials before SPF. Varloteaux *et al.* reported that annealing an aluminum alloy before deformation can lead to sintering of pre-existing cavities by diffusion [73].

These low levels of cavitation after superplastic forming without the use of an applied hydrostatic (back) pressure provide opportunities for the manufacturing of components which require strict control of cavitation levels to enable the desired mechanical properties to be obtained. G.J. Mahon, [82] reported that the material processing route influences the cavitation behavior of the materials. AA 7475 sheets of Waldman-type manufactured offer the higher application potential. The major benefit in using the Waldman route can be seen when the cavitation levels produced during biaxial forming are examined. Although with the decrease of sheet thickness the cavitation in the component is found to increase, the level of cavitation in the material of Waldman-type manufactured is much lower than that of the Rockwell-type [83].

The main feature in Waldman-type route is the lower number of larger size particles compared with Rockwell-type route [82]. In addition to the precipitate distribution, another feature of the microstructure not apparent is the amount of solute left in solid

solution after the heat treatment, since it has been suggested that this can also influence grain size as a consequence of recrystallization at shear bands produced during cold rolling.

Despite the similar grain sizes produced in the two materials, Waldman-type route provides materials with much lower susceptibility to cavitation [82]. This implies that the cavitation characteristics are not only controlled by the grain structure of the materials, but also by other mechanisms which are controlling the number of potential cavity nucleation sites in the two materials prior to superplastic forming. The matrix strength in the Waldman-type route will be lower as a consequence of deliberate solute removal from the matrix taking place during cooling down of heat treatment. This softer matrix implies that it will be easier to accommodate matrix flow in the vicinity of the large Fe-containing intermetallics, which is often associated with the large cavities after superplastic deformation. It is suggested that a softer matrix contributes in part to the low cavitation tendency of the sheet produced via the Waldman-type route by preventing microcavities opening up during cold rolling.

2.3 MICROTTEXTURE EVOLUTION

2.3.1 Grain Boundary Analysis

Grain boundary plays an important role in material properties. There are two important progresses in early 1980s which have radically changed the course of grain boundary research. The first one is the proposition of the concept of ‘grain boundary engineering’ or ‘grain boundary design’. Grain boundary engineering is the

exploitation of materials with boundary populations with super properties, in order to improve the overall properties of the materials. There have been some evidences of its application since grain boundary engineering was first introduced in 1984 [84-86]. However, progress towards understanding the fundamental aspects which underpinned grain boundary engineering is proceeding at a slower rate. The second process is the advent of superior experimental techniques that greatly facilitate the measurement of grain boundary in bulk polycrystalline. The most notable advancement is the development of Electron Backscattering Diffraction (EBSD), which is applied in SEM with minimal specimen preparation requirement. Recently, an exciting development is the automated capturing and indexing of an EBSD pattern. Using fully automated EBSD system thousands of boundaries can be analyzed, overcoming the traditional problem of small sample populations that may not provide statistically valid representations.

It is common in the literature for all the boundary properties, phenomena and behavior to be known as ‘grain boundary properties’. In practice, these are:

- Cavitation
- Corrosion
- Diffusivity
- Embrittlement
- Energy
- Fracture
- Migration
- Mobility

- Precipitation
- Resistivity
- Segregation
- Sliding

This grain boundary phenomenon categorization does not imply that each other is mutually exclusive. There is an underlying common dependency on boundary structure that links various manifestations of boundary behavior. All the phenomena listed above have sharp discontinuities in values for special boundaries, which have formed the subjects of many investigations. The response and behavior of a particular material grain boundary are a consequence of the following combination : (1) grain boundary geometry. (2) grain boundary solutes, and (3) extrinsic grain boundary structure. It has been suggested that the properties of boundaries are dependent more on the defect structure than on the perfect structure.

Migration and sliding are most important grain boundary phenomena concerning with the material creep and superplasticity. It is also important to know the position of the boundary plane. The position of the boundary plane is defined by the direction of its normal referenced to the crystal axes of both interfacing grains. The movement of a boundary parallel or perpendicular to its plane, i.e. grain boundary sliding and migration respectively, is a function of grain boundary mobility and in turn, diffusivity. Other important phenomena are precipitation, intragranular degradation and energy minimization.

In principle, five degrees of freedom is needed for geometrical description of a grain boundary, although the curvature of grain boundary plane will make the description more complex. The lattice misorientation between two neighboring grains and the orientation of the boundary plane account for three and two freedom, respectively.

Misorientation is most frequently expressed as an angle/axis pair, which involves one and two independent parameters for angle and axis respectively. Essentially, the axis of misorientation is a direction which has the same Miller indices in both grains, and the misorientation angle is the angle between the two grains by which one grain could rotate about the axis to make two grains superimposed. For the cubic crystal system there are 24 different symmetry-related ways in which the misorientation matrix, and in turn angle/axis, can be expressed. Usually, the misorientation is expressed by the solution which contains the lowest angle.

Misorientation is extensively used to describe grain boundary since it shows directly some elements of grain boundary structure. However, the determination of grain boundary plane normal is a more complex process. The current measurement technique of boundary plane normal is less accurate and time consuming. Therefore, reported data about microtexture and misorientation is scarce and semi-quantitative.

Another important way to characterize grain boundary is the coincidence site lattice (CSL). CSL refers to a three dimensional superlattice consisting of lattice points from the crystal lattices of two grains which are superimposed. A grain boundary is a two dimensional entity where two lattices conjoined; hence a CSL, common to both grains is physically applicable to describe a grain boundary. In theory CLS can be formulated

for any value of coincidence ration (Σ -value), however, only the relatively low Σ -value grain boundaries have physical significance to engender effects on its properties.

2.4 ELECTRON BACKSCATTERED DIFFRACTION (EBSD)

Electron Backscatter Diffraction (EBSD) is the most recently developed SEM based diffraction technique. A stationary electron probe impinges on a tilted sample of crystalline material in a scanning electron microscope. A diffraction pattern – the electron backscattering pattern-is formed on a phosphor screen placed near the sample. The phosphor screen is monitored by low light level television camera and the image passed to a PC for display and processing. By using of EBSD it is possible to collect and analyze large sample populations of individual orientations in an acceptable time span. The development of EBSD and its commercial availability as an addition to most SEM is a significant factor in the considerable interest that has been generated recently in the measurement of local texture [87].

2.4.1 Development of EBSD

The observation of backscatter Kikuchi patterns was reported in 1954. The potential of these Kikuchi patterns for the determination of microtexture was not fully appreciated until the 1970s when a series of papers by Venables and co-workers reported observing the patterns in an SEM, named them electron backscattering patterns and

showed that they had significant advantages over SACPS in the field of what they called 'microcrystallography'. The key advance which converted EBSD into a practical experimental tool occurred in the 1980s when Dingley implemented real-time imaging of the Kikuchi patterns with on-line computer interrogation, plus a more convenient method for determining the position of the pattern source points. The second crucial development was the implementation of a calibration routine whereby a crystal of known, standard orientation was mounted on a holder inclined precisely at a predetermined angle which was also used to mount the specimen [87].

Nowadays, EBSD is a well-accepted and important technique for obtaining crystallographic information in SEM. EBSD system is now commercially available as a package, consisting in its most basic form of low-light video TV camera control unit with foot switch and computer interface, a high resolution monitor, a microscope interface including phosphor screen, retraction mechanism, vacuum sealed window, camera mount and specimen mount, a calibration crystal and a software package.

2.4.2 Application of EBSD

2.4.2.1 Orientation

The physical properties of materials such as Young's modulus, hardness, plasticity, permeability, etc. are often anisotropic with respect to the crystallographic direction in which they are measured. Many materials, particularly after processing, possess a preferred orientation, known as a texture. EBSD can probe not only the proportions of

each orientation component present in a specimen, but also the distribution of these components in the microstructure. To date, the most common application for EBSD has been local orientation analysis of fabricated alloy products, where it is possible to follow the evolution of orientation, and related property changes, as a function of thermomechanical treatments.

2.4.2.2 Misorientation

An important consequence of measuring orientations on a site-specific basis using EBSD is that the orientations between crystals can be accessed—in other words, the grain or phase boundaries can be investigated if the orientations on either side of the interface are known.

2.4.2.3 Phase Identification

Using EBSD can also identify complex phases. Where EBSD is particularly useful, is to distinguish between phases having similar chemistries. For example, oxides, carbides or nitrides of an element may be difficult to distinguish on a chemistry basis in the SEM unless a calibrated, fully quantitative procedure is carried out. However, the crystallography of these phases can often be differentiated unambiguously.

2.4.2.4 Strain Assessment

The existence of strain in materials affects their properties such as tensile strength or toughness. By using EBSD, strain in the lattice can be manifested because strain blurs the Kikuchi lines in the diffraction.

2.4.2.5 True Grain Size

Traditional grain size measurements rely on observation of grain boundaries in an image of the microstructure. It has become apparent since the advent of EBSD that not all grain boundaries are revealed by the conventional etching route. This is especially true for the so-called ‘special’ boundaries, including twin and low angle boundaries. Heavily twinned microstructures, because of their complexity, are especially problematic for grain size measurements. Since a grain is defined essentially as a unit of uniform crystallographic orientation, EBSD is an ideal tool for grain size measurement.

2.4.2.6 Application Examples

The application of EBSD is still under exploration. Many researchers have already done good works in this area and materials involved include Al alloy, stainless steel, titanium alloy, Fe-Ni alloy, steels, etc. [88-91]. Unfortunately, the investigation of the microstructure of titanium alloys by using EBSD is limited.

Garmestani *et al.* [92] investigated the effect of superplastic deformation mechanism on texture of titanium alloy using EBSD technique. Pole figures of samples strained to 33%, 66%, 108% at 927°C with an initial rate of $2 \times 10^{-4} \text{s}^{-1}$ were studied. Bieler *et al.* [93] studied the microstructural evolution of Ti-6Al-4V alloy using EBSD and determined how microstructure develops by transformation from β to α .

2.5 SUMMARY

SPF of CP titanium alloy has not been given the appropriate amount of attention that the alloys deserve. In spite of the commercial success of CP titanium alloy, the knowledge about superplasticity of the alloy is still not well understood. The investigations of the superplasticity mechanism, related phenomena and microstructure evolution are important for achieving desired mechanical behaviors of the material. It would be fruitful to gain a profound understanding in the deformation behavior; deformation mechanisms and microstructural evolutions of CP titanium alloy at high temperatures in order fully exploit this alloy. Gaining a better insight of the elevated temperature deformation and the superplastic deformation capability of CP titanium alloy would prove worthwhile in encouraging more engineers and product designers to choose this alloy.

CHAPTER 3: EXPERIMENTAL PROCEDURES

3.1 MATERIAL

Commercially Pure titanium alloy sheet and Ti-6Al-4V alloy were employed in this studied. These materials have been cross-rolled to a thickness of 1.5 mm and annealed to achieve isotropic mechanical properties. The chemical composition of the two types of material is showed in Table 3-1 and the microstructure of CP titanium is showed in Fig. 3-1. In the initial state, the microstructure of the CP titanium alloy consists of all α -phase. The typical grain size is approximately 12.7 μm determined using the linear intercept method.

Fig. 3-1. Optical micrograph showing microstructure of initial sample.

Table 3-1. Composition of Commercially pure titanium alloy (wt%).

Element	C	Fe	N	Al	O	V	H	Ti
wt%	0.012	0.14	0.015	6.4	0.14	4.0	0.004	Balance
wt%	0.01	0.16	0.008	---	0.108	---	0.0015	Balance

3.2 HIGH TEMPERATURE TENSILE TEST

3.2.1 Specimen

The Samples for the tensile tests were electro discharged machined from the as-received material with the tensile axes oriented parallel to the rolling direction (Fig. 3-2). The geometry of the specimen is illustrated in Fig. 3-3. The gauge length and width of the specimen are 11 mm and 4 mm, respectively, while the thickness is 1.5 mm. Prior to testing, all specimens were polished using colloidal silica to remove scratches on the surface.

Fig.3-2. Illustration of the cutting direction of sample.

Fig.3-3. Illustration of the specimen geometry, sample thickness is 1.5mm.

3.2.2 High Temperature Uniaxial Tensile Test

Uniaxial tensile tests of CP titanium alloy were performed using Instron 8500 testing machine equipped with a electrical resistance furnace chamber. The furnace can heat up to temperature of 1000°C and maintains a temperature fluctuation of less than 5°C.

The tensile tests were performed in temperature range of 600°C, 750°C and 800°C at constant crosshead displacement velocity, with their corresponding initial strain rate from 0.0001/s to 0.1/s. The time required to raise the temperature to the desired value greatly depends on the test temperature, which could range from 50 to 90 minutes. To achieve the stabilization of temperature, test was started 3 minutes after the preset temperature had been reached. Prior to straining, the temperature of the specimen was further verified using a thermocouple put in contact with the gauge of the specimen. The variation of stress and strain was monitored continuously by a computer equipped with an automatic data acquisition system. All tests were repeated three times and the average values were calculated. Unless specifically noted, all the strains reported in this thesis are engineering strain rather than true strain.

3.3 OXYGEN PICK UP TEST

Oxygen pick up tests were carried out in air between 800 and 900°C for exposure periods up to 150 minutes. Samples employed in this experiment are the same as samples used in tensile tests. The surface of the sample were polished using 1000 grit sand paper followed by 30 minutes ultrasonic cleaning and degreasing in acetone. The

weight of each sample varies from 4.0 gram to 4.1 gram. After weighting, all samples were tied with a stainless wire and suspend within the furnace. Every 10 minutes, a sample will be taken out of the furnace to check the weight gain while the rests were still kept inside the furnace. Samples must be cooled and weight in 30 seconds in order to avoid moisture pickup. Acculab balance was used in this test, and the error can be controlled less than 0.001 grams.

3.4 MICROSTRUCTURE AND MICROTTEXTURE

3.4.1 Metallographic Examination

After tensile testing, the deformed specimens were cooled rapidly to room temperature by forced cooling in order to preserve the microstructure. The metallographic samples were prepared along L-T plane as shown in Fig. 3-4. Samples were cut from desired sections, mounted, ground, and polished by colloidal silica sequentially. They were then etched using reagent (10ml nitric acid +5ml hydrofluoric acid + 85ml distilled water) for 5 to 10 seconds. The metallographic samples were used for microstructure examination, grain size determination, and EBSD test.

Fig.3-4 Illustration of the specimen geometry.

3.4.2 Grain Size Measurement

The linear intercept method which can be used for counting equiaxial grains as well as distinctly no-equiaxed microstructures was employed. Images for measurement were first captured by optical microscope. Images were then sent for analysis using Image Pro+ software. The average grain size then was calculated from measurements on more than 500 grains, which were collected on more than 10 different regions.

3.4.3 Scanning Electron Microscopy (SEM) Examination

A JEOL JSM-5600LV scanning electron microscope (SEM) was employed to investigate the surface morphology of specimens. In order to increase the conductivity, samples were sputtered with a thin layer of gold. The SEM is also employed with an

Energy Dispersive X-ray spectroscopy (EDX) attachment which was used identify chemical elements and their compositions.

3.4.4 Microtexture Determination

EBSD test was performed using Leica360 with an attachment of TSL EBSD test system. EBSD samples were sectioned on L-T section on gauge part and the center plane of tensile specimen. The specimens were mechanically polished using 400-4000 grit papers. Final polishing was done by using colloidal silica. During polishing, care was taken to avoid surface deformation. This was achieved by using small pressing force (3 lbs). This is to reduce the influence of the surface smoothness and surface polishing residual stress of the sample on the corresponding Kikuchi pattern quality.

Fig. 3-5 shows the basic layout of the components of an EBSD system produced by TSL Instruments Microanalysis Group. The symmetry relationship and the calibration routine are illustrated in Fig. 3-6 and Fig. 3-7. In TSL system, a single crystal germanium having surface normal [001] is accurately positioned to the sample holder in order to keep the crystal normal coincident with the holder normal and [011] is positioned parallel to the X axis of the detector. The calibration method used in TSL relies on the movable phosphor screen relative to the specimen. During movement of the screen, the only point in the pattern whose coordinates remain unchanged is the PC, as illustrated on Fig. 3-6, and the distance can also be calculated by entering the known angular separation of the two zone axes of the screen, as illustrated on Fig. 3-7.

Fig. 3-5. Illustration of the components of a typical EBSD system.

Fig. 3-6. Illustration of the calibration method used in TSL system, i.e., calibration by change of screen position, the pattern center and sample normal could therefore be determined.

Fig. 3-7. Calibration of the distance between camera and sample; two zone axes of known angular separation used to calculate the camera to sample distance in the TSL system.

CHAPTER 4: SUPERPLASTIC BEHAVIOR OF COMMERCIALLY PURE TITANIUM ALLOY

4.1 INTRODUCTION

SPF is widely employed for the processing of complex shaped components of high strength materials, such as titanium alloys. Tests of superplastic property of materials have been carried out for many years. Extensive superplastic properties data are helpful to achieve successful SPF of the materials. Many researchers in the superplasticity area have published good reviews on the superplastic testing and property characterization of different alloys and ceramic [94, 95].

The most widely used methods to determine the superplasticity of a material are uniaxial and biaxial stress tests. The material behavior in the biaxial stress test is close to that of actual SPF processing. On the other hand, the uniaxial tensile test needs only simple setting up and usually can cover more extensive temperature and strain rate range. As the uniaxial test results generally show the similar tendency as the biaxial test results, it is therefore not surprising that uniaxial tests have been employed in most of the investigations on superplasticity.

In the present work, the uniaxial tensile tests were performed at 600, 750 and 800°C with an initial strain rate of 10^{-1} to 10^{-4}s^{-1} . The technique of conducting elevated temperature tensile testing has been described in detail in Chapter 3. The elongation-

to-failure of CP titanium alloy at different temperatures under constant strain rate are presented and discussed.

4.2 UNIAXIAL TENSILE TEST RESULTS

The results of high temperature uniaxial tensile test are presented in Table. 4-1 and Fig. 4-1.

Table 4-1. Summary of high temperature uniaxial tensile test results of CP titanium alloy.

Temperature (°C)	Strain rate (s ⁻¹)	Elongation (%)
600	0.1	90
600	0.01	155
600	0.001	188
600	0.0001	180
750	0.1	132
750	0.01	186
750	0.001	160
750	0.0001	127
800	0.1	131
800	0.01	132
800	0.001	133
800	0.0001	124

Fig. 4-1. Variation of elongation-to-failure as a function of strain rate at different temperatures.

4.3 DISCUSSION

It can be observed from Fig. 4-1 and Table 4-1 that there are two optimum conditions for deformation of this alloy. One is at 600°C with an initial strain rate of 0.001/s and another is at 750°C with an initial strain rate of 0.01/s. The elongations-to-failure values obtained under these conditions are 188% and 186% respectively. However, the values of elongation of all samples are not very high. In general, a material exhibiting elongation-to-failure in excess 200% when uniaxially loaded can be classified as superplastic. In other words, this material does not show good superplasticity under these conditions.

4.3.1 Grain Growth

The microstructures of the deformed samples were examined by optical microscope. Deformed specimens were sectioned along the L-T plane of the deformed sample as shown in Fig. 3-4. The microstructures of the grip and gauge section of sample deformed at different temperature are shown in Fig. 4-2 to Fig. 4-4 and the average grain size of different section of the deformed samples are shown in Table 4-2. Comparing the microstructures of these deformed samples with that of the as-received sample, two features are worthy of notice.

- 1) The first is that the grain size of the deformed sample is much larger than that of the as-received sample. At high temperatures (750°C and 800°C), grain sizes of this alloy dramatically grew even at a high strain rate (0.1/s). At a lower temperature (600°C), excessive grain growth also took place if the strain rate was very low (0.0001/s).
- 2) Another phenomenon is that the grain size of the gauge section is much smaller than that of the grip section. Many fine grains were found at the gauge region. These fine grains observed at the gauge region can be presumed as new grains that have been dynamically recrystallized under the influence of stress and elevated temperature. This assumption is valid since the isochronous grains at the grip section of the specimen that were not under the influence of stress coarsened.

Table 4-2 Average grain size of different sections of deformed specimen.

Test temperature(°C)	Strain rate (s ⁻¹)	Holding time (minutes)*	Grain size at gauge part (μm)	Grain size at grip part(μm)
600	1×10 ⁻¹	3.2	13.1	18.9
600	1×10 ⁻²	5.6	13.6	20.2
600	1×10 ⁻³	34.3	13.9	22.0
600	1×10 ⁻⁴	303.0	28.3	90.2
750	1×10 ⁻¹	3.2	34.0	87.1
750	1×10 ⁻²	6.1	39.1	105.6
750	1×10 ⁻³	29.5	41.2	113.0
750	1×10 ⁻⁴	231.3	43.6	140.6
800	1×10 ⁻¹	3.2	39.4	110.6
800	1×10 ⁻²	5.3	40.8	128.3
800	1×10 ⁻³	25.8	41.6	130.4
800	1×10 ⁻⁴	214.6	43.9	152.6

* Holding time does not include the heating time.

It is well accepted that the grain size plays a very important role during the superplastic forming. A fine and stable microstructure is the most basic requirements for materials to exhibit structure superplasticity. In this work, the characteristics of the static grain growth and dynamic recrystallization of the alloy were studied and discussed in Chapter 6 and 8. The term ‘dynamic’ is used here to describe the grain growth which occurs under the influence of stress, and also to differentiate it from the ‘static’ growth which takes place without straining.

Fig. 4-2. Optical micrograph of sample deformed at 800°C with an initial strain rate of
(a) 0.1/s, (b) 0.01/s, (c) 0.001/s and (d) 0.0001/s.

Fig. 4-3. Optical micrograph of sample deformed at 750°C with an initial strain rate of (a) 0.1/s, (b) 0.01/s, (c) 0.001/s and (d) 0.0001/s.

Fig. 4-4. Optical micrograph of sample deformed at 600°C with an initial strain rate of (a) 0.1/s, (b) 0.01/s, (c) 0.001/s and (d) 0.0001/s.

It is obvious that the grain growth took place not only during the deformation process, but also during heating up process. For the heating-up process, it took about 50, 80 and 90 minutes for the furnace to reach 600, 750 and 800°C, respectively. For the deformation process, the duration varies from 3 minutes to more than 300 minutes. In order to minimize the grain growth during heating-up process, “furnace pre-heating” is attempted in this study. Tests were carried out by first heating-up the furnace to the desired temperature, and then quickly setting the sample on the tensile machine. The tensile test was carried out 3 minutes after the preset temperature had been reached again. By using this method, the sample did not undergo the long heating-up process. So, the grain growth during the heating up process can be neglected.

Fig. 4-5 shows the elongation-to-failure values obtained by this method. The elongation-to-failure value obtained by the conventional method is also presented in this figure for comparison. It can be seen from this figure that only a very limited increase in elongation can be obtained by using the ‘furnace pre-heating’ method. The reason for this is that the material has a relatively high grain size in the as-received condition. As mentioned in early, the average grain size is 12.7 μm for the as received materials. The large grain size is not suitable for GBS, in view of the fact that only grains with an average size of less than 10 μm can be formed by GBS [8, 96]. On the other hand, the grain growth rate of this alloy is very fast, especially at high temperatures (750 and 800°C). Grain sizes of this alloy grow dramatically during the deformation process. This explains why the alloy does not show good superplasticity under the above-mentioned condition.

Fig. 4-5. Variation of elongation-to-failure as a function strain rate at different temperatures.

4.3.2 Cavitation

During SPF process, the presence of cavitation is often a concern because cavitation beyond a critical level is unacceptable due to its adverse effect on the properties [64]. It is well known that cavitation is observed in a large number of alloys such as aluminum, copper, zinc and ceramic and intermetallics [64-69]. It has been demonstrated that the mechanical properties of the materials would be significantly reduced when the cavity ratio exceed certain value, e.g., approximately 1%. In the present study, cavitation was observed in CP titanium alloy during SPF (Fig. 4-6). The nucleation of the cavities, their growth and coalescence lead to cavitation failure. However, in the present study, it was found that the cavity phenomenon is influenced by temperature. At high temperature, e.g. 750°C and 800°C, no cavitation was found in the deformed samples. Detailed investigations into the cavitation phenomenon as well as related mechanisms and its effect on the superplasticity of the CP titanium alloy will be discussed in the Chapter 7.

Fig. 4-6. Optical microstructure of the sample deformed at 600 °C with an initial strain rate of 0.001/s.

4.3.3 Oxidation

It is well accepted that titanium alloy will be oxidized when exposed at high temperature. SEM picture of the deformed sample shows that oxide film had been formed on the surface of the commercially pure titanium as shown in Fig 4-7 (a). XRD analysis shows that the oxide film consisted of TiO_2 (Fig 4-7 (b)). In the present study, the oxidation behaviour of the CP titanium alloy as well as its effect on the superplasticity of the alloy is discussed in Chapter 5.

Fig. 4-7. (a) SEM image and (b) XRD analysis of the of oxide film.

4.4 SUMMARY

Uniaxial tensile tests were conducted at different temperatures to investigate the superplasticity of the CP titanium alloy. Due to the fast grain growth and cavitation phenomena, the alloy does not show good superplasticity. The maximum elongation obtained at 600°C with an initial strain rate of 0.001/s and 750°C with an initial strain rate of 0.01/s. It is also found that dynamic recrystallization can be found on the gauge section of the deformed samples. Another interesting phenomenon is that oxide film is formed on the surface of the alloy.

CHAPTER 5: EFFECTS OF OXIDATION ON THE SUPERPLASTIC BEHAVIOR OF TITANIUM ALLOYS

As discussed in Chapter 4, during high temperature deformation of the CP titanium alloy, oxide film can be found on the surface of the sample. In this chapter, the studies focus on the oxidation behavior of the titanium alloys as well as its effect on the superplasticity of the titanium alloys. A coating method is also attempted to increase the ductility of the titanium alloys during high temperature deformation.

5.1 OXIDATION BEHAVIOUR

5.1.1 Experimental Procedural

In order to get a better understanding of the effect of oxidation on the ductility of the titanium alloys, not only the CP titanium alloy, but also Ti-Al-4V titanium alloy were chosen to study in the present study. The sample preparation has been detailed in chapter 3. One group of samples was tested in an atmosphere of argon (Ar) while another group was tested without any inert gas protection. When using argon protection, the Ar flowed in from the bottom of the furnace by an inlet as showed in Fig. 5-1. The Ar inflow rate is 20L/ min. After testing, the formed specimen was cooled rapidly to room temperature to by forced cooling in order to preserve the microstructure.

Fig. 5-1. Schematic diagram of the furnace set.

5.1.2 Results and Discussion

The variation of elongation-to-failure values of CP titanium and Ti-6Al-4V alloy as a function of strain rate of the two groups of samples are shown in Fig. 5-2 and Fig. 5-3 respectively. These results clearly indicated that the tensile elongations of samples deformed under Ar protection are higher than that of those without Ar protection at all temperatures for all the two type alloys. This is an obvious evidence that oxidization can degrade the ductility of the titanium alloys. It is also noted that the difference in elongation-to-failure between Ar-protected and without Ar protection samples is influenced by temperature and initial strain rate. At lower temperatures (600°C for CP titanium alloys) or high strain rate (10^{-1}s^{-1}), the difference is small, at a high temperature (900°C for Ti-6Al-4V alloy) or low strain rate (10^{-3}s^{-1}), the difference is large.

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Fig. 5-2. Variation of elongation-to-failure value of CP titanium alloy as a function of strain rate at (a) 600°C, (b) 750°C and (c) 800°C.

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Fig. 5-3. Variation of elongation-to-failure value of Ti-6Al-4V alloy as a function of strain rate at (a) 800°C, (b) 850°C and (c) 900°C.

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Fig. 5-4 and Fig. 5-5 show the variation in ultimate tensile strength and yield strength of the two types of alloy as a function of strain rate for different testing temperatures. It can be seen from these figures although oxidation has an obvious influence on the ductility of the CP titanium and Ti-6Al-4V alloys, it has little effect on the Ultimate Tensile Strength (UTS) and yield strength of these alloys (Fig. 5-4 and Fig. 5-5). From these figures it is apparent that the UTS and yield strength remains almost unaffected. This would mean that the strain-rate-sensitivity coefficient, m , would remain unchanged.

Fig. 5-4. (a) Variation of UTS and (b) yield strength of CP titanium alloy as a function of strain rate at different temperatures.

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Fig. 5-5. Variation of (a) UTS and (b) yield strength of Ti-6Al-4V as a function of strain rates at different temperatures.

5.1.2.1 Characterization of the Oxide Film

It is well known that when titanium alloy is exposed to the atmosphere at high temperature, oxidation will happen on the surface of the alloy [17, 18]. Fig. 5-6 shows the optical micrographs of the cross section of the deformed Ti-6Al-4V and CP titanium alloy. It is clear from these pictures that a thick layer of oxide film was found on the surface of sample. For the Ar protected samples, no such oxide layers were found on the surface. At room temperature, the oxide film formed on the surface of titanium alloys is a very stable, self-healing film. However, at high temperature, the film is not dense. Inspection at a higher magnification (Fig. 5-7) shows that there are many small cavities and microcracks inside the oxide film.

Fig. 5-6. Optical micrograph of oxide film on the surface of (a) Ti-6Al-4V and (b) CP titanium alloy.

Fig. 5-7. Optical micrograph of oxide film on the surface of Ti-6Al-4V.

The weight gains observed for the two alloys plotted against exposure time between 600 and 900°C are displayed in Fig. 5-8. It can be deduced from this figure that the thickness of oxide film is influence by exposure time and temperature. The higher the temperature or the longer the exposure time, the thicker the oxide film.

Fig. 5-8. Weight gains against time for Ti-6Al-4V and CP titanium alloy oxidized in air between 600°C and 900°C.

In order to obtain a better understanding of the oxidation materials, the oxide film that formed at high temperature was examined. Fig. 5-9 shows the EDX analysis of the oxide film that formed on the surface of the CP titanium alloy. XRD analysis of oxidized samples for different exposure periods and temperatures identified the presence of only TiO_2 (rutile) as shown in Fig. 5-10. However, for the Ti-6Al-4V alloy, according to [17], the oxide film consisted of mostly $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 (rutile). Fig. 5-11 shows the SEM picture of the cross section of the oxide film that formed on the surface of Ti-6Al-4V. It is noted from this picture that many white needle-like materials scattered in the gray substrate. EDX quantitative spot measurements were made to detect the chemical composition of the white and gray areas. It can be concluded from analysis that the white material is Al_2O_3 . For the gray material, according to Frangini [17], it is highly likely that it is VO_3 dissolved in the TiO_2 . Fig. 5-12 represents the EDX mapping result for the cross section of the oxide film of Ti-6Al-4V alloy. The result showed that the Al element distribution is almost homogeneously all over the oxide film. There was no evidence of the formation of alternate layers of TiO_2 and Al_2O_3 that was described by Du *et al* [17].

Fig. 5-9. EDX analysis of the oxide film formed on the surface of CP titanium.

Fig. 5-10. XRD analysis of the oxide film formed on the CP titanium.

Fig. 5-11. SEM micrograph of oxide film formed on the Ti-6Al-4V.

Fig. 5-12. EDX Mapping of the oxide film formed on the Ti-6Al-4V.

Further investigations indicated that at the early stage of oxidation, a thin film of TiO_2 (rutile) would develop quickly as soon as the titanium alloys were exposed to air at high temperature. Once the film was formed, the substrate would be separated from its environment. However, as the oxide film is not dense, oxygen can still diffuse inward and react with titanium to form TiO_2 or $\text{TiO}_2 + \text{Al}_2\text{O}_3$. As a result, the thickness of the oxide film increases with increasing exposure time.

With the growth of the oxide film, the issue of how the oxide film and substrate would keep good contact needs to be addressed. At the initial stages of oxidation, it is possible to maintain contact between the oxide film and substrate by plastic flow of the oxide film. Since the plasticity of the oxide film is limited, cracks would form between the oxide film and the substrate once a critical thickness of the oxide film is exceeded. The stress caused by mismatch in expansion coefficients between the oxide film and the substrate can be released by cracking initially at the edge of the specimen and then expanding progressively through the entire specimen surface. Once such crack is formed, a new layer of TiO_2 will quickly form on the substrate. This layer would again separate the substrate from its environment in the crack where the conditions might be similar to the bulk atmosphere. Oxygen from the outside would again diffuse inward and react with the substrate to form TiO_2 and Al_2O_3 . As a result, the oxide film observed under optical microscope consists of many layers as shown in Fig. 5-13. The oxidation mechanism of the titanium alloys is schematically described in Fig. 5-14.

Fig. 5-13. Optical micrograph of the cross section of the oxide film formed on the surface of CP titanium alloy.

Fig. 5-14. Schematic illustrating the oxidation process of CP titanium alloy.

5.1.2.2 Modeling for “Stress Oxidation Cleft”

Since the oxide film is very brittle, it cannot be elongated as much as the substrate. During tensile testing, clefts were formed on the oxide film as shown in Fig. 5-15. It is also noted from Fig. 5-15(a) that all the clefts formed approximately at right angles to the direction of the tensile stress. The substrate adjacent to the cleft was exposed to air and the substrate was subjected to further oxidation (Fig. 5-15(b)). So, the clefts tended to propagate. As the cleft penetrates further into the materials, it eventually reduces the supporting cross section of the material to the point of structure failure from overload. This explains why the two types of titanium alloys tend to exhibit lower ductility as compared to Ar-protected samples at high temperatures. On the other hand, the propagation of the “stress oxidation cleft” depends on temperature and exposure time. For low temperatures or fast strain rates tests, failure occurs before the surface nucleated clefts penetrate significantly. This would explain why the difference in elongations value between Ar protected samples and those without Ar protection sample is small at low temperatures or fast strain rates. However, during tensile testing, both the UTS and yield strength are recorded at the early stage of the process. Bearing in mind that at this stage the oxide film is very thin when compared with the thickness of the metal sheets, and the cleft has not been formed on the surface of the sample, so it has little or no influence on the UTS and yield strength. On the other hand, once the cleft is formed, it will decrease the strength of the alloy and this is shown in Fig. 5-16. It can be seen from Fig. 5-16 that at the early stage of the deformation, the difference in stress between two CP titanium samples is very limited. However, at the later stage of the deformation, because some clefts have been formed

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on the surface of the specimen, the stress of the sample which is protected under Ar is higher than that of sample without Ar protecton; and the difference in the stress experienced by them increase with increasing strain.

Fig. 5-15. Clefts on the surface of the oxide film.

Fig. 5-16. Stress-displacement curve of CP titanium samples deformed at 800°C with an initial strain rate of 0.001/s.

Based on the above-mentioned observations and analysis, a schematic illustration for cleft initiation and expansion when deformed at high temperatures without Ar protection is shown in Fig. 5-17.

Fig. 5-17. Illustration of (a) oxidation (b) cleft initiation and (c) cleft propagation during high temperature tensile test without Ar protection.

Supposing that the oxide film has been formed on the surface of the titanium alloy, as shown in Fig. 5-17(a), under tensile stress, an initial cleft will be formed in “A” area and the area “B” in the substrate will be further oxidized (Fig. 5-17(b)). The cleft will further propagate approximately at right angles to the direction of the tensile stress (Fig. 5-17(c)) and area “C” will be further oxidized.

In order to verify the proposed model, the observations in this work were limited to the sample tested at initial strain rate of $10^{-3}/s$ at $900^{\circ}C$. Inspection of cleft characteristics in the center portion of the specimen strained to 150% showed that cleft had formed and penetrated to the substrate as shown in Fig. 5-18. The direction of the cleft is perpendicular to the stress direction. No such cleft was observed in the samples that protected with Ar. This supports the model proposed here.

Fig. 5-18. Illustration of initial cleft during high temperature tensile test.

5.2 PREVENTION OF OXIDATION IN Ti-6Al-4V DURING SUPERPLASTIC FORMING USING THERMAL SPRAYING

As discussed in the previous section, oxidation on the surface of titanium alloy can cause oxide film and degrades the ductility of the alloy. In order to prevent oxidation, superplastic deformation of these alloys can be carried out under Ar protection. Although this method can protect titanium alloys from oxidation during SPF processes, it greatly increases the cost of the processing and needs complicated equipments. In this section, oxygen barrier coating were applied onto the surface of Ti-6Al-4V alloy prior to superplastic forming by plasma spray and the effects of the coating on the mechanical properties were studied.

5.2.1 Plasma Spray

Zircon (ZrSiO_4 or $\text{ZrO}_2 \cdot \text{SiO}_2$) was selected as the candidate material for the coating layer due to its excellent thermal shock resistance and corrosion resistance. A layer of Zircon coating layer was applied onto the surfaces of Ti-6Al-4V sheets using SG100 Plasma System. Operating Parameters for spraying are listed in Table 5-1. The average thickness of the coating layer is about $25\mu\text{m}$.

Table 5-1 Operating Parameters of the Plasma Spray

Flow of Argon	65 scfh
Flow of Helium	58scfh
Flow of powder carrier gas (Ar)	20scfh
Spray distance	120mm
Net energy	12kW
Power feeding rate	15g/min

5.2.2 Room Temperature Tensile Tests

The uniaxial tensile tests were carried at 800, 850, 900°C and room temperature with initial strain rate from 10^{-1}s^{-1} to 10^{-4}s^{-1} . Fig. 5-19 shows the comparison of UTS, yield strength and percentage elongation between the uncoated and coated samples at room temperature. It can be observed that the coating layer has little or almost negligible effect on the various properties of Ti-6Al-4V alloy at room temperature. The properties themselves also remain relatively constant through the different strain rates.

Fig. 5-19. Variation of (a) UTS, (b) yield strength and (c) elongation as a function of initial strain rate at room temperature

5.2.3 High Temperature Tensile Tests

The results of tensile tests at elevated temperatures are presented in Fig.5-20. The elongations of samples without coating and samples with Ar Protection are also showed in this table for comparison. The pictures for these samples before and after test are showed in Fig.5-21.

Fig. 5-20. Variation of elongation-to-failure value of different samples as a function of strain rate at (a) 800°C, (b) 850°C and (c) 900°C.

Fig. 5-21. (a) Tensile specimen (I) Uncoated and (II) Coated tested at 800°C and strain rate (/s) of: (B) 0.1, (C) 0.01, (D) 0.001 and (E) 0.0001 in comparison to (A) untested specimen. (b) Tensile specimen (I) Uncoated and (II) coated tested at 850°C and strain rate (/s) of: (B) 0.1, (C) 0.01, (D) 0.001 and (E) 0.0001 in comparison to (A) untested specimen. (c) Tensile specimen (I) uncoated and (II) coated tested at 900°C and strain rate (/s) of: (B) 0.1, (C) 0.01, (D) 0.001 and (E) 0.0001 in comparison to (A) untested specimen.

Upon closer analysis of the Fig. 5-20, it can be seen that the elongations of coated samples are higher than those of uncoated samples at all temperature for all strain rates. The difference in % elongation between coated samples and uncoated samples is influenced by temperature and initial strain rate. At a lower temperature (800°C) or a high strain rate (10^{-1}s^{-1}), the difference is small, at a higher temperature (900°C) or a low strain rate (10^{-4}s^{-1}), the difference is large. A possible reason for this could be due to the success of the zircon coating in preventing the formation of oxide film during the high temperature conditions of the tensile tests.

Fig. 5-22. Pictures of samples (a) before and (b) after exposing to air at 900 °C.

Fig 5-22 shows the pictures of two types of samples before and after exposing to air at 900°C for 60 minutes. It clear shows that oxide film has been formed on the surface of uncoated sample while no obvious change occurred on the surface of the coated sample. The optical micrograph shows that no oxide film was observed under coated layer (Fig. 5-23). This is a good support that the Zircon coated layer can prevent oxidation at high temperature.

Fig. 5-23. Optical micrograph showing coated layer after air oxidation at 900°C.

As discussed in the previous section, oxidation can cause oxide film on the surface of titanium alloy and render clefts nucleated in these areas under tensile stress. Relatively low ductility of the uncoated specimen is due to the propagation of clefts nucleated in oxide film as illustrated in Fig. 5-15. Elsewhere, in a study involving titanium alloy, it has shown that transgranular cracks developed in the oxide film did not penetrate significantly beyond the oxide film in creep test of relatively short duration [18]. In other words, for short duration tests, failure occurs before surface nucleated clefts penetrate significantly beyond the oxide film. On the other hand, when samples deformed at low strain rates, clefts have enough time to propagate. This explains why the difference in elongation between coated and uncoated samples is relatively small when deformed at high strain rate. Also, at low temperature, the oxidation on the surface is not as serious as at high temperature because the thickness of oxide film is determined by exposing temperature. The possibility of generation of clefts on oxide

film areas is relatively low. This explains why the difference in elongation between coated samples and uncoated samples is relatively high when tested at high temperatures.

Fig. 5-20 also indicates that the % elongations of coated samples is not as high as that of those with Ar protection at high temperature with an initial strain rate of 10^{-2}s^{-1} . The difference in elongation between Ar protected samples and coated samples is 2%, 16%, 21% at 800, 850 and 900°C respectively. Further investigation on the coating surface behavior during tensile test indicated that when samples strained over 300%, surface cracks will form on the coating layers.

Fig. 5-24 is the picture of the coated layer of the sample strained to 350% at 900°C with a strain rate of 10^{-3}s^{-1} . Areas “A” are the coating layer and “B” areas are the crack area. EDX analysis on the two areas indicates that significant oxygen appears in crack area. This indicates that oxygen has invaded into the substrate through the crack. Fig. 5-25 is optical micrograph of cross section of the sample. It clearly shows that oxygen rich phase has been formed in the crack area. Compared with the substrate; the ductility of the coated layer is very limited. During tensile test, when the substrate elongated, the coated layer cannot keep up with the substrate. Due to the mismatch in elongation between the coating surface and substrate, cracks will form on the coating layer and lead the substrate exposing to air. Oxide film will form in these areas and these oxygen rich phases will cause cracks. This process is illustrated in Fig. 5-26. This explains the reason why the % elongations of coated samples are lower than that of Ar protected samples. In other words, the coated layer can not protect the substrate from oxidation all the time all over the surface. However, it can protect all the

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substrate at the early stage and part of the surface all the time during high temperature tensile test. From this point, the advantage of this method is obvious. Despite the crack problem on the coated layer, the coating method still protects substrate from oxidation in a great degree and increases the elongation during high temperature tensile tests.

Fig. 5-24. Picture of the surface of the coated sample deformed at 900°C.

Fig. 5-25. Optical micrograph of coated sample strained to 350% at 900°C with a strain rate of 10^{-3}s^{-1} .

Fig. 5-26. Illustration of the crack formation process on the coating surface (a) Sample strained 300%. (b) Sample strained over 300%.

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Variation in ultimate tensile strength and yield strength, as a function of strain rate is shown in Fig. 5-27. It is apparent that the difference in UTS and yield strength is very small at all temperatures. The result is reasonable, because compare with the thickness of the sample, the thickness of the coating layer and oxygen rich zone is very thin; they have little or no influence on the overall mechanical properties.

A logarithmic plot of yield stress versus strain rate at different temperature is performed (Fig. 5-28). The strain rate sensitivity index, m , which can be determined by the slope of the curves, shows no significant difference between the coated and uncoated samples at all test temperatures. This means that the both the coated and uncoated samples could be deformed by the same superplastic mechanisms and the mechanisms do not change with the coating.

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Fig. 5-27. Variation of (I) UTS and (II) yield strength as a function of strain rate at (a) 800, (b) 850 and (c) 900°C.

Fig. 5-28. Graph of Log (Yield stress) vs Log (Strain rate) for (a) 800, (b) 850 and (c) 900°C.

5.2.4 Superplastic Forming Test

Superplastic forming test was performed using a Murdock 140-10001 100 ton press. The coated and uncoated sheets were formed in a conical die at 980°C with a constant argon press of 1.3 MPa for a period of 30 minutes. The parameters used during forming are shown in Table 5-3. After forming, the coating layer was then removed with 5% HF.

Table 5-2. Operating parameters for the superplastic forming process.

Temperature	980°C									
Ram force	500psi									
Time (mins)	1	2	3	4	5	6	12	18	24	30
Upper psi	10	20	35	50	65	80	150	220	290	300

Fig. 5-29 shows the pictures of two formed cones of both coated and uncoated Ti-6Al-4V. For the uncoated sheet, oxide film formed on the bare Ti-6Al-4V sheet. However, in the case of the coated sheet, the original bright surface finish is retained simply by cleaning the coating layer with 5% HF. EDX analysis shows that the cleaning process removes the coating entirely, leaving a surface identical to that of pure Ti-6Al-4V alloy (Fig. 5-30).

Figure. 5-29. Superplastic Formed cones: coated (left) and uncoated (right).

Fig. 5-30. EDX analysis of cleaned Ti-6Al-4V.

An interesting point about the cleaning process that warrants further investigation. According to [18], during the spraying process, zircon will dissociate into ZrO_2 and SiO_2 and the as-sprayed coating comprised of zirconia and silica. It has documented that zirconia is reactive to both hydrochloric acid as well as nitric acid. However, various concentrations of these two particular acids fail to remove the coating.

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Hydrofluoric acid, on the other hand, removes the coating even at very low concentrations. Within the coating, only the silica constituent is susceptible to hydrofluoric acid.

The question remains as to why HF acid succeeds in removal of the coating while the other two acids fail. One possibility is that silica forms the base of the coating, with the zirconia component bonded to this silica. Hence once the silica base is dissolved by the hydrofluoric acid, the zirconia is washed away as well, leading to the removal of the coating.

5.3 CONCLUSIONS

In this study, the oxidization behavior of the titanium alloys and its effects on the superplasticity of the alloys have been investigated. Zircon coating layer was applied onto the surface of Ti-6Al-4V alloy by plasma spraying prior to superplastic forming and the effects of the coating layer on the mechanical properties of Ti-6Al-4V were also studied. The following conclusions have been made.

1. When exposed to air at high temperatures, oxide films will form on the surface of the titanium alloys. The thickness of the oxide film increase with increased exposure time and temperatures.
2. Oxide film on the surface of the titanium alloy can induce “stress oxidation clefts” and decrease the ductility of the alloy and this is significant at high temperatures. However, the oxide film has only a little effect on the UTS and yield strength of the alloy.
3. Coating layer can protect the substrate from oxidation and increase the elongation-to-failure value of the Ti-6Al-4V alloy. The coating layer has little effect on the UTS and yield strength of the alloy at all temperatures and it could be easily removed by 5% HF after forming to reveal the original metallic surface finish.

CHAPTER 6: STATIC GRAIN GROWTH OF COMMERCIALLY PURE TITANIUM ALLOY

As discussed in Chapter 4, average grain size of the deformed sample is much larger than that of the as-received sample. Especially at high temperatures (750°C and 800°C), the grains grow dramatically even at a high strain rate (0.1/s). At a lower temperature (600°C), excessive grain growth can also take place if the strain rate is very low (0.0001/s). In this chapter, the studies focus on the static grain growth of the alloy at different temperatures.

6.1 TEMPERATURE DEPENDENT OF STATIC GRAIN GROWTH

Static grain growth was performed by heating up the specimens in the furnace to the specified test temperature and held for 1.0 hour. The specimens were then quenched in water to preserve the microstructures. Images for measurement were first captured by optical microscope. Images were then sent for analysis using Image Pro+ software. The average grain size then was calculated from measurements on more than 500 grains, which were collected on more than 10 different regions. The purpose of this test is to investigate the thermal stability of the CP titanium alloys at different temperatures.

Fig. 6-1 (b) to (d) depict the microstructures of samples exposed to 600, 750 and 800°C for 1.0 hour. For comparison reasons, microstructure for the as-received CP

titanium alloy is also presented in Fig. 6-1 (a). From Fig. 6-1, it can be seen that the grains are thermally unstable and highly dependent on the temperature. Fig. 6-2 shows the average grain size of these samples and it can be seen from this figure that grain growth of the CP titanium alloy is very fast. The average size increased to 30.1, 120.2 and 130.1 μm when test temperatures were at 600, 750 and 800°C, respectively. These data also give us an indication that grain growth at 600°C is less obvious compared to exposure at 750°C and 800°C.

Fig. 6-1. Microstructure of (a) as-received and samples exposed to (b) 600 (c) 750 and (d) 800°C, for duration of 1 hour.

Fig. 6-2. Average grain size of samples exposed to different temperatures for 1 hour.

6.2 TIME DEPENDENCE OF STATIC GRAIN GROWTH

During the superplastic deformation process or elevated temperature tensile test, the superplastic alloys need to be heated up to the optimum deformation temperature which takes a specified period of time. In the previous section (section 6.1), it has been demonstrated that CP titanium alloy is thermally unstable at high temperature and therefore, during this heating process the material will experience static grain growth. And in the following section, studies are focused on the time dependence of static grain growth.

Chapter 6

Static Grain Growth of Commercially Pure Titanium Alloy

To investigate the time dependence of static grain growth, test specimens were exposed to 600, 750 and 800°C for exposure periods up to 5 hours. Every 10 minutes, a sample is taken out from the furnace and quenched. The microstructure is studied and the average grain size is calculated and plotted. Typical microstructural evolutions for the exposure time of 30, 60, 90 and 120 minutes at different temperatures are shown in Fig. 6-3, Fig. 6-4 and Fig. 6-5 respectively.

Fig. 6-3. Optical microstructure of CP titanium at 600°C when exposed for a period of (a) 30 (b) 60 (c) 90 (d) 120 minutes.

Fig. 6-4. Optical microstructure of CP titanium at 750°C when exposed for a period of (a) 30 (b) 60 (c) 90 (d) 120 minutes.

Fig. 6-5. Optical microstructure of CP titanium at 800°C when exposed for a period of
(a) 30 (b) 60 (c) 90 (d) 120 minutes.

The variation of average grain size against holding time at different temperatures is showed in Fig. 6-6.

Fig. 6-6. Variation of average size against exposure time at different temperatures.

From the above discussion, it can be seen that the microstructure of the CP titanium alloy is not thermal stable and the grain growth is very fast at high temperatures. In this work, tensile specimens took approximately 50, 80 and 90 minutes (3000s) for reaching 600, 750 and 800 °C. Excessive Grain growth would take place during this period. It is well accepted that a fine and stable microstructure is one of the most basic requirement for a material to exhibit structural superplasticity [9]. The large grain size is not suitable for grain boundary sliding (GBS), in view of the fact that only grains with an average size of less than 10μm can deform by GBS [8, 96]. This is one of the reasons why the alloy does not show good superplasticity during high temperatures deformation.

CHAPTER 7: CAVITATION PHENOMENON OF COMMERCIALLY PURE TITANIUM

7.1 INTRODUCTION

It is well-established that during superplastic deformation most materials develop cavities, which grow and coalesce, leading to cavitation damage [64, 66, 97-107]. Such damage in turn gives rise to premature failure of the material, thereby, limiting the use of superplastically formed components. For the CP titanium alloy, as mentioned in Chapter 4, cavities can be found on the samples deformed at 600°C. However, for samples deformed at relatively high temperatures (750 and 800°C), no cavities can be found. These results give an indication that the cavitation is temperature dependent. In this chapter, we report and analyze experimental data obtained in an investigation that focuses on the detailed quantitative evaluation of cavitation of the CP titanium alloy during tensile test. The effect of temperature on the cavitation phenomena as well as related mechanisms are investigated.

7.2 EXPERIMENTAL DETAILS

In order to investigate the effect of temperature on the cavitation behavior. Uniaxial tensile tests were performed at room temperature, 400°C, 600°C, 750°C and 800°C with an initial strain rate of 0.01/s. Deformed specimens were sectioned along the L-T plane of the deformed sample as shown in Fig. 3-4. The specimens were polished by silica paste and electro polished by using 90% Acetic+10HClO₄. For optical studies,

samples were etched using 10%HF+5%HNO₃+85%H₂O for 5 seconds. In the present work, cavitation ratio measurements were conducted on the top area of deformed samples as shown in Fig. 7-1. Images for cavitation ratio measurement were first captured by optical microscope. Images were then sent for analysis using Image Pro+ software. The cavitation ratio was calculated by dividing the cavity area by the total image area. In the present study, only cavities larger than 0.5 μm were counted, to reduce measurement errors.

Fig. 7-2. Schematic of the deformed tensile specimen. Cavitation ratios are investigated on the shaded area of interest.

7.3 RESULTS AND DISCUSSION

7.3.1 The Effect of Temperature on the Cavitation Ratio

The variation of cavitation ratio against temperatures is shown in Fig. 7-2 and optical micrographs of the specimens deformed to failure are shown in Fig. 7-3. It can be seen from these figures that many cavities can be found on the sample deformed at deformed at room temperature, 400°C and 600°C. These cavities are randomly

Chapter 7 Cavitation Phenomenon of Commercially Pure Titanium

distributed and the cavity size varies over a wide range. Fig. 7-2 indicates that the cavitation ratio decreases with increasing test temperature and when then temperature above 750°C, the cavitation ratio decreases to zero. The maximum cavitation ratios are 5.2%, 4.3%, 0.55% for samples deformed at room temperature, 400°C and 600°C respectively.

Fig. 7-2. Variation of cavitation ratio against temperature.

Fig. 7-3. Microstructure of samples deformed at (a) room temperature, (b) 400°C, (c) 600°C, (d) 750°C and (e) 800°C.

7.3.2 Cavity Formation and Growth

In order to identify the cavitation ratio and cavity initiation sites, detailed quantitative evaluation of cavitation was conducted. Samples were strained to different strain levels at different temperatures and the cavities were studied from the center of the gauge. Fig. 7-4 shows the SEM micrograph of the samples strain to 15% at 400°C. These pictures show that cavities are formed along the grain boundary or the triple points. Many similar micrographs were examined from different deformation conditions, and in the overwhelming number of cases at the lower strain levels, cavities were found to at grain boundaries.

Fig. 7- 4. SEM picture of the deformed sample strained to 15% at 400°C.

The variation of cavitation ratio as a function of strain level at different temperatures is shown in Fig. 7-5. From Fig. 7-5 it can be seen that critical strain level for cavity initiation is 10% and 15% for samples deformed at room temperature and 400°C. However, for samples deformed at 600°C, the value increases dramatically to 80%.

Fig. 7-5. Variation of cavitation ratio as a function strain level at different temperatures.

Further studies show that above the critical strain, not only the size of cavities, but also the population density of cavities increase with increasing strain. The population increase is directly related to the emergence of new small size cavities. This gives an indication that new cavities are continuously formed and are also enlarged with increasing strain. As a result, the cavitation ratio increases with increasing strain. This leads to some cavities coalescence as shown in Fig. 7-6. In the present study, no significant evidence for cavity interlinkage along to the stress axis, but there are some evidence for cavity interlinkage perpendicular to the stress axis as shown in Fig. 7-6.

Fig. 7-6. Optical microstructure of the deformed sample (Tensile axes was horizontal).

A major characteristic of cavitation in superplastic alloys is that cavities usually display an aligned configuration; a group of cavities aligned in a specific direction is referred to as a cavity stringer [97]. In most cases, cavities stringer align themselves parallel to the tensile axis and in a few occasions they show alignment perpendicular to the tensile axis. However, in the present studies, no such phenomenon can be found. These cavities are randomly distributed and cavity size varies over a wide range.

There are two opposing viewpoints concerning cavity nucleation [109]. Some researchers [110] suggested cavities may pre-exist in many superplastic alloys, and this suggestion is supported by Silveti [111]. On the one hand, several recent analyses have demonstrated that, at least in some superplastic alloys, there is no evidence to support the concept of pre-existing defect [112, 113].

For CP titanium alloys, did the cavities nucleate on pre-existing defects or did they truly nucleate independently? For the present study, the preferred viewpoint is that these cavities do not pre-exist but nucleate with strain. This is because that the alloys had been annealed at high temperature. Any possible stress concentration/ dislocation pile-ups following cold work would be annealed-out. Although a few pre-existing defects were indeed found in the as-received alloy, the number is very limited. The temperature-dependent critical strains (Fig. 7-5) indicate that cavities nucleate with strain.

Fig. 7-7. SEM picture of the as-received CP titanium alloy.

7.4 CONCLUSIONS

Cavitation caused by superplastic straining of a CP titanium alloy under uniaxial tension was systematically studied. The observations made in this work are listed as follows.

- 1) Cavitations can be found during high temperature deformation of CP titanium alloy and this phenomenon is temperature dependent. When the test temperature is above 750°C, no cavities can be found in the deformed samples.
- 2) Cavities are formed at the grain boundary and triple points. During deformation, both the size and population density of cavities increase with increasing strain. The maximum cavitation ratios are 5.2%, 4.3%, 0.55% for samples deformed at room temperature, 400°C and 600°C respectively.

CHAPTER 8: ENHANCEMENT OF DUCTILITY BY DYNAMIC RECRYSTALLIZATION

As mention in Chapter 4, Dynamic Recrystallization (DRX) phenomenon can be found during high temperature deformation of the commercially pure (CP) titanium. The positive contributions of dynamic recrystallization on the superplasticity of Al-Mg alloys, Al 2219, Al 7475, Co₃Ti and Mg-3Al-1Zn alloys have been well documented [114-119]. In this chapter, the idea of refining the grain structure of CP titanium alloy by DRX was put forward and its effectiveness demonstrated. A ‘two-stage deformation method’ was proposed to improve the elongation-to-failure.

8.1 DYNAMIC RECRYSTALLIZATION

This section presents the dynamic recrystallization (DRX) of the alloy during high temperature deformation. The effects of temperature and strain rate on the microstructures of the alloy were systematically investigated to find the optimum DRX condition. Subsequently, the effects of DRX on the microstructure, grain boundaries misorientation and strain rate sensitivity index, i.e. m -value were discussed.

8.1.1 Microstructure Evolution

In order to obtain a better understanding of the dynamic recrystallization phenomenon of this alloy, microstructures of samples deformed at different conditions were

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examined. The linear intercept procedure was employed for measuring the grain size. In the present work, fine grains are defined as grains having a diameter of $\leq 10\text{ }\mu\text{m}$. The volume fraction of fine grains ratio measurements was measured on the gauge section of deformed samples. The images for measurement were first captured by optical microscope. The images were then analyzed using Image Pro+ software. The volume fraction of fine grain ratio was calculated by dividing the fine grain area by the total image area. The effects of employing different combinations of temperature and strain rate on the percentage of fine grains attainable are depicted in Fig. 8-1 and the average grain size from different parts of the deformed sample is shown in Table 8-1.

Table 8-1 Average grain size of different parts of deformed specimen.

Test temperature($^{\circ}\text{C}$)	Strain rate (s^{-1})	Holding time (minutes) *	Grain size at gauge part (μm)	Grain size at grip part(μm)
600	1×10^{-1}	3.2	13.1	18.9
600	1×10^{-2}	5.6	13.6	20.2
600	1×10^{-3}	34.3	13.9	22.0
600	1×10^{-4}	303.0	28.3	90.2
750	1×10^{-1}	3.2	34.0	87.1
750	1×10^{-2}	6.1	39.1	105.6
750	1×10^{-3}	29.5	41.2	113.0
750	1×10^{-4}	231.3	43.6	140.6
800	1×10^{-1}	3.2	39.4	110.6
800	1×10^{-2}	5.3	40.8	128.3
800	1×10^{-3}	25.8	41.6	130.4
800	1×10^{-4}	214.6	43.9	152.6

*Holding time does not include the heating time.

Fig. 8-1. Volume fraction of fine grains attainable at fracture.

It can be seen from Fig. 8-1 that the highest volume fraction of fine grains (24.1%) can be obtained when the sample is deformed at 600°C with an initial strain rate of 0.001/s. It can also be seen from this figure that grain refinement by dynamic recrystallization becomes less effective when the test temperature is at a high temperature (800°C). This is because the rapid grain growth which offset the positive effects of DRX. Consequently, the percentage of fine grains attainable never exceeds 5% for all the chosen strain rates. Moreover, due to the fact that specimen which deforms at higher strain rates will fail at a shorter period; hence DRX process is interrupted before its completion. So, it was also difficult to achieve high volume fraction of fine grains at all temperatures when the strain rate is 0.1/s or faster.

To further investigate the DRX phenomenon, specimens were tested using the optimum superplastic deformation conditions determined earlier in Chapter 4, i.e. at 600°C with an initial strain rate of 0.001/s. During the tests, specimens were strained to different strain levels, unloaded and immediately cooled by forced air. Specimens

were sectioned from the gauge section. Fig. 8-2 shows the evolution of recrystallized microstructures and their corresponding grain size distribution charts. The average grain size at different strain levels is shown in Fig. 8-3.

At the beginning of the deformation, i.e. $\epsilon=0\%$, the microstructure consists of equiaxed grains. Because of static grain growth during the heating-up process, the as-received microstructure had transformed into a coarse-grained structure whose average size was $18.9\text{ }\mu\text{m}$ as shown in Fig. 8-2(a). Most of the grains are equiaxed grain with grain size larger than $10\text{ }\mu\text{m}$. The microstructure and grain size distribution chart shows that at this stage, very little fine grains can be found and the percentage of the fine grain area is only 0.1% .

At $\epsilon=10\%$, the coarser grain boundaries started to appear jagged as a result of the applied stress, as shown in Fig. 8-2(b). Careful examination of the microstructure shows that most grains are extended along the stress direction. Inspection at a higher magnification shows that some equiaxed fine grains appear along the grain boundaries and triple points (Fig. 8-4). At this stage, most of the sizes of the new formed grains vary from 1.2 to $2.0\text{ }\mu\text{m}$ and the fine grain area is around 1.0% . Although the percentage of fine grain area is very low at this stage, the average grain size of the deformed sample decreases to $12.8\text{ }\mu\text{m}$ measured by using liner intercept method.

Fig. 8-2. Optical microstructure and grain size distribution of samples strained to: (a) 0%; (b) 10%; (c) 40% and (d) 80% at 600 °C with 0.001/s.

Fig. 8-3. Average grain size at different strain levels when deformed at 600°C with an initial strain rate of 0.001/s.

Fig. 8-4. Optical micrograph of the deformed sample.

Fig. 8-2(c) depicts the microstructure at $\epsilon=40\%$. Comparing with Fig. 8-2 (b), more fine grains can be observed in this figure. However, the distribution of these fine

grains is not homogeneous. It clear indicates that the microstructure characterized by a bimodal microstructure: fine equiaxed region (or recrystallized region) with grain size less than 10 μm sandwiched by coarse band structure. The average grain size decrease to 10.1 μm and the fraction of fine grain increase to 18% at this stage.

When $\varepsilon=80\%$, the amount of fine grains reaches 25%, and the average grain size decrease to 9.7 μm . At this strain level, the average grain size is smaller than that of the as-received sample and the distribution of fine grains is relatively homogeneous. However, many coarse grains with grain size larger than 10 μm can still be found in Fig. 8-2(d). It can be seen from Fig. 8-2(d) that coarse grains are surrounded by fine grains. Further investigation indicates that from 80% strain and onwards the change in terms of the percentage of fine grains attainable was minimal. Studies also showed that beyond 80% strain, the average grain size increase with increasing strain due to grain growth at this temperature (Fig. 8-3).

The above observations revealed that a maximum ratio of fine grain area and minimum average grain size can be obtained when the sample is strained to 80%. For samples deformed at this level, the average grain size is 9.7 μm and the fraction of fine grain area is 25%. However, many coarse grains still exist in the deformed samples and the distribution of the fine grains is not homogeneous.

8.1.2 Effect of DRX on the Misorientation Angle

The misorientation of grain boundaries of the polycrystalline materials can influence their strength, ductility behavior, etc [121, 122]. In the region of superplasticity, high angle grain boundaries are usually desired for achieving grain boundary sliding (GBS). There have been few investigations into the mechanisms of formation and evolution of boundaries in superplastic alloys that exhibit recrystallization. The absence of a systemic study on this issue is partially due to the low efficiency of traditional analysis techniques. In most cases, diffraction patterns have been studied using TEM. This equipment allows detailed microstructure characterizations, but analysis of many grains is time consuming. The emergence of Electron Backscatter Diffraction (EBSD) permits statistically representative studies of microstructure [123-132]. In this work, the effect of DRX on the distribution of the grain boundary misorientation was characterized by using electron back scattered diffraction (EBSD) technique. EBSD measurements were carried out using a scanning electron microscope (SEM; JEOL 360) equipped with a TSL EBSD system. The SEM was operated at an accelerating voltage of 20kV and EBSD measurements were performed with a step size of 1.0 μm .

Several EBSD relative maps from the samples strained to 10%, 40% and 80% are presented in Fig. 8-5. The left column shows the grain size map. Their shapes are related to the grain size. The darker the shade, the larger the grain size in this area. The middle column in Fig. 8-5 shows the fine grain map. Black areas in this map indicate that grains in these areas have a grain size smaller than 10 μm . The right column shows the misorientation maps. Dark lines in these maps refer to misorientation angles

higher than 60° . In the literature, the grain boundaries have been classified as low angle, intermediate angle and high angle boundaries. But the line for such a separation has not been universally defined. In the present study, we defined the boundaries with a misorientation angle less than 30° as low angle boundaries and those angle boundaries greater than 60° are treated as high angle boundaries. The rest within 30 - 60° are classified as intermediate angle boundaries.

Several interesting features are worth noting in these maps:

- (i) The fraction of fine grain area increase with increasing strain and the distribution of fine grains are not homogeneous. This feature is consistent with the optical micrographs as shown in Fig. 8-2.
- (ii) The density of high angle also increases with increasing strain. Further investigation on Fig. 8-5 revealed that the distribution of the high angle boundaries is not homogeneous over the microstructure, with the high angle boundaries mainly located in the fine grain regions. This implies that most of the fine grains have high angle boundaries.

Fig. 8-5. EBSD relative maps of samples strained to: (a) 10%; (b) 40%; and (c) 80% at 600 °C with 0.001/s. Left, grain size map; center, fine grain map (black areas denote fine grain area); right, high angle misorientation map (dark lines denote very high angle grain boundary with misorientation angles above 60°).

Fig. 8-6 shows the distribution of the misorientation angles between 5° and 95° of the as-received sample, sample strained to 10%, 40% and 80%. The average misorientation angles deduced from the histograms were 48° , 51° and 56° for sample strained to 10%, 40% and 80%, respectively. An interesting point can be seen from Fig. 8-6 is that a strain-induced shift in the mode of misorientation distribution from high frequency of low-angle boundaries to a high frequency of high-angle boundaries can be observed. The fractions of low, intermediate and high angle misorientation boundaries for the sample strained to 10% are 31.9%, 32.8% and 35.3% respectively. At 80% strain, the corresponding value transfer to 21.0 %, 32.9% and 46.1%.

Fig. 8-6. Histograms showing the misorientation angle distributions sample strained to different levels.

From the above discussion, it can be seen that DRX not only decrease the average grain size of the CP titanium alloy, but also increase the misorientation angle of the grain boundaries. It has been repeatedly reported that low angle boundaries are converted to high angle boundaries in some alloys when they deformed at high temperatures [133-138]. The rapid increase in misorientation and decrease in average grain size during superplastic deformation has been investigated by several researchers [137-139]. There are two mechanisms involving the decomposition of coarse structure and increase in misorientation.

(i) One mechanism [137] is that at the early stage of deformation, dislocation sliding is dominant. With further deformation, climb process occurred and the dislocations arrange themselves as subgrain boundaries. The subgrain boundaries divided the initial large grains into many fine subgrains. The subgrains boundaries absorb the dislocations coming from the subgrains and thus the misorientation between subgrains increases. Some subgrain boundaries were indeed found in the deformed sample as shown in Fig. 8-7 and absorption dislocation, of course, will result in an increase in boundary misorientation. However, as shown in Fig. 8-7, the distribution of subgrain boundaries is relatively homogeneous. If the increase in the boundary misorientation is caused by dislocation absorption, the high misorientation boundaries would distribute homogeneously. The EBSD maps do not support this mechanism because this mechanism can not explain why the distribution of the fine grains is not homogeneous for the CP titanium.

Fig. 8-7. Subgrain of sample strain to 80% at 600°C with an initial strain rate of 0.001/s. (Red lines in the map denote subgrain boundaries with misorientation less than 10°)

(ii) Another possible mechanism responsible for these phenomena is localized grain boundary sliding (GBS) [140]. As discussed earlier, the average grain size is relatively large (18.9 μm) at the beginning of deformation. According to [8, 96], only grains with an average size of less than 10 μm can deform by grain boundary sliding (GBS). So, GBS is not the predominant mechanism during deformation. This is also verified by strain rate sensitivity m -value as discussed later. On the other hand, many very high angle boundaries exist in the as-received material and this is confirmed by Fig. 8-8. These high angle boundaries can provide the starting sites for localized GBS [140]. Because the extent of GBS is very limited, its contribution to the total strain is not significant. However, it can lead to accelerated dynamic recrystallization by the following processes [120, 140]: (a) as GBS takes place, dislocations are introduced to

accommodate the strain incompatibility and the absorption of these dislocations into boundary will increase misorientations between adjacent subgrains; (b) the GBS causes rotation of the adjoining subgrains, thereby introducing additional high angle boundaries which are also able to slide. Repetition of this process rapidly transforms low angle boundaries into high angle boundaries. As a result, more and more fine grains with very high angle boundaries are formed as the strain increase.

Fig. 8-8. Histograms showing the misorientation angle distributions of the as-received material.

For these processes, three phenomena will be observed on the deformed microstructure:

- (a) Because the GBS can only happen at high grain boundaries, as a result, most of the newly formed fine grains will congregate rather than be homogeneously distributed.

- (b) These fine grains will have relatively high grain boundary angles.
- (c) For a coarse grain undergoing the dynamic process, a misorientation angle gradient is expected to exist from the edge region to the center region because the edge subgrains were affected by the adjacent GBS while the subgrains at the center were not.

Evidence supporting these predications is shown in Fig. 8-9. In this figure, red lines denote subgrain boundary with misorientation angles less than 10° while dark lines denote high angle grain boundary with misorientation angles above 60° . The rest within 10 - 60° are denoted by green lines. It can be seen from Fig. 8-9 that at the outside of the coarse grain, many fine grains with high misorientaton can be found. These fine grains surround the coarse grain like a “necklace”. In the center of the course grain, there is no high grain boundary, only a few subgrain boundaries with misorientation less than 10° . Between the center and the “necklace”, some fine grains can also be found but the misorientation is not as high as that of the ‘necklace region’.

Fig. 8-9. Misorientation map of sample strain to 40% at 600°C with an initial strain rate of 0.001/s.

8.1.3 Effect of DRX on the m -value

From the above-mentioned phenomena, it can be seen that the Dynamic Recrystallization process not only decreases the average grain size of the CP titanium, but also increases the average misorientation angle. It is well known that fine grain and high misorientation are favorable for GBS. The presence of a high percentage of fine grains with high misorientation grain boundary also strongly suggests that at the strain level of 80%, grain boundary sliding (GBS) might act as the predominant deformation mechanism.

The most important mechanical characteristic of a superplastic material is its strain rate sensitivity of flow stress, referred to as m -value. For superplastic behavior, m -value would be greater than 0.3 [8]. Since it is of interest to know the degree of superplasticity that the CP Titanium alloy undergoes at various strain rates and temperatures, the strain rate sensitivity (m -values) was obtained to better understand the deformation mechanisms. From the formula that relates stress and strain rate as follows:

$$\sigma = k\dot{\epsilon}^m \quad (8-1)$$

where the σ is the true flow stress, k is a constant and $\dot{\epsilon}$ is the true strain rate. A logarithmic plot of true stress versus strain rate is performed to obtain the gradient of the linear graph which corresponds to the m -values at the respective temperatures and strain rates.

$$\log \sigma = m \log \dot{\epsilon} + \log k \quad (8-2)$$

In order to investigate the effect of DRX on the deformation mechanism of the CP titanium alloy, two group of samples were used to check the m -value of the sample before and after DRX.

For group I, samples were strained to failure at 600°C with different initial strain rates. In order to obtain the m -value of the sample before DRX, a logarithmic plot of yield stress versus strain rate is performed. The m -value would simply be equal to the gradient of the curve as shown in Fig. 8-10.

For group II, Samples were first strained to 80% at 600°C with an initial strain rate of 0.001/s. The aim of this step is refining the coarse microstructure and increasing the average grain boundaries by utilizing DRX. The second step was carried out with different initial strain rates at the same temperature and the Log yield stress versus Log strain rate curve in this step is also plotted in Fig. 8-10.

Fig. 8-10. Graph of Log (stress) vs Log (strain rate).

In can be deduced form Fig. 8-10 that the m -value of group II are higher that that of the group I. For group I, the m -values were around 0.2 and for group II, the m -values at the second stage vary form 0.3 -0.4. This imply that the deformation mechanism of the CP titanium alloy were change by DRX and at this stage, GBS is the predominant mechanism

8.2 FLOW STRESS ANALYSIS

Stress-strain curves are capable of providing clues on the many complex internal process that are involved during elevated temperature deformation. To date, different types of flow curves have been observed and reported for various alloys. By now, four different types of curves observed in superplastic materials have been identified. These curves can be summarized into Table 8-2.

Table 8-2. Different types of stress-strain curves for superplastic materials [141].

Types of stress-strain curve	Brief description
Flat (F)-type	Well-behaved curve showing a steady flow stress with strain.
Hardening (H)-type	Continuous strain hardening.
Softening (S)-type	A predominantly strain softening type curve.
Complex (C)-type	Exhibit both exaggerated strain hardening and strain softening.

The engineering stress-strain curves of the sample deformed at 600°C with an initial strain rate of 0.001/s is shown in Fig. 8-11. In order to characterize the curves into the types listed in Table 8-2, this curve was converted into true stress-strain curves (Fig. 8-12) using the following relationships assuming uniform cross section within the gauge

region. This assumption is valid since the gauge section is basically deforming uniformly, prior to the onset of plastic necking.

The true stress σ_T can be expressed in terms of engineering stress σ_e by:

$$\sigma_T = \sigma_e (\epsilon_e + 1) \tag{8-3}$$

Whilst, the true strain ϵ_T can be expressed in terms of engineering strain ϵ_e by:

$$\epsilon_T = \ln(\epsilon_e + 1) \tag{8-4}$$

Fig. 8-11. Engineering stress vs engineering strain of the sample deformed at 600°C with an initial strain rate of 0.001/s

Fig. 8-12. True stress vs true strain of the sample deformed at 600°C with an initial strain rate of 0.001/s.

Softening (S) type curves can be observed in Fig. 8-12. It shows the true stress as a function of true strain at 600°C with an initial strain rate of 0.001/s. The curve exhibit a continue drop in flow stress, especially at the later stage of the deformation, the drop rate is rapid. Two reasons may be attributed to the decrease in flow stress as follows:

1) Deformation mechanism.

As mentioned in the previous sections, at the initial stage of the deformation, the average grain size is relative large (18.9 μm), so, grain boundary sliding (GBS) is not the predominant mechanism and this is verified by the m -value. Only some localized GBS can take place. However, as the strain increasing, more and more fine grains with high grain boundaries appeared as a result of the DRX. Subsequently, the flow stress decrease as the grain size is reduced.

2) Cavitation

Another factor attributing the decrease in flow stress is the initiation of cavities. As discussed in Chapter 7, many cavities can be found on the deformed samples. For samples deformed at 600°C, initial cavities can be found at the grain boundary or triple point when the sample strained to 80%, and the cavitation ratio increase with increasing strain. As a result, the flow stress decrease with increasing strain.

8.3 ENHANCED DUCTILITY BY ‘TWO-STAGE DEFORMATION METHOD’

Chapter 6, 7 and section 8.1 have present in-depth investigation and analysis into the cavitation, static and dynamic grain growth phenomena of the CP titanium alloy. Due to rapid grain growth and cavitation, the alloy does not show good superplasticity at high temperature. Also, it is apparent that fine grains can be obtained through dynamic recrystallization, and this process not only decrease the average grain size but also increase the misorientation angle and strain rate sensitivity index, i.e. m -value.

Grain size refinement can be used as a powerful means in increasing the ductility of materials [115-119, 142, 143]. Takuda and his coworkers [143] have reported that the superplasticity of Mg alloy can be substantially improved by first refining the grains of the rolled alloy through predeformation process. A maximum elongation-to-failure of 345% was reported. However, their paper did not elucidate the essential deformation mechanisms underlying the tensile elongation improvement. Very recently, T. Mohri .

[144] have demonstrated that a rolled Mg-9Al-1Zn alloy can be made to deform superplastically after going through dynamic continuous recrystallization which resulted in the formation of fine grains. A maximum elongation of 604% was attained after the grain refinement process. Dynamic recrystallization of other superplastic materials such as Co₃Ti and Duralumin [115-119] have also been reported by several other authors.

Recognizing the capability of CP titanium alloy to dynamic recrystallize, a ‘two-stage deformation method’ was employed to enhance the superplasticity of the CP titanium alloy in this study. For the first stage (Stage I), deformation is aimed at refining the coarse microstructure, whereas the second stage (Stage II) is carried out at higher temperature to avoid the cavitation.

The three key parameters which govern the amount of dynamic recrystallization undergone by the material are temperature, strain rate and strain level. Section 8.1 has presented the capability of the CP titanium alloy sheet to undergo dynamic recrystallization for achieving a fine and relative homogeneous microstructure. It can be concluded that the optimum condition for DRX is 600°C with an initial strain rate of 0.001/s. The strain level should not be over 80% to avoid cavitation.

Table 8-2 lists the results of the elevated temperature tests performed using single and ‘two-stage methods’. Even though Sample 1 was deformed under optimum condition, i.e. at 600°C with an initial strain rate of 0.001/s; its elongation-to-failure was limited to 188%. Its failure was due to cavitation, which has been discussed in detail in

Chapter 7. Sample 2 was independently deformed at 750°C with an initial strain rate of 0.01/s, achieving an elongation-to-failure of 186%, resulting microstructure consisted of coarse grain. Sample 3 was tested using the ‘two-stage deformation method’. It was first strain to 80% at 600°C with an initial strain rate of 0.001/s, and then quickly unloaded the sample. For the second stage, the deformation is carried at 750°C with an initial strain rate of 0.01/s. (In order to avoid static grain growth during the heating up process, all these tests were carried out by using pre-heating method, i.e. tests were carried out first heating up the furnace to the desire temperature, and then quickly set the sample on the tensile machine.) By using the ‘two-stage deformation method’, the elongation-to-failure value increased to 243%. The fractured specimen is shown in Fig. 8-13. Apparently, the ‘two-stage deformation method’ has again proven its effectiveness in enhancing the elongation-to-failure value of the CP titanium alloy.

Table. 8-3. Summary of uniaxial tensile test results of CP titanium alloy deformed under different conditions

Sample number	Test temperature °C	Strain rate, /s	Elongation-to-failure, %
1	600	0.001	188
2	750	0.01	186
3	600⇒750	0.001⇒0.01	243

Fig. 8-13. Deformed specimen under different conditions.

8.4 CONCLUSIONS

- 1) Grain refinement of CP titanium alloy can be accomplished via dynamic recrystallization (DRX). The optimum DRX conditions were found to be at 600°C with an initial strain rate of 0.001/s, attaining the highest volume fraction of fine grains whose average is $\approx 9.7 \mu\text{m}$ at strain of 80%. Grain refinement by DRX becomes less effective at higher temperatures (750°C and 800°C) due to rapid grain growth.
- 2) The distribution of the recrystallized fine grains on the deformed sample is not homogeneous during the deformation. At the early stage of the deformation, fine grains are formed at the grain boundaries and triple points. As strain increases, the fine grain ratio increases and most fine grains congregate together around coarsen grains.
- 3) EBSD study shows that the fraction of high angle boundaries and the average misorientation angle increase with increasing strain when deformed at 600°C with an initial strain rate of 0.001/s. The distribution of the high angle boundaries is not homogeneous. Most of the high angle boundaries are concentrated in the fine grain areas.
- 4) The strain rate sensitivity rate index was also changed by DRX. The m -value is around 0.2 before the DRX. When the strain level arrived at 80%, m -value transformed to 0.3-0.4.

- 5) The ‘Two-Stage Deformation Method’ is proposed to enhance the maximum elongation-to-failure attainable during uniaxial tensile test. Aiming at refining the coarse microstructure, Stage I is carried out at 600 with an initial strain rate of 0.001/s, whereas Stage II is carried out at the 750°C with an initial strain rate of 0.01/s to avoid cavitations. The maximum elongation attainable by this method is 243%.

CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

In this work, the superplastic deformation behavior of commercially pure titanium alloy was studied by using uniaxial tensile test at different temperatures with different initial strain rates. Investigations on microstructures evolution, oxidation behavior, cavitation phenomenon, dynamic recrystallization as well as related mechanisms were carried out. The key objective of this work was to improve the ductility by exploiting its superplastic capabilities. A 'two-stage deformation method' is also proposed to further enhance the superplasticity of the commercially pure titanium alloy. The following conclusions can be drawn:

- 1) Commercially pure titanium alloy does not show good superplasticity when deformed between 600 and 800°C. The maximum elongation-to-failure values attainable are 188% and 186% when deformed at 600°C with an initial rate of 0.001/s and 750°C with an initial strain rate of 0.01/s respectively.
- 2) When exposed to air at high temperatures, an oxide film will form on the surface of titanium alloys. The oxide film is not dense and the thickness of the oxide film increase with increasing exposure time and temperatures.
- 3) Because the oxide film is brittle, during tensile test, 'stress oxidation clefts' are generated in the oxide film and then propagate perpendicular to the stress

direction. This process decreases the ductility of the alloy and this is significant at high temperatures. However, the oxide film has little effect on the ultimate tensile stress and yield strength.

- 4) Zircon coating layer applied onto the surface of Ti-6Al-4V alloy by plasma spraying can protect the alloy from oxidation and dramatically increasing the elongation. Coating layer has little influence on the UTS and yield strength of the alloy both at room temperature and high temperature. The zircon coating layer could be easily removed by 5% HF after forming to reveal the original metallic surface finish.
- 5) Cavitations can be found in the deformed samples at lower temperatures (below 600°C) during uniaxial tensile test and this phenomenon is temperature dependent. The cavitation ratio decreases with increasing test temperature.
- 6) Cavities are formed at the grain boundary and triple points. As strain increasing, not only the size of the cavity, but also the number of cavities increases with increasing strain. The maximum cavitation ratios are 5.2%, 4.3%, 0.55% for samples deformed at room temperature, 400°C and 600°C respectively.
- 7) The microstructure of the CP titanium alloy is not thermally stable at high temperature. When deformed at 750°C and 800°C, grain sizes of this alloy grow dramatically even at a high strain rate (0.1/s). At a lower temperature

- (600°C), excessive grain growth can also take place if the strain rate is very low (0.0001/s).
- 8) Grain refinement of CP titanium alloy can be accomplished via dynamic recrystallization (DRX). The optimum DRX conditions was found to be at 600°C with an initial strain rate of 0.001/s, attaining the highest volume fraction of fine grains whose average is $\approx 9.7 \mu\text{m}$ with a strain to 80%. Grain refinement by DRX becomes less effective at higher temperatures (750°C and 800°C) or fast strain rate.
- 9) The distribution of the recrystallized fine grains on the deformed sample is not homogeneous during the deformation. At the early stage of the deformation, fine grains are formed at the grain boundaries and triple points. As strain increases, the percentage of fine grain increases and most fine grains congregate together around the coarser grains.
- 10) EBSD study shows that the fraction of high angle boundaries and the average misorientation angle increase with increasing strain when deformed at 600°C with an initial strain rate of 0.001/s. The distribution of the high angle boundaries is not homogeneous. Most of the high angle boundaries are concentrated in the fine grain areas.

- 11) The strain rate sensitivity rate index was also changed by DRX. The m -value is around 0.2 before the DRX. When the strain level reached at 80%, m -value transforms to 0.3-0.4.
- 12) A 'Two-Stage Deformation Method' is proposed to enhance the maximum elongation-to-failure attainable during uniaxial tensile test. Aiming at refining the coarse microstructure, Stage I is carried out at 600 with an initial strain rate of 0.001/s, whereas Stage II is carried out at the 750°C with an initial strain rate of 0.01/s to avoid cavitations. The maximum elongations attainable by this method is 243%.

RECOMMENDATIONS & SUGGESTION

- 1) Increasing the elongation-to-failure value by coating method.

Oxidation on the surface of the CP titanium alloy can cause oxide film and this film degrades the ductility of the alloy. Coating method is a good way to protect the substrate from oxidation and this technology is widely used in many areas. A thin layer of coating layer can be applied to the surface of the alloy by spraying method to protect the alloy from oxidation during high temperature deformation. Zircon is recommended as a coating material because this material has excellent mechanical properties at high temperatures.

- 2) Study on the modifications of the grain boundary character distribution (GBCD)

During the superplastic deformation, GBCD plays an important role on the cavity nucleation and growth of the material. In the present study, pre-existing defects is the main reason for cavity nucleation. However, study on the relationships between GBCD and cavity nucleation and growth of the CP titanium alloy would generate important information of the material behaviour and this is an attractive research area worthy of further exploration.

PUBLICATIONS

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2. M.J. Tan, X.J. Zhu, Thiruvarudchelvan, K.M. Liew, "Superplasticity in Ti-15V-3Cr-3Sn-3Al beta titanium alloy", Journal of Materials Processing Technology, Accepted.
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