CHAPTER 1 INTRODUCTION

Because of the large amount of Si particles, the hypereutectic Al-Si-X alloys typically have outstanding wear resistance, low thermal expansion and good casting characteristics [1,2]. They have received broad attention due to their potential applications to components of automobiles and compressors, such as spiral scrolls, pistons, engine blocks, pumps bodies, etc [3-5].

Most of the hypereutectic Al-Si-X alloy parts are currently produced by casting or ingot metallurgy (IM) routes. However, these castings or IM parts normally have coarse Si particles, even though modifying treatments are used [6]. Additionally, they can exhibit pronounced gravitational segregation of Si particles, because the Si particles are slightly lighter than the melt and tend to float as the castings solidify slowly [6]. These segregated large Si particles may shorten the life of the tools used in machining and they also dramatically degrade the mechanical properties [1,2].

Making the Si particles small and uniform thus has become a key objective when fabricating hypereutectic Al-Si-X alloys of high quality. To make the Si particles fine and uniform in hypereutectic Al-Si-X, solidification of the alloy melt should be quick [2]. There are many conventional rapid solidification processes (RSPs) such as gas atomization and melt spinning [7-9]. However, these RSPs usually produce powders or ribbons, and their products need further treatment by PM method to form bulk materials [10-17].

The Al-Si-X powders or ribbons are difficultly sintered due to their surface oxide films [10]. In the last decade, some techniques such as powder forging [11-15] and powder extrusion [16-17] have been developed to overcome this difficulty. However, besides the cost issue in these methods, they still do not easily achieve net-shape forming of complex parts such as engine block, pump bodies, etc. The difficulty in net-shape forming is primarily attributed to the poor formability of the Al-Si-X powder preforms in cases involving deformation in solid state. For instance, a backpressure is often required [13-15] in conventional powder forging machines, complicating the design of the forging molds and the machines, increasing costs.

Since the discovery of the unique rheological behavior of non-dendritic semi-solid slurries in the early 1970s [18], forming a metal in its semi-solid state becomes feasible if the metal has the so-called “non-dendritic” microstructure [19-22]. In order to easily achieve net-shape forming, several new semi-solid metal-forming (SSMF) processes have been developed [19-34]. Thixocasting [20-22] is an SSMF process in which the net-shape forming is performed using a die-casting machine and feedstock of semi-solid slurries that are fabricated by heating a “non-dendritic” feedstock in a solid state to a semi-solid state.

The non-dendritic feedstock used for thixocasting is typically made by ingot casting method and is mostly produced by continuous casting with electro-magnetic stirring [23] of the melt during solidification. Currently, the hypoeutectic Al-Si-X alloys that contain less than 12 wt% Si are the most popularly used in thixocasting process [22]. However, hypereutectic Al-Si-X alloys that contain more than 12 wt% Si are now still not popular used in thixocasting process [24-25]. This is because the feedstock of the hypereutectic Al-Si-X alloys with fine microstructures is difficultly fabricated using conventional ingot method, as the solidification during cooling is so slow that the coarsening and segregation of the Si particles may readily occur [6,25].

Recently, P.J. Wars and J. Valer [35-37] also developed a net-shape forming process that combines semi-solid and powder processing. They fabricated the semi-solid feedstock of hypereutectic Al-Si-X alloys by spray forming of billets followed by extrusion. An Al-25Si-5Cu oil pump housing has been shown to be successfully thixocast using this feedstock [36]. However, this approach has various disadvantages, including a low spray forming yield rate of only 60% to 80% because of over spray [36], and higher cost because of increased investment in spray forming equipment.

The atomized powder generally has very fine microstructure owing to rapid solidification [8]. Powder process thus has the potential to become an alternative method of fabricating the semi-solid feedstock with fine microstructure [38-44]. It was considered possible to use consolidated powder preforms, rather than spray formed billets, to net-shape a hypereutectic Al-Si-X alloy. Consequently, a new idea for net-shape forming by combining techniques of PM and thixocasting process was proposed in this study. This proposed novel process is introduced here as “powder thixocasting”, which is utilized to compare with the conventional PM routes such as “powder forging” or “powder extrusion”.

The aim of this study is to evaluate the feasibility of this new method, powder thixocasting. In this study, hypereutectic Al-25Si-2.5Cu-1Mg-0.5Mn alloy was selected as demonstration the feasibility of this idea. At first, Al-25Si-2.5Cu-1Mg was prealloyed in melt and gas atomized into spherical powder. The hypereutectic powder is then used as the semi-solid feedstock for thixocasting by means of powder consolidation. The consolidation was performed at elevated temperatures to increase the density of the consolidated preforms. Then the densified preforms were heated into semisolid state, before being thixocast. The consolidation mechanism of the proposed powder processing was also investigated in this study. The effects of processing parameters on the microstructure and tensile strength of thixocast specimens were also examined. Finally, the mechanical properties and wear performance of the powder thixocast materials were studied.

The wear behaviors of the Al-Si-X alloys are known to depend strongly on Si contents [45-48], size of primary Si particles [49], element additions [50-54], composed by dispersed reinforcement [55-58], and processing routes [59-65]. Besides, the wearing test conditions such as applied load, counter sliding body and sliding speed also greatly affect the wear behaviors of the Al-Si alloys [66-70]. Because the wear tests do not have standard procedures, two Al-Si-Cu-Mg alloys produced by conventional method were also undertaken to evaluate the wear performance of the powder thixocast Al-25Si-2.5Cu-1Mg alloy. Wear experiment results show that the powder thixocast alloy has better wear performance as well as more promising microstructures and mechanical properties than the conventional alloys.

Chapter 2 deals with the literature reviews of semi-solid forming techniques. Chapter 3 introduces about hypereutectic Al-Si-X alloys and then describes the conception and the experimental details of the powder thixocasting. Chapter 4 reports the effort on achieving net-shape forming of Al-25Si-2.5Cu-1Mg alloy by using the powder thixocasting process that is mentioned in Chapter 3. The influence of processing parameters on the success of the process and the mechanism of powder thixocasting are also detailed in this Chapter.

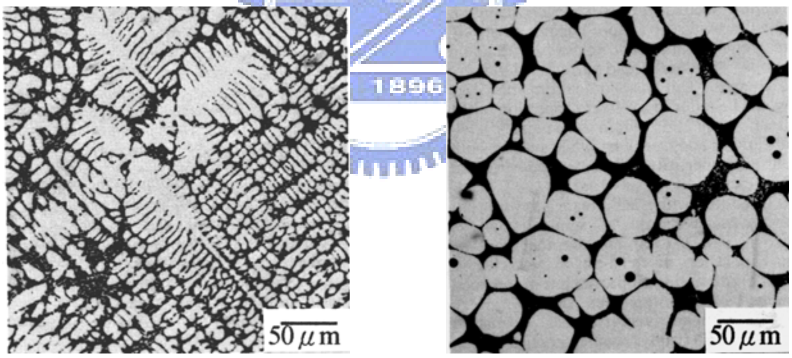
After the process was developed successfully, the properties of the thixocast Al-Si-Cu-Mg alloy were subsequently examined. In order to show the advantage of the new process, Al-Si-Cu-Mg alloys fabricated by conventional process were also investigated. Chapter 5 describes the results of the microstructures and mechanical properties of these alloys. Chapter 6 describes their dry sliding wear performance. From Chapters 5 and 6, the new process is clearly demonstrated to be feasible in net-shape forming of aluminum alloy with high integrity and superior performance. Finally, Chapter 7 makes a general conclusion, and Chapter 8 gives a broad concept for future work in this field.

CHAPTER 2 SEMI-SOLID METAL FORMING

2.1 What is Semi-Solid Metal Forming (SSMF)

Semi-solid metal forming (SSMF) [18-34] is a net-shape metal forming process in which metal alloys are processed in semi-solid state, where the alloy has part liquid and part solid. Traditionally, metal alloys are processed either in the solid states by wrought processing such as rolling, extrusion, forging or in liquid state by casting methods such as gravity casting, pressure die casting etc. However, metal alloys also can be processed in its semisolid state, if they have a solidification mushy zone.

The SSMF process was first discovered in 1970's by Flemings and his coworkers [18,20], and it has been practice for at least 30 years. The success of SSMF is based on the non-dendritic or globular microstructure. Figure 2.1 demonstrates an example of the dendritic and non-dendritic microstructures for a commercialized A356 aluminum alloy that was produced by conventional casting and SSMF, respectively.



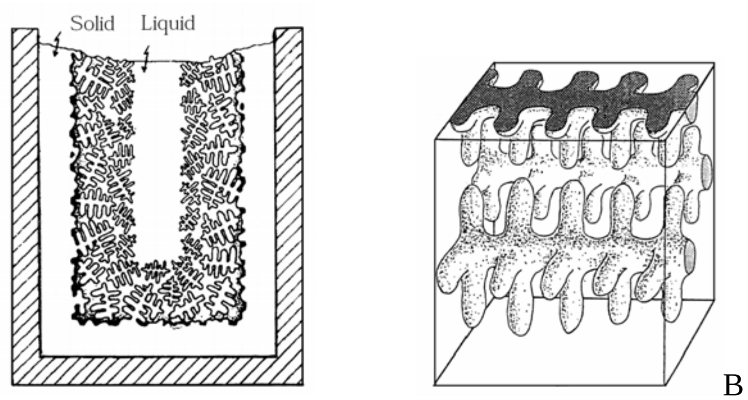
(a) (b)

Figure 2.1 Microstructures of Al-7.0Si-0.35Mg aluminum alloys with (a) dendritic and (b) non-dendritic aluminum grains [71]

Base on mechanical agitation method, David Spencer also discovered the essential rheological properties of the non-dendritic slurry [18]. The mechanism and rheological properties of the dendritic and globular material will be detailed in following sections.

A. Dendritic grains in conventional casting

Figure 2.2 schematically shows the dendritic grains that usually exhibit in conventional solidification. However, dendritic microstructure is not suitable for SSMF process, because it causes many solidification defects including filled or unfilled hot tears, liquid-solid separation during semi-solid deformation [20].



(a) (b)

Figure 2.2 Schematic diagrams of dendritic grains

(a) dendritic grains exhibit in the mushy zone at interface between solid and liquid phase during solidification (b) typical 3-D diagram of the dendritic grains.[20]

Dendritic growth normally arises when a crystal nucleus grows in a supercooling melt [72-74]. Figure 2.3 demonstrates a constitutional supercooling is present in an alloy melt that is solidified directionally. During directional solidification, latent heat of crystal growth is extracted through the solid, from right side to left side in Fig 2.3. As the dendrite grows, solute atoms are continuously rejected from the solidified dendrite, which builds a high solute concentration in front of the dendrite. The high solute concentration causes equilibrium liquidus temperature T_L to be lower in the melt near the dendrite than in the melt far away from the dendrite. A constitutional supercooling area near the dendrite will present if the actual melt temperature Tq is lower than T_L, as shown in Fig.2.3. The constitutional supercooling is believed to be responsible for the dendritic microstructures that exist in conventional metal casting.

Besides the effect of solute rejection, the latent heat dissipation during crystallization will also result in supercooling effect. Briefly speaking, dendritic growth will tends to occurs more often than flat interface growth in metal solidification because dendritic growth make the rejected solute and dissipated latent heat to be redistributed more efficiently than does flat interface growth.

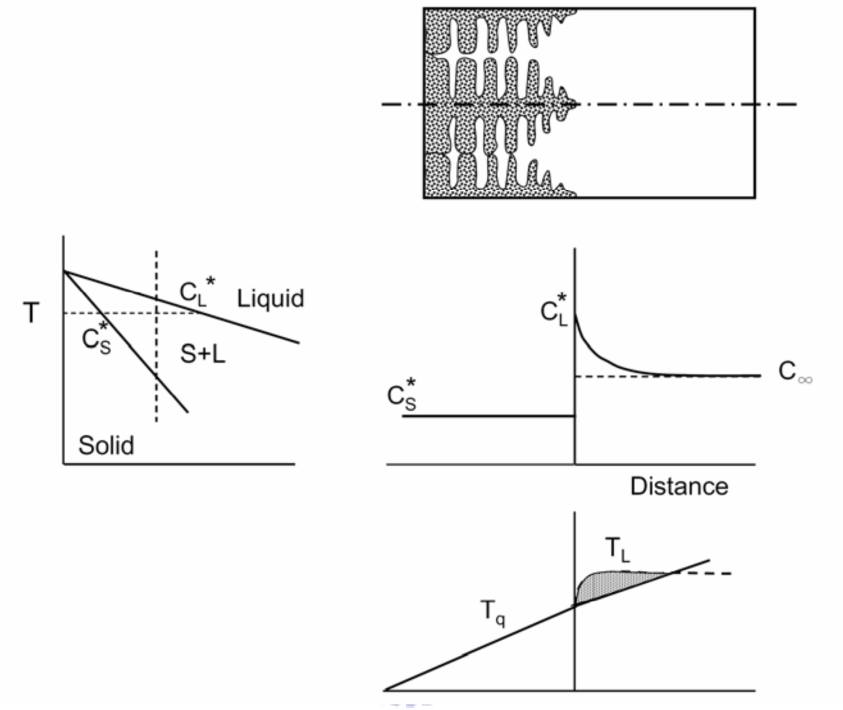


Figure 2.3 Concentration and temperature fields of dendrite

T_q is the alloy temperature and T_L is the equilibrium liquidus temperature, showing an area of constitutional supercooling in front of a tip of a growing dendrite as solute rejection continues during solidification. [74]

B. Non-dendritic grains obtained by melt stirring

Non-dentritic or globular microstructure is the basic requirements for SSMF process. The essential rheological properties of a non-dendritic Pb-15%Sn alloy semi-solid slurry was first discovered at MIT by Flemings and his student, David Spencer, in early 1971 [18]. David Spencer occasionally found a "non-dendritic" grain structure, when he conducted a hot-tear experiment to Pb-15%Sn alloy for his doctoral thesis. He found that "non-dendritic" grains could be produced by continuously agitating the alloy melt during solidification. This discovery initiated the SSMF process because it facilitates the metal forming processes to be undertaken at semi-solid state.

Many mechanisms explain the grain spheroidisation during stirring the melt [20, 32,33]. One was proposed by Flemings [20] and is depicted in Fig. 2.4. As solidification begins, agitating the melt results in formation of new grains (Fig. 2.4 a). Then, each dendrite continuously grows dendritically (Fig. 2.4 b). With continuing shear and time during solidification, the dendrite morphology becomes that of a “rosette” (Fig. 2.4 c), as a result of ripening, shear, and abrasion with other grains. Ripening proceeds during further cooling (Fig. 2.4 d). With sufficiently slow cooling and high shear, the particles become shperoidal, usually with a small amount of entrapped liquid (Fig. 2.4 e). This mechanism is like that for the ripening process, in which reducing surface area acts as the driving force. However, the mechanism is bases on the hypothesis that the solute concentration and temperature gradient near the crystallized grains are redistributed uniformly due to the vigorous stirring. Thus, the dendritic growth is depressed, since fluid flow homogenizes the distribution of the solute concentration and the dissipated latent heat around the dendrite.

An entirely different mechanism has been proposed by Vogel et al. [32] and discussed by Doherty et al. [33], and is schematically depicted in Fig.2.5. They suggest that dendrite arms bend under the flow stresses and the plastic strain is accommodated by dislocation generation. At the melting temperature, the dislocations can climb and coalesce to form grain boundaries. When the misorientation between grains across a boundary exceeds about 20^{o}, liquid interface energy, the liquid will now wet the grain boundary and rapidly penetrate along it, separating the arm from its stalk.

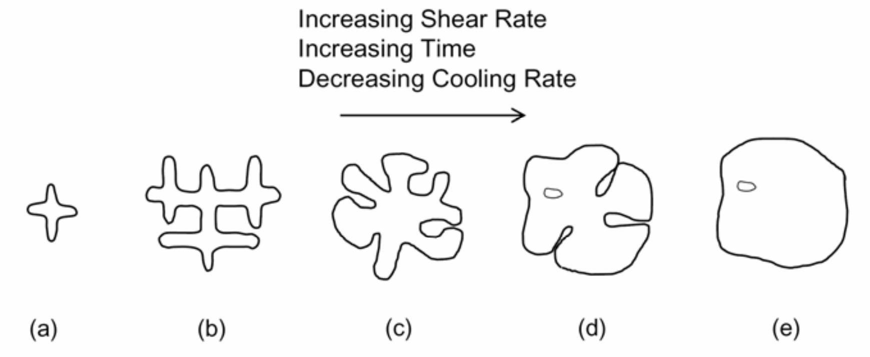


Figure 2.4 Schematic evolution of solidified crystal with vigorous agitation

(a) initial dendritic fragment, (b) dendritic growth, (c) rosette, (d) ripened rosette, and (e) spheroid. [20]

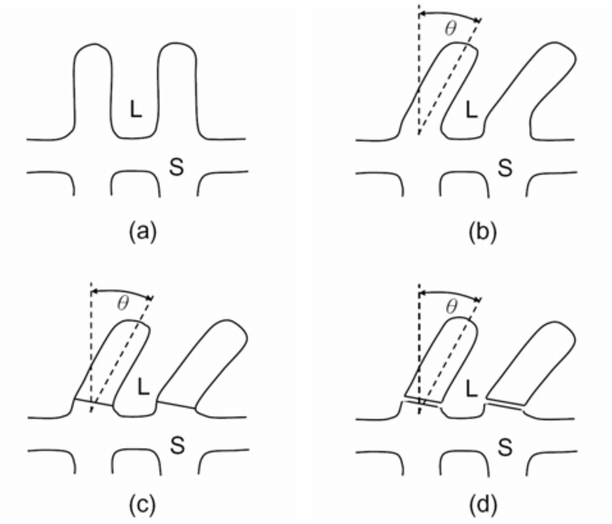


Figure 2.5 Model of grain boundary fragmentation mechanism

(a) undeformed dendrite; (b) after bending, (c) reoganisation of lattice bending to give grain boundaries, and (d) for $\gamma_{gb} > \gamma_{s/l}$*, grain boundaries have been wetted. [33]*

Figure 2.6 demonstrates the typical engineering methods to examine whether or not a semi-solid metal is of non-dendritic structure and is suitable for SSMF process. A “non-dendritic” semi-solid metal can easily be cut off with a knife by hand if of high fraction of solid, or look like porridge if of high fraction of liquid.

(a) (b)

Figure 2.6 Semi-solid state aluminum alloy with non-dendritic solid grains. (a) if consisting of high fraction of solid, semi-solid metal can easily be cut with a butter knife, (b) if of high fraction of liquid, it looks like porridge. [22]

C. Fabrication of non-dendritic feedstock

Figure 2.7 shows various technologies that have been developed to produce the non-dendritic materials or so-called SSMF billets. SIMA (Strain Induced Melt Activated) and RAP (Recrystallisation And Partial melting) are the methods [21, 22], where material is worked in the solid state (eg. by extrusion or rolling) and then is heated to a semi-solid temperature in which recrystallisation occurs and the liquid penetrates the recrystallised boundaries to give the required microstructure. SIMA is based on hot working (above the recrystallisation temperature) and RAP on warm or cold working (below the recrystallisation temperature). MagnetoHydroDynamic (MHD) [23] fabricates SSMF billets by combining techniques of direct cooling casting and magneto-hydrodynamic stirring. Presently, MHD is the most popular methods to produce hypoeutectic Al-Si-X commercialized SSMF billets. MHD solves the problem of erosion of the agitator that directly contact with aluminum melt during the mechanical stirring. Alternatives are the chemical grain refining where a highly grain refined alloy is achieved for the billet [21, 22]. Finally, SSP (single slug production) is a route that using rapid solidification to fabricate ultra-fine grain structure for the billet. When heated to semi-solid temperature, the ultra-fine grains suspend in the mushy semi-solid slurries and such slurries can behave similarly to the non-dendritic slurries.

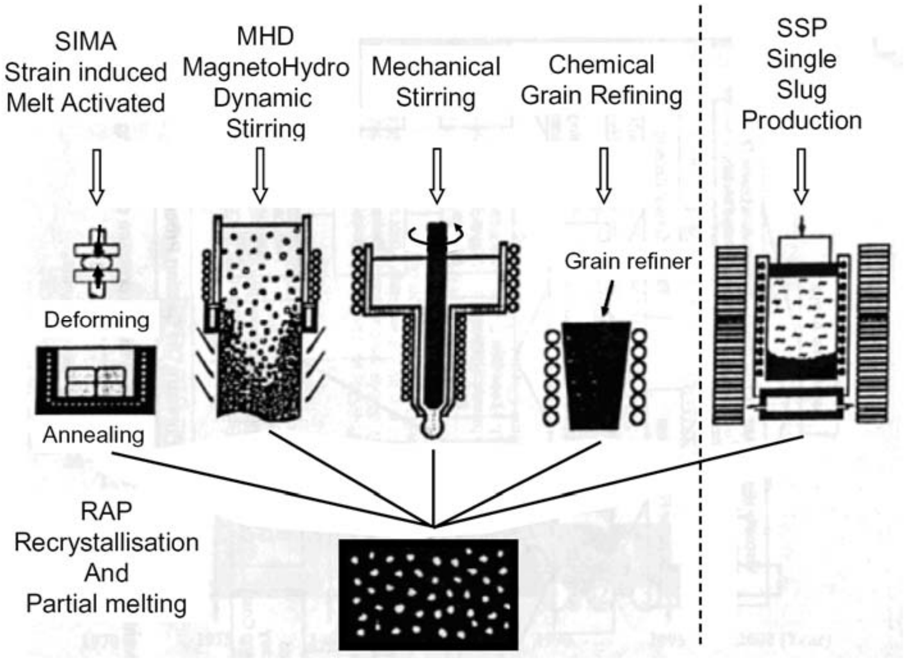


Figure 2.7 Methods of producing non-dendritic materials for SSMF [21]

D. Rheological behavior of the non-dendritic semisolid slurry

SSMF takes the advantages of the pseudo-plastic and thixotropic behaviors of semi-solid metal slurries [18,19]. Because of these behaviors, the SSMF slurries have adequate strength for robotic handling, facilitating transfer from the heating furnace to the press machine. Besides, the high shearing rates during injection cause the semi-solid alloy to flow like a very viscous liquid and fill the mould cavities smoothly and without entrapping gases.

Figure 2.8 a schematically depicts a semi-solid metal slurry that is deformed under a τ shear stress. If the microstructure consists of spheroids of solid in a liquid matrix, its viscosity (η) normally is time and shear rate ($\dot{\gamma}$) dependent.

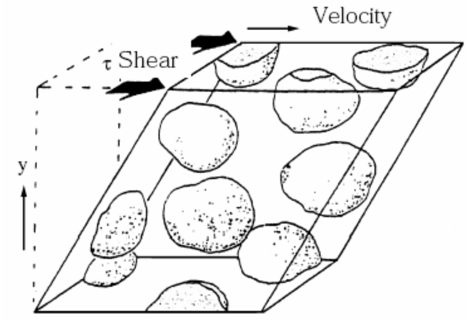
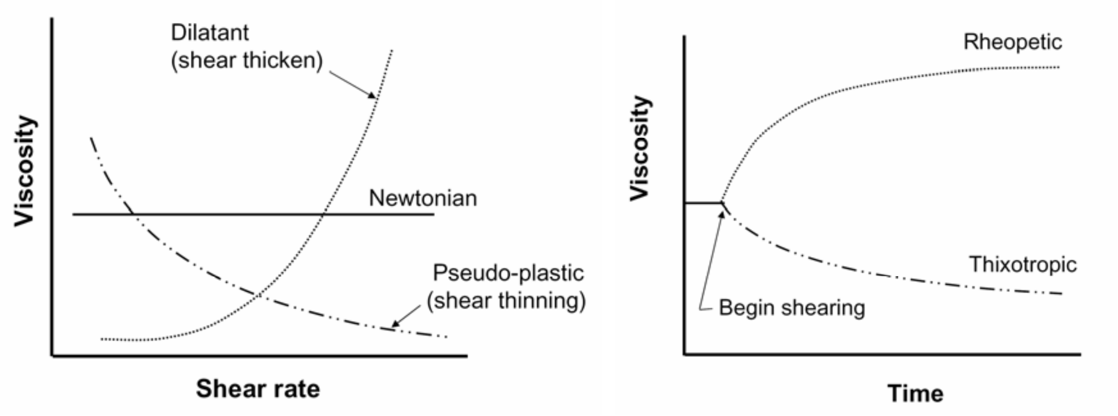


Figure 2.8 Schematic flow of a semi-solid metal slurry under a shear stress.

Figure 2.9 a shows typical shear-dependent flow curves. Newtonian fluids, such as water and some low-molecular-weight mineraloils, display viscosity that is independent to shear rate. Pseudo-plastic or shear thinning fluids display viscosity reduction while the shear rate increases. Semi-solid metal or other colloidal systems are the examples. The colloidal structure of solid particles and liquid matrix breaks down while shear rate increases, displaying reduced viscosity. Dilatant or shear thickening flow, which is unusual in colloidal systems, displays viscosity increases with shear rate.

Figure 2.9 b shows typical time-dependent flow curves. Time-dependent flow measures the increase or decrease in viscosity with time, while a constant shear is applied. The flow is called thixotropic if viscosity decreases with time, or rheopetic if it increases. Semi-solid metal slurries usually exhibit thixotropic property, while they are sheared. Thixotropic behavior describes a degradation of the colloidal structure during agitation. This structure degradation is suggested to be referred to the dendritic structures that are broken to get a globular structure during agitation.

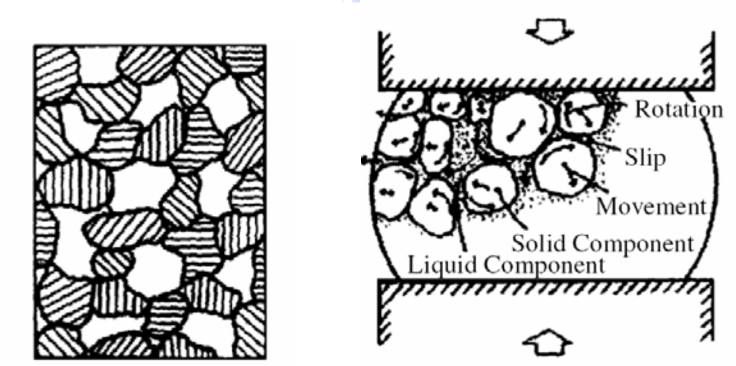


(a) (b)

Figure 2.9 Typical flow viscosity curves.

(a) shear-dependent flows and (b) time-dependent flows

Figure 2.10 further explain the pseudo-plastic behavior of a semi-solid metal slurry. Figure 2.10 a shows the slurry behaves like a solid if it is not sheared. This meaning that it can be handled as a solid when at rest. However, if the slurry is pressed, the slurry can be easily plastically deformed through rotation or sliding of the solid grain particles. This means that the semi-solid slurry can flow like a liquid when injected into a mold cavity to be shaped into a component.



(a) (b)

Figure 2.10 Plastically deforming a semi-solid metal slurry.

(a) A solid framework of semi-solid slurry, (b) movement of solid particles during deforming the semi-solid slurry [34]

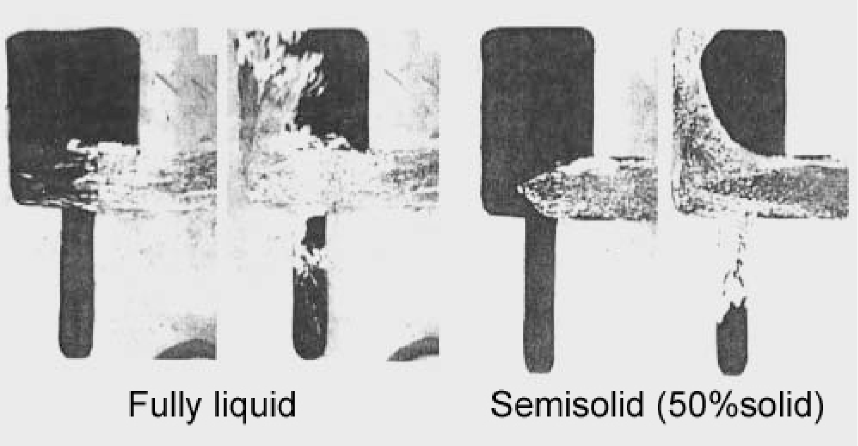
E. Advantages of SSMF

SSMF fabricates industry parts with very high quality, which is mainly resulted from its highly smooth flow of metal during formation. Smooth flow of semi-solid slurries is demonstrated in Fig 2.11, which shown flow front of liquid is much more turbulent than that of semisolid slurry. In conventional die casting, molten metal sprays into the die, leading to higher levels of porosity and poor quality of castings. Contrarily, metal flow is very smooth in SSMF, thus the SSMF achieves low porosities and gas hole. Shrinkage in SSMF parts is minimized because of the high solids content and the much lower temperatures involved with SSMF than conventional casting.

The “semi-solid” material has unique flow characteristics and low heat content. The resulting castings have little or no porosity and die life is improved compared to traditional die and squeeze casting. Compared with the superheated liquid metal, SSM has lower temperature, lower shrinkage and a more stable flow pattern. Therefore, the rheomolding process can produce net-shape metal or metal-matrix composite parts continuously at lower cost.

The advantages of SSMF process are summarized and listed below [21]:

- Low casting temperature of about 580 °C → Low consumption of energy
- Less heat removal → Long life of mold
- Earlier mold opening → Less cycle time
- Very little shrinkage and little or no porosity → Heat treatability & Enhanced mechanical properties
- Much less loads for forging and extrusion → Much higher reduction in one step



(a) (b)

Figure 2.11 Flow front of a fully liquid and a semisolid slurry [75]

Table 2.1 lists major problems of metal forming processes, based on the three categories- liquidus, solidus and semisolid processes. Liquidus processes inevitably have the casting defects including gas holes, shrinkages and segregations etc, leading to low quality of cast parts. Solidus processes are costly and difficult in net-shaping complex parts, although it can achieve high properties.

SSMF also has needs to be overcome some difficulties, although it solves the aforementioned major problems in conventional liquidus and solidus processes. The main problems or difficulties of SSM will be detained in next paragraph.

Table 2.1 Metal forming processes and their major problems [21]

Feed Metal	Manufacturing Process	Major Problems
Liquid	- Gravity casting - Pressure die Casting	- Turbulence, air entrapment, shrinkage porosity, macrosegregation - High thermal impact on machines or mold leading to their short life - Low production rate due to long solidification time
Solid + Liquid	Semisolid Metal Forming (SSMF)	- Suitable operating temperature range is narrow - Dendritic grains cause macro-segregation and “non-filled” hot cracks
Solid	- Powder Metallurgy - Forging, