

## CHAPTER 2

### Literature Review

#### 2.1 Superplasticity

Superplastic alloys are capable of undergoing extensive, neck free, tensile deformation without fracture. There are two types of superplasticity. The first type, environmental superplasticity, is observed in material subjected to special environmental condition, e.g., thermal cycling through a phase change. The second type, structural superplasticity is observed in fine-grained materials. Structural superplasticity is a universal phenomenon. Appropriate structure preparation (grain refinement) can transform most of the polycrystalline to the superplastic state (Padmanabhan et al., 2001). A detailed review of structural superplasticity is given in present study.

In 1996, Rajagopalachary and Kutumbarao identified superplasticity as the phenomenon in which large tensile elongations are achievable in polycrystalline materials under certain condition of strain rate, temperature and a suitable microstructure. Superplastic materials are able to undergo large uniform strains prior to failure in excess of 200% or more. As reported by Higashi in 1992, the current world record for elongation in metal stands at 8000% elongation in commercial bronze as shown in Figure 2.1 (Chandra, 2002 and Nieh et al., 1997). Superplasticity has been observed in several kinds of materials, such as metals (including aluminium, magnesium, iron, titanium and nickel based alloys), ceramics (including monolithics and composites), intermetallics (including iron, nickel, titanium base) and laminates (Xing et al., 2004).

Although materials do not exhibit superplasticity at their original state by commercial process or naturally, a wide range of materials under specific loading condition display superplastic behavior. Most of these materials do require some special processing conditions to achieve the microstructural requirements necessary for superplasticity. Mabuchi and Higashi reported some of these processing in their article. However, some materials such as Ti-6Al-4V alloy display superplasticity without any special structural preparation. This alloy exhibit superplastic behavior by their commercial process (Chandra, 2002).

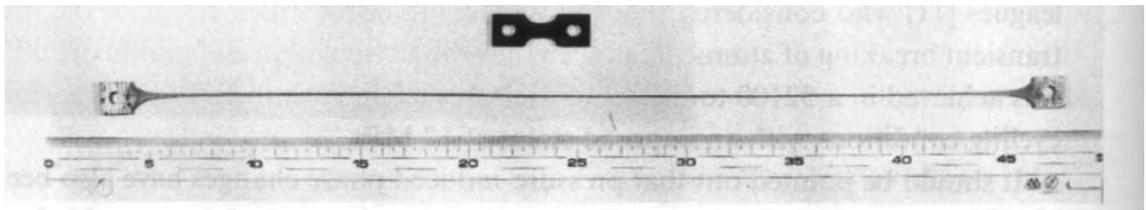


Figure 2.1 A demonstration of superplasticity in Cu-Al alloy with 8000% elongation  
(Source: Chandra, 2002 and Nieh et al., 1997)

### **2.1.1 History of Superplasticity**

Rosenhain, Houghton and Bingham initially observed phenomena of superplasticity on a eutectic alloy of Zn-Al-Cu in 1920 (Internet source 2). This traditionally brittle material showed an elongation up to 60%. Jenkins also reported a tensile elongation of 410% for the Pb-Sn eutectic at room temperature in 1928. However, in 1934, Pearson reported his spectacular observations on Bi-Sn eutectic alloy that showed a tensile elongation of 1950% without failure. Moreover, Pearson also

discovered that the size and the shape of the grains of superplastic alloys did not seem to change during the deformation (Internet source 4). After Pearson, many researches had been carried out to explore further in superplasticity.

By the late 1960s, considerable research related to superplasticity was carried out and attention was drawn to its application in the industry. Recently, application for the Zn-22%Al eutectoid and other superplastic alloys based on copper, titanium, stainless steel and nickel have been developed for industrial application (Tsuzuka et al., 1991).

### **2.1.2 Characteristics of Superplasticity**

Study of superplastic deformation received much attention because of its attractive behavior to produce the complex net shape structure at low or intermediate temperature. Superplastic behavior in materials has been reported associated with three main characteristics:

- (1) a fine grain size (on the order of 1  $\mu\text{m}$  to 10  $\mu\text{m}$ ),
- (2) deformation temperature more than 0.5  $T_m$  (where  $T_m$  is the melting point), and
- (3) a strain-rate sensitivity factor  $m$  more than 0.3 (Hertzberg, 1996).

#### **2.1.2.1 High Strain Rate Sensitivity**

The most important characteristic of a superplastic material is the strain-rate sensitivity factor, or the  $m$ -value in the well-known flow stress-strain relation. Strain rate sensitivity values are derived from the flow stress and the corresponding strain rate.

Higher  $m$ -value delay necking deformation because the higher the strain rate sensitivity value, the higher is the local stress, which would be required for neck formation. In areas where necking has begun already, the local reduction in the cross-sectional area causes an increase in the local strain rate. Therefore, an increase in stress is required to continue deforming at the reduced cross-sectional area (Vairis, 2008). The strain rate sensitivity exponent can be calculated from the relation

$$m = \frac{\partial(\ln \sigma)}{\partial(\ln \dot{\epsilon})} \quad (1)$$

The flow stress-strain rate relation express by the following equation.

$$\sigma = \frac{F}{A} = k \dot{\epsilon}^m \quad (2)$$

Where  $\sigma$  = plastic flow stress

$F$  = applied force

$A$  = cross-sectional area

$k$  = constant

$$\dot{\epsilon} = \frac{1dl}{l dt} = -\frac{1}{A} \frac{dA}{dt} = \text{strain-rate}$$

$m$  = strain-rate sensitivity factor

While the  $m$ -value of normal plastic deformation is less than 0.2, the  $m$ -value for most of superplastic materials lies within the range of 0.4 ~ 0.8. The slope in Figure 2.3

corresponds to the  $m$ -value. Region 1 is a low strain-rate region where the deformation occurs due to diffusion. Region 2 is the region of superplastic deformation with an  $m$ -value more than 0.4. Region 3 is a high strain-rate region where the deformation occurs due to dislocation creep. This is where plastic deformation occurs with the elongated grains during the deformation (Hasan, 2005). Superplastic deformation normally takes place at low strain rates and high homologous temperatures in material with thermally stable, fine and equiaxed grains. Decreasing grain size or increasing temperature increases the maximum strain rate sensitivity.

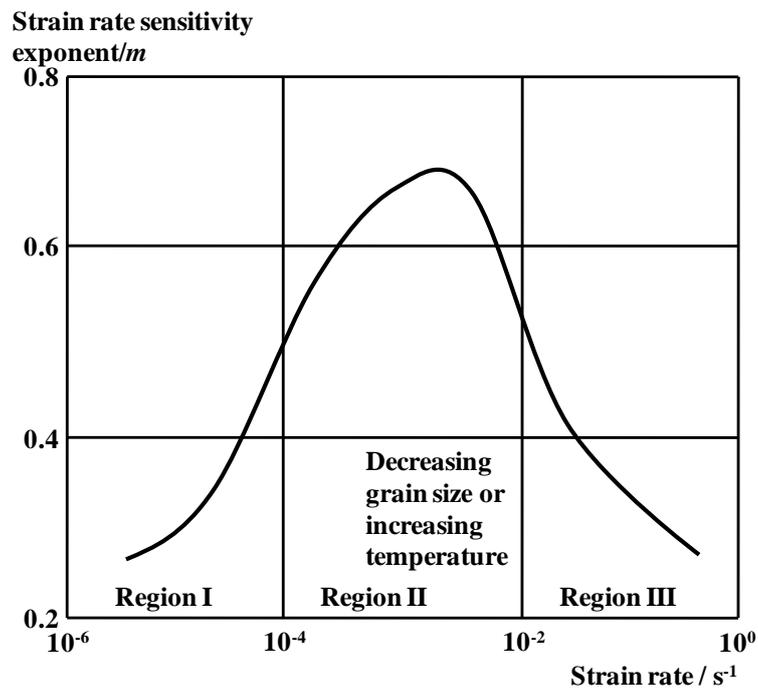


Figure 2.2 Strain rate sensitivity exponent versus strain rate

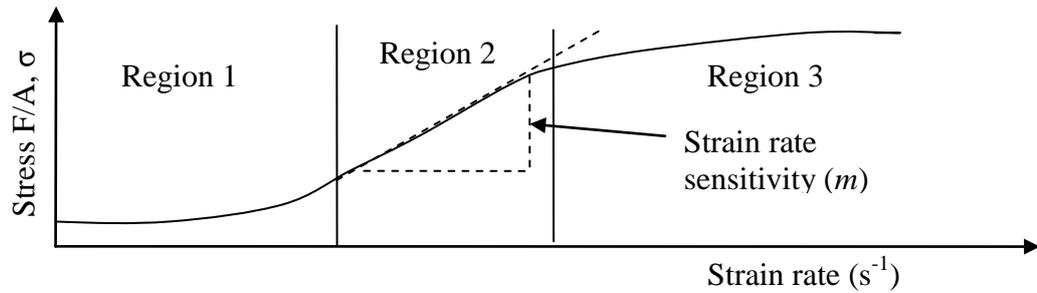


Figure 2.3 Stress versus strain rate with superplastic behavior

### 2.1.2.2 Fine Grain Size

Fine grain size is one of the main characteristics that strongly influence superplasticity. Ductility of materials increases as the grains sizes become finer. Metals are not normally superplastic unless their microstructure is fine grained, typically 1-10  $\mu\text{m}$ , in diameter and structure must also be stable at the temperature of deformation.

Small grain size and stable structure is dependent on a restricted grain growth. Dispersed particles of a second phase that are present at the matrix grain boundaries restrain grains growth to maintain a fine grain size at the superplastic forming temperature and for the times involved during superplastic forming. As it is achievable either in 2 phases system of the eutectic or eutectoid types, many superplastic materials are based on a eutectoid (e.g. Fe-C), eutectic (e.g. Al-Ca), or monotectoid (e.g. Zn-Al) compositions (Internet source 1).

Besides, grain boundary sliding is the predominant deformation mechanism in superplastic materials. Evenly distributing the second phase of material facilitate grain boundary sliding. Reducing the grain size of the material ( $<10 \mu\text{m}$ ) can advance grain boundary sliding (Cheong et al., 2001).

### **2.1.2.3 Temperature**

Temperature is also one of the critical parameters in superplastic deformation. Superplasticity involved deformation and movement of matter such as gas particles, solid particles and liquid particles. Such matter movement is temperature dependent.

Superplasticity in most materials commonly occurs at elevated temperature. Operational temperature for superplastic behaviours is normally greater than  $0.5 T_m$  ( $T_m$  is the melting point of material expressed in Kelvin). Superplastic deformation only exist in most of the alloys when the deformation temperature is greater than  $0.4 T_m$ . Metal does not strain harden because the microstructural evolution of metal achieve equilibrium between recovery and hardening at these temperatures. Superplastic deformation temperature should be controlled at a certain limit as a too high temperature may disrupt structural stability and result in a loss of superplasticity.

### **2.1.3 Mechanism of Superplasticity**

The exact nature of superplastic deformation mechanisms have been the subjects of interest for a very long time and still not well understood until nowadays. Researchers had proposed several models of mechanisms for superplastic deformation (Langdon, 1970; Mukherjee, 1971; Gifkins, 1976; Arieli and Mukherjee, 1980; Langdon, 1991; Zelin and Mukherjee, 1996).

There is research attributed the high ductility obtained in steel at high temperature to two causes. i) one is the ease of dislocation annihilation and of sub-boundary formation, which decrease the material's strength; ii) the second cause is the

bulging and motion of high angle grain boundaries, which isolate the cracks formed at original boundaries and inhibit grain boundary sliding. Furthermore, recent studies support that the dominant strain producing mechanism in superplasticity is grain boundary sliding (Chandra, 2002). The motion of individual grains or clusters of grains relative to each other accumulate strain in a given direction by sliding and rolling at the region along the grain boundary surface. Therefore, the grain shape and size remains identical before and after deformation, although there is some difference in grain shape during the accommodation. Figure 2.4 shows how grain boundary sliding occurs.

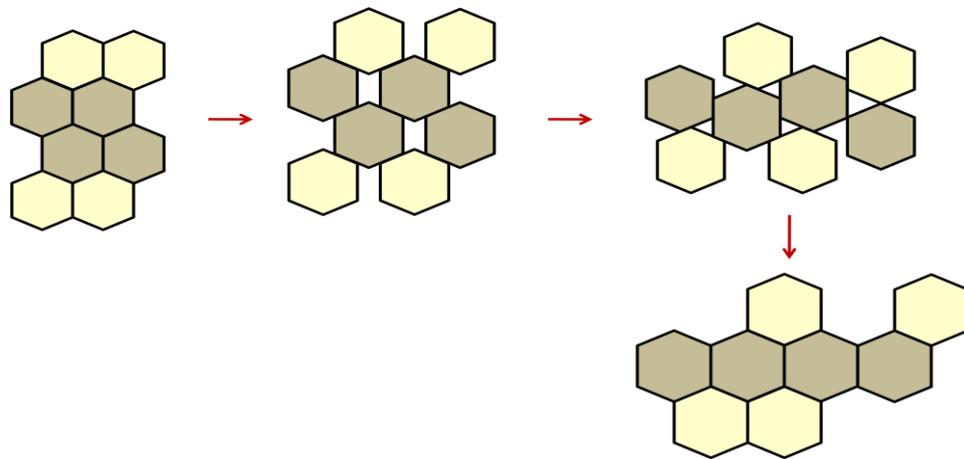


Figure 2.4 Grain boundaries sliding (Internet source 3)

Grains retain equiaxed or nearly equiaxed shape after being deformed for several hundred percent elongation (Zelin and Mukherjee, 1996). Grains should be equiaxed because grain boundary between adjacent matrix grains should be high angle (i.e. disordered) so that grain boundary can experience a shear stress, allowing grain boundary sliding to occur. Low-angle boundaries, such as those obtained during warm working, do not slide readily under shearing stresses (Internet source 3).

Grains change their neighbors and emerge at the free surface from the interior (Chandra, 2002). This is different from plastic deformation where grains become elongated and the location of grain neighborhood remains unchanged when a tensile force is applied. Figure 2.5 (a) and (b) explains the evolution of microstructure during superplastic and plastic deformation.

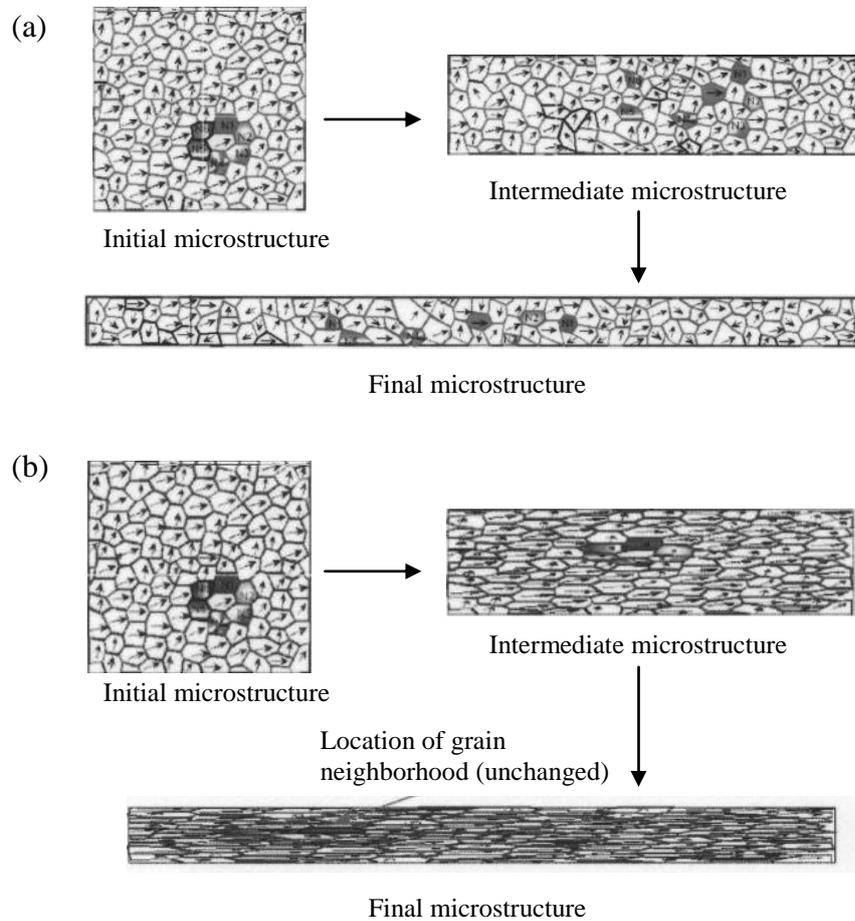


Figure 2.5 Evolution of microstructure during (a) superplastic and (b) plastic deformation (Source: Chandra, 2002)

There are three general groups of accommodation mechanisms (Mukherjee, 2002): (a) diffusional accommodation, (b) accommodation by dislocation motion and

(c) combined model with elements of dislocation and diffusional accommodation. For diffusional accommodation, the mass flow is due to the diffusion process in the vicinity of grain boundaries. When a load is given to a material, the deformation is due to grain boundary diffusion and sliding, because of strain. Figure 2.6 (a) illustrates this process. Accommodation by dislocation motion can be understood by dividing the grain into two parts; the core inside the grain, and mantle at the grain boundary, as shown in Figure 2.6 (b). In order for the grain to slide, the dislocations that move onto the grain boundary are accumulating at the triple point of grain boundary. From there, the dislocations move into the mantle due to stress concentration. Thus, the dislocation motion inside the mantle results in the grain rotation. Figure 2.6 (c) shows the process of accommodation by dislocation motion. Figure 2.6 (d) shows the third group of accommodation that combines dislocation and diffusion processes.

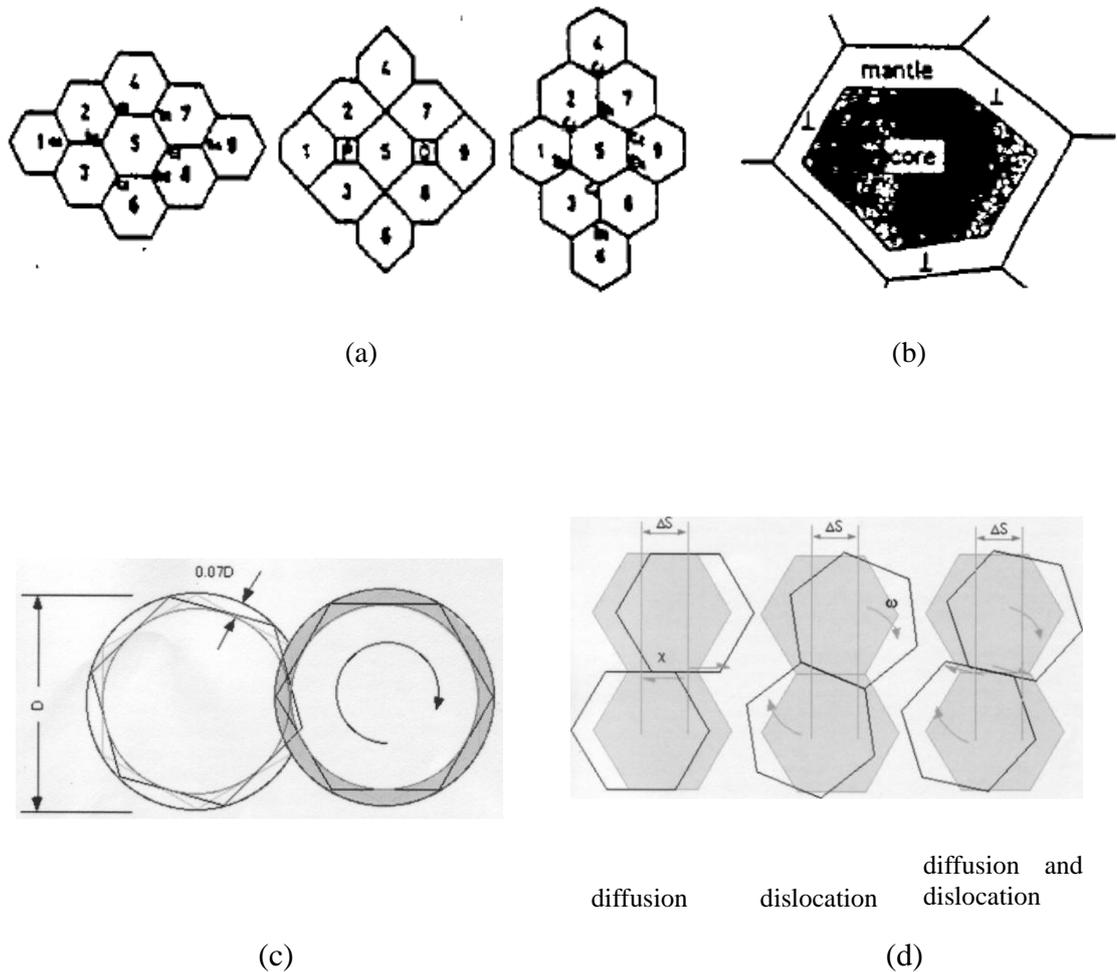


Figure 2.6 Basic accommodation mechanisms of superplasticity (a) diffusional accommodation (b) accommodation by dislocation motion (c) dislocation motion inside the mantle results in the grain rotation (d) combined model with elements of dislocation and diffusional accommodation (Zelin and Mukherjee, 1996)

Besides grain boundary sliding (GBS), other mechanisms include diffusion processes, especially diffusion creep, and dislocation gliding within the grains (Sedlacek, 1986). High strain rate sensitivity, as high as 0.5 to 1.0, is found when grain boundary sliding and or diffusion induced deformation makes a significant contribution to plastic flow. When dislocation glide is the sole process contributing to plastic flow,  $m$  value are

usually lower. If the contribution to superplasticity from grain boundary sliding and/or diffusion induced plastic flow is significant, then it could occur in compression or for that matter in any state of stress. There have been only a few studies devoted to superplasticity in compression (Rajagopalachary and Kutumbarao, 1996).

The favourable deformation rate for superplasticity commonly lies in the range between  $10^{-5} \text{ s}^{-1}$  and  $10^{-2} \text{ s}^{-1}$ . The superplastic optimum level can be attained under this condition (Sedlacek, 1986).

#### **2.1.4 Application of Superplasticity**

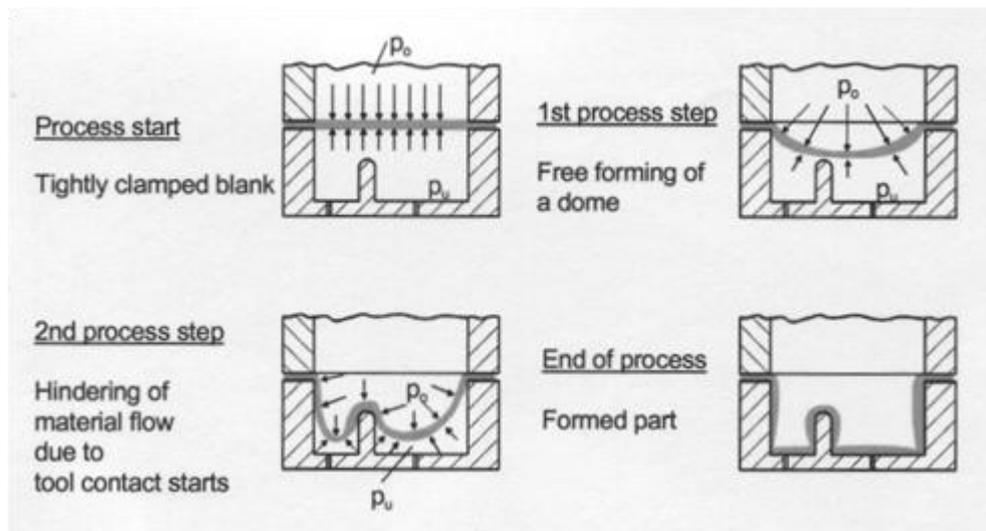
Applications of superplasticity have been broadly exploited in many fields. Most of the applications are in the aerospace area (Friedrich and Winkler, 1991; Tsuzuka et al., 1991; Hefti, 2004; Li and Guo, 2005) and have been further applied in non-aerospace area. Aerospace area used superplastic nickel-based alloys to form turbine discs with integral blades, and superplastic titanium alloys to produce fan and compressor blades for aeroengines. For other applications, superplastic aluminum alloys has been used in complex surface profiles and decorative panels for internal and external cladding of buildings and high-speed train (Superform Metals Limited, 1988). Aluminum automotive components made using a hot blow forming process are reducing vehicle weight and increasing the fuel efficiency of today's cars.

The superplastic forming (SPF) give a dramatically effect on the material formability increment and consolidates many parts into one to produce highly integrated, net-shape components (Li and Guo, 2005). This minimizes the number of parts, fasteners, tools and assembly operations required for complex parts. Figure 2.7(a)

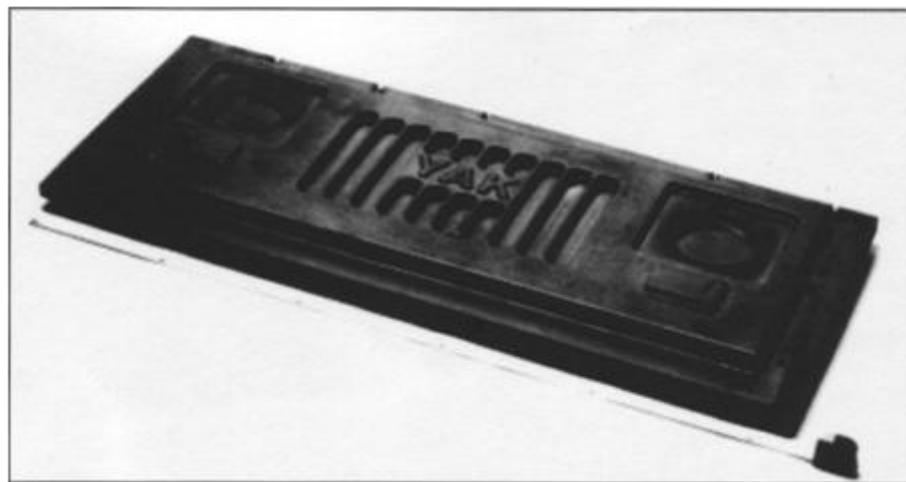
illustrates the SPF process and Figure 2.7(b) shows a tool insert for a Landrover front part, formed by superplastic forming.

The manufacture of complex cellular structures always combines superplastic diffusion bonding (SDB) with superplastic forming (SPF). Compared to other diffusion bonding processes, the SDB process offers a shorter joining time at lower pressure, with parent metal strength (Jauhari et al., 2002). The acceleration of SDB by superplastic deformation is closely connected with the development of grain boundary sliding in the material (Lutfullin et al., 1995). In addition, the fine grain size of the material can be preserved thus ensuring the same mechanical properties before and after bonding process. Figure 2.8(a) shows the process steps of superplastic diffusion bonding and superplastic forming in the manufacture of a box profile. Figure 2.8(b) shows a hollow box profile with closed chambers.

All of these applications reveal the great contribution of well-known superplastic forming (SPF) and superplastic diffusion bonding (SDB) application.

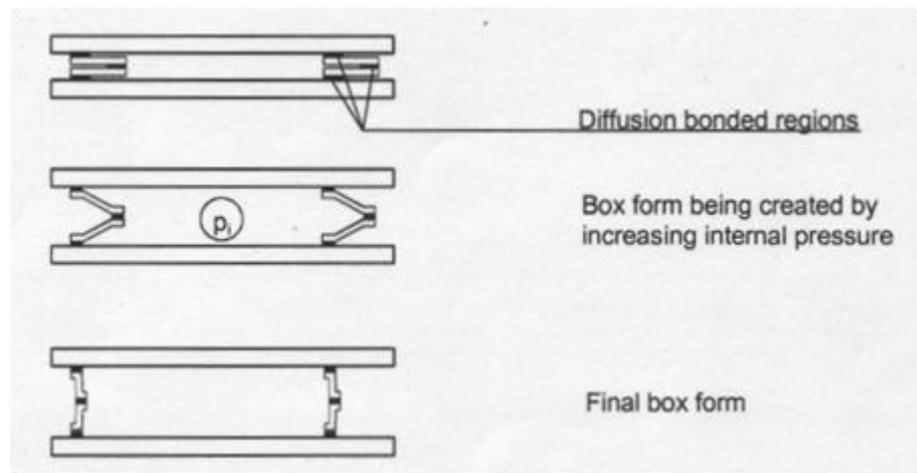


(a)

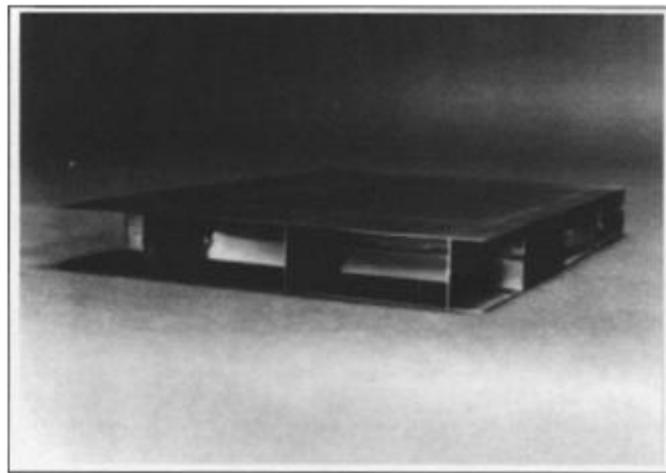


(b)

Figure 2.7 Superplastic forming (a) SPF process (b) Tool for a Landrover front part  
(Source: Siegert and Werle, 1994a)



(a)



(b)

Figure 2.8 Superplastic diffusion bonding and superplastic forming (SDB/SF) (a) SDB/SPF process steps (b) SDB/SPF formed component (Source: Siegert and Werle, 1994b)

## 2.2 Boronizing

Boronizing is a type of diffusion coating using thermochemical treatment. Boron atoms diffuse into a metal surface to form metal borides.

Thermochemical treatment techniques have been well investigated and used widely in the industry. This is a method where nonmetals or metals penetrate by thermodiffusion followed by chemical reaction into the surface. By thermochemical treatment, the surface layer changes its composition, structure, and properties. Carburizing, nitriding, carbonitriding, chromizing, and aluminizing are the most popular methods for industrial applications. Among these coating techniques, boronizing, being a thermochemical process, is used to produce hard and wear-resistant surfaces (Biddulph, 1977). The surface hardness of the resulting boride layer can exceed 2000 Hv and has a good resistance to abrasive and adhesive wear (Çelikyurek et al., 2006). The hard compound layer can have a depth in a range from 0.0005 in to 0.002 in (12  $\mu\text{m}$  to 50  $\mu\text{m}$ ) (Budinski, 1988). For instance, Sen et al. (2005) proved that the hardness of borides is much higher than that of the unborided substrate. The microhardness value of before and after borides formed on the steel substrate were about 280 Hv and 1446-1690 Hv, respectively. This can be attributed to the presence of FeB, Fe<sub>2</sub>B and CrB.

The characteristic of this boride layer depends on the physical state of the boride source used, boronizing temperature, treatment time, and properties of the boronized material (Meric et al., 2000). Many researches of boronizing have been done on ferrous material. According to Jain and Sundararajan in 2002, boriding of ferrous material is generally performed at temperature between 840°C and 1050°C. The process can be carried out in solid, liquid or gaseous medium. The most frequently used method is pack

boriding, a process similar to pack carburizing. Pack boriding involves placing the component in the powder mix and sealing it in a container. The container is then heated up to the required temperature for the required time and cooled in air (Jain and Sundararajan, 2002).

The boronized surface layer is very hard, the friction coefficient is very low, no extra heat treatment is required after boronizing, it has considerable resistance against some acid, base, and metal solutions, and high temperature oxidation. Boronized steel can resist wear and oxidation without losing their tribological properties even at surface temperatures of up to 1000°C. In addition, powder form boronizing has many advantages, including ease of treatment, ability to achieve a smooth surface and simplicity of the required equipment (Meric et al., 2000). Generally, during boronizing of ferrous or titanium alloys, boride grains tend to grow as columnar aggregates, which usually cause the formation of tooth-like coating/substrate interfaces (Li et al., 2006).

Kaestner, Olfea, and Rieb (2001) had carried out plasma boriding of pure titanium and the titanium alloy  $TiAl_6V_4$  at 700-900°C. This experiment led to the formation of a layer on the surface consisting of TiB and  $TiB_2$  resulted in relatively high hardness and adhesion strength. Besides, Li et al. (2006) modified the surface properties of  $Ti_3SiC_2$  using boronizing method. Vickers hardness test of  $Ti_3SiC_2$  increase from 3.7 GPa to a maximum 9.3 GPa, and the wear resistance of  $Ti_3SiC_2$  also significantly improved. The result of these studies indicated that boronizing is a promising way to improve the surface property.

The boronizing process can actually be traced back to an article published in 1895, in which Henry Moissan described a method of hardening iron at red heat in a vapor of volatile boron halides (most likely  $BCl_3$ ). The application of boronizing to industry

followed about 60 years later. However, only when powder pack boronizing was developed in the late 1960s did boronizing become wider spread (Arnim Kuper, 2003).

### **2.2.1 Mechanism of Boronizing**

During boronizing, boron is absorbed into the surface layer of a piece of metal. The boron which is derived from a solid, gaseous or liquid substance depend on the boron source state has intimate contact with the metal surface by means of a chemical reaction that does not directly involve the metal but may be catalyzed by the presence of the metal. Absorption of boron into the surface layer set up a gradient from surface layer to the core. In response to the boron content gradient, movement of boron atoms occurs by diffusion away from the surface layer. Boron potential of the surrounding environment and the boronizing temperature determine the boron content in the metal surface layer. However, if the chemical balance in the environment yields a certain amount of boron potential, the boron content will not exceeded regardless of the boronizing temperature. Through a paste boronizing study, Campos and his team (2004) found that different thickness of boron paste over the material surface with constant temperature and time show the variability of the diffusion coefficient of boron in  $Fe_2B$  phase. He explained that boronized layer depend on the boron potential at the external surface of the substrate. The mobility of boron in the formed phase is determined by the balance mass equation that considers the concentration profiles in the corresponding interphases layer–substrate, the thermodynamic equilibrium in the growth of the iron boride layer.

Boron atoms diffuse rapidly into the surface layer at first, as there is a large difference between the boron potential of the atmosphere and the boron content of the surface layer of metal. As the content of boron in the surface layer increases, boron absorption rate diminishes. At initial stage, the boron amount diffused away from the surface toward the core is small as the boron gradient is small and therefore the driving force is small. Nevertheless, as the boron content at the surface increases, driving force for boron diffusion increases and therefore more boron is absorbed into the surface layer.

Diffusion is easier in some materials than others are. Diffusion is almost nonexistent at temperatures up to 800F (425°C), but is very rapid at 1700F (925°C). Diffusion of boron into the substrate can start at temperatures as low as 750F (400°C). Boron atoms has about the atomic size as carbon, hence it diffuses easily into steels and many other metal (Budinski, 1988). Both Sen et al. (2006) and Meric et al. (2000) showed the thickness of the boride layer increase with treatment time and affect by process temperature.

### **2.2.2 Pack Boronizing**

Medium for boronizing process can be either in solid, liquid or gaseous form. Gas offers a number of distinct technical advantages as diffusion medium, for example, for nitriding, case hardening and chromizing. However, owing to unsolved problems and serious deficiencies that remain unrectified, gas- and liquid-phase boronizing have not become state-of-the-art (Internet source 4). For example, environmental contamination, toxic, explosive and nature problems always become shortcoming of

molten salt baths boronizing and gas phases boronizing. Therefore, technological variants of boronizing process are solely from solid or powder pack boronizing.

Powder pack boronizing process is simple, economical, original and industrially reliable (Goeriot et al., 1981). It was used extensively in present application due to its technological and economical advantage. In the process, the work piece is placed in a suitable container and embedded in the boronizing agent, which is the activated boron carbide. In order to minimize consumption of boronizing agent, the container and the work piece should be of the same shape. To avoid complications, boronizing should be performed in a protective gas atmosphere, which may be pure argon, pure nitrogen or a mixture of hydrogen and either argon or nitrogen. This is accomplished by either packing the containers into a protective gas retort then heat-treating them in a chamber furnace, or else boronizing directly in a retort furnace with the necessary protective gas supply. It is important to note that oxygen-bearing compounds adversely affect boronizing. For this reason, use should not be made of gases containing CO (Internet (Internet source 4). Figure 2.9 shows the schematic of powder pack boronizing.

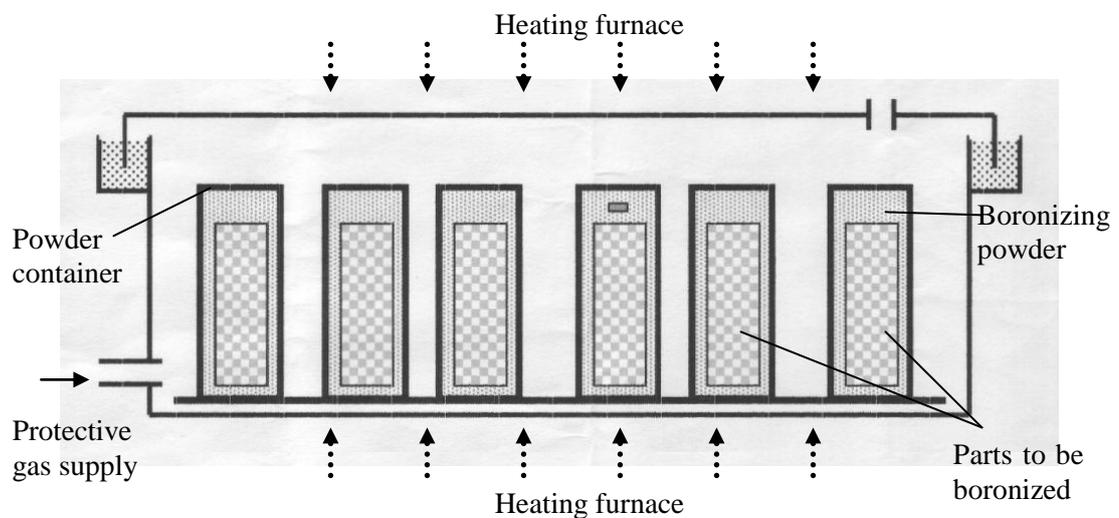


Figure 2.9 Schematic diagram of powder pack boronizing (Internet source 4)

High cost of boronizing agent and protective environment has severely discouraged commercial applications of powder pack boronizing. One way to bring down the cost of the boronizing process is to reduce the boronizing powder pack thickness around the component to the minimum required level without compromising on the properties of the boride coating. Jain and Sundararajan (2002) concluded that a minimum pack thickness of 10 mm is required to obtain boride coatings of optimum thickness, microstructure and properties in low carbon steel.

Boronized layer thickness increased with the decrease in carbon content of the material (Meric et al., 2000). Furthermore, boronized layer adhered well to carbon steels and high chromium steels but results with very highly alloyed steels such as 18-10 stainless steel were not satisfactory (Goeuriot et al., 1981). In high concentrations, alloying elements such as carbon (0% - 2%), nickel (0% - 14%) and chromium (0% - 26%) tend to favour the formation of relatively flat and thin boride layers, even when these layers are highly textured, in contrast with the single-phase acicular Fe<sub>2</sub>B layer obtained on low carbon steels, which can penetrate deep inside the material.

The concentration profiles developed during boronizing revealed different behaviours: carbon segregates towards the matrix, nickel segregates towards the surface, whereas chromium is scarcely affected. The segregation of nickel to the surface at high boron activities severely hinders the successful boronizing of highly alloyed steels, e.g. austenitic stainless steels (Goeuriot et al., 1982).

### 2.2.3 Superplastic Boronizing

SPB is the combination of two processes: (1) boronizing process and (2) superplastic deformation. The basic principle of SPB process is to conduct boronizing while the specimen is undergoing superplastic deformation.

In previous research on superplastic boronizing, the process was conducted through tension loading method. The specimen was undergoing heat treatment to obtain ultrafine grains for superplastic deformation. A tensile specimen is held and pulled in solid boronizing agents containing  $B_4C$ ,  $KBF_4$  and  $SiC$  in a tensile test machine at  $760 \pm 3$  °C. Specimen was pulled to an elongation of about 160% in 4 hours, no necking being observed. Fine equiaxed boride grains were observed in the superplastically boronized specimens, whilst 'comb-like' acicular borides were observed in the conventionally boronized specimens. Compared with the conventionally boronized specimens, the fracture strength, toughness and maximum flexure of the specimens treated with SPB were increased by 8%, 18% and 15% respectively (Xu et al., 1997).

Recently, Hasan (2005) carried out SPB on DSS using compression method. SPB process provides a much faster boronizing rate than the CB process. During the SPB, the superplastic deformation created high densities of vacancies, dislocations and sub-grain boundaries. These defects were movable under the superplastic deformation processes, increasing the rate of atomic diffusion. Boron atoms will diffuse into the vacancies in the grains and grain boundaries, producing a faster boronizing process.

The comb-like morphology of CB was due to the preferential growing direction in  $FeB$  and  $Fe_2B$ , which is along one direction only,  $\langle 001 \rangle$ . In other orientations, the growth of boride grains is slow and will be suppressed soon while they meet other

grains. In SPB, the rotating and sliding of equiaxial and fine grains during the superplastic deformation process will rotate the new formed boride nuclei. The growth of borides with preferential crystallographic orientation will soon stop because of the turning effect and further growth of these nuclei will be continued in random orientation. The rotation-growth mechanism finally produces a boride layer with fine equiaxial grains (Hasan, 2005).

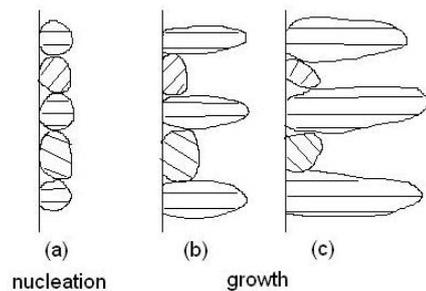


Figure 2.10 The boride layer formation mechanism during conventional boronizing (a) nucleation (b) and (c) growth. (Source: Hasan, 2005)

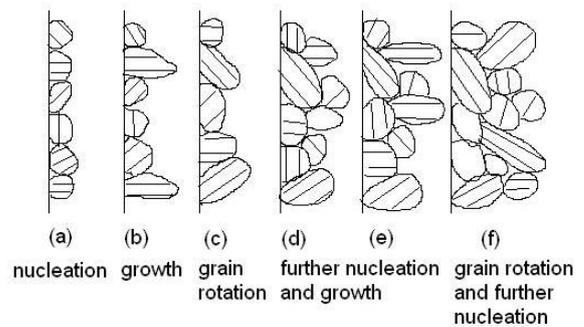


Figure 2.11 The boride layer formation mechanism during SPB. (Source: Hasan, 2005)

In present study, a new approach of SPB under compression was introduced with main objective to understand the behaviors of boronizing under huge plastic deformation. Although the study looks similar to that of SPB under tension, the mode of deformation used here is considered more practical and easy as well as having the advantage to avoid the problem of necking. For this fundamental study, the effect of strain on boronizing was studied and the results obtained were analyzed and compared with that from the CB one.

## 2.3 Boronizing Substrate

### 2.3.1 Duplex Stainless Steel

The DSSs are defined as a family of stainless steels consisting of a two phase aggregated microstructure of  $\alpha$ -ferrite and  $\gamma$ -austenite (Han and Hong, 1999).

Brief history of DSS was written by Alvarez-Armas (2008) stated that these alloy steels have existed for more than 70 years. The early grades were alloys of chromium, nickel and molybdenum. The first wrought DSSs were produced in Sweden in 1930 and were used in the sulfite paper industry. These grades were developed to reduce the intergranular corrosion problems in the early high-carbon austenitic stainless steels. In the early 1980s, a second generation of duplex steels was introduced with improved welding properties mainly through nitrogen alloying. The most common duplex grade today is EN 1.4462 or 2205 (UNS S31803/S32205), which has a nominal composition of 22% Cr, 5% Ni, 3% Mo, and 0.16% N. This steel is used in a great number of applications in a wide variety of product forms. Many duplex grades become commonly known by a number that reflects their typical chromium and nickel contents, e.g. 2205 with 22% Cr and 5 % Ni.

DSS exhibited an  $\alpha$  single phase just below the liquidus temperature, but the phase transformation of  $\alpha$  single phase into  $\alpha+\gamma$  duplex phases occurred below 1320°C. Since the volume fraction of  $\gamma$  phase increases with decreasing temperature below 1320°C, the precipitation of fine  $\gamma$  phase in  $\alpha$  matrix phase improved the hot ductility at temperatures between 950°C and 1100°C. The grain growth is effectively suppressed at

high temperature due to the two phase aggregated microstructure causing a fine grained microstructure that encourage superplastic behavior (Han and Hong, 1999).

Figure 2.12 shows the microstructure of roughly 50% austenite and 50% ferrite of DSS. The blue ferrite phase surrounds the yellow austenitic phase. Figure 2.13 shows a phase diagram of Fe-Cr-Ni alloy. As shown by the dashed line in the diagram, DSS solidifies initially as ferrite, then transforms on further cooling to a matrix of ferrite and austenite. In order to avoid formation of brittle intermetallic phases, the usable temperature range of DSS is restricted in the range of 223 K to 553 K (Internet source 5).

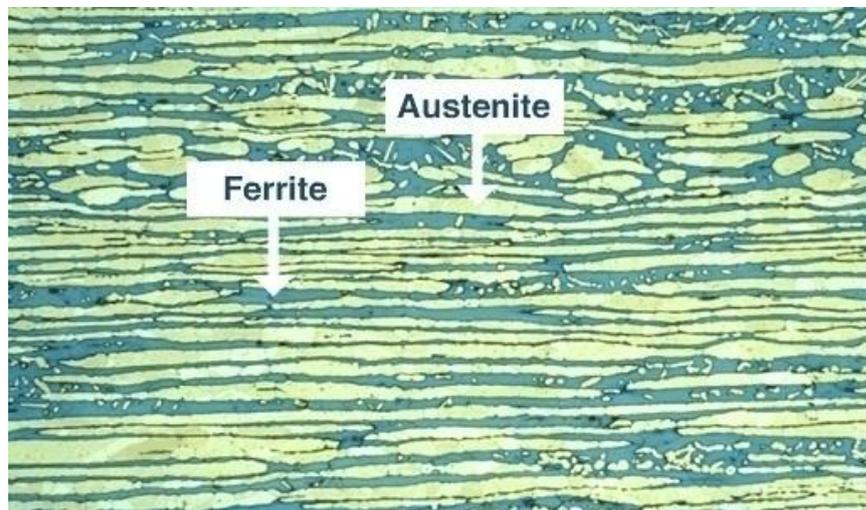


Figure 2.12 Microstructure of DSS (Internet source 7)

### Fe-Cr-Ni Phase Diagram

Dashed Line shows solidification of a typical Duplex

The Red region denotes a mixture of Ferrite and Austenite

Temperature in °C

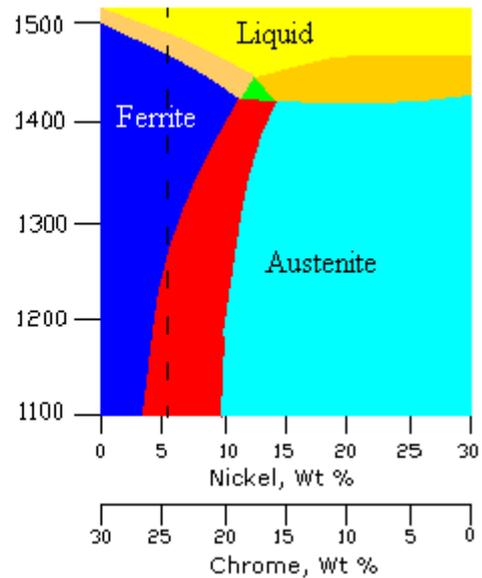


Figure 2.13 Fe-Cr-Ni phase diagram (Internet source 5)

With balanced ferrite/austenite microstructures, DSSs are very well known for their superior corrosion resistance and high strength compared to other stainless steel. As such, they are suitable for constructional and petrochemical applications. DSSs are widely utilized in the oil and gas production and transmission, petroleum industries, petrochemical process plants, shipbuilding, transportation and for pulp and paper production equipments (Jauhari et al., 2007).

### **2.3.2 Superplastic Duplex Stainless Steel**

DSS is widely known for its refined grain and structure exhibit superplasticity. DSS with fine grain microstructure has the ability to show superplastic behavior since the grain growth is effectively suppressed at high temperature due to the two phase aggregated microstructure (Han and Hong, 1999).

Han and Hong (1999) stated that Hayden et al. did the first reported investigation on the superplasticity in DSS in 1967. This investigation showed 500% elongation in 25Cr-6.5Ni-0.6Ti hot rolled DSSs at a temperature of near 1273 K. Researches done by Gibson et al. (1968) and Smith et al. (1976) reported that additional cold working and hot rolling enhanced superplasticity in DSS. Enormous elongation above 1000% was reported in cold rolled 25Cr-6.5Ni-0.6Ti DSS.

A thermomechanical process consists of solution treatment followed by cold rolling is an essential stage in producing superplastic DSS. These processing steps provide the stable finest microstructure at the deformation temperature and enhance superplasticity. The tensile elongation of superplastically deformed DSS increased with increasing amount of reduction during cold rolling (Han and Hong, 1997). The fine-grained duplex microstructure is obtained through the precipitation of the second phase particles when the thermomechanically treated DSS is heated up at test temperature (Han and Hong, 1999). The microduplex structure consists of  $\alpha$  subgrains and fine  $\gamma$  particles (Tsuzaki et al., 1996). Figure 2.14 shows microstructure of thermomechanically treated DSS after it has been heated up at test temperature, prior to a tensile test. A fine structure with grain size smaller than 5  $\mu\text{m}$  was obtained.

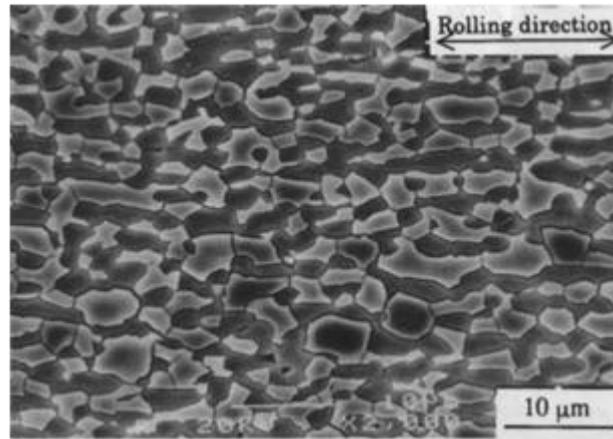


Figure 2.14 Microstructure of fine grain DSS (Source: Miyamoto et al., 2001)

The phenomenon of superplastic deformation in DSS has been termed dynamic continuous recrystallization by Tsuzaki et al. (1996). He suggested that the role of dynamic recrystallization is to keep the grain size fine suitable for the grain boundary sliding. The grain boundary sliding is considered the controlling mechanism for superplastic deformation in DSS and the role of the dynamic recrystallization is to transform the low angle grain boundaries into high angle grain boundaries suitable for sliding (Han and Hong, 1999). The disorientation angles between the neighboring  $\gamma$  grains increased with increasing strain, thus dynamic recrystallization transformed the low angle grain boundaries into high angle grain boundaries during the deformation so that they were suitable for sliding. From these studies, Han and Hong (1999) concluded that the grain boundary sliding assisted by dynamic recrystallization is the controlling mechanism for superplastic deformation of DSS.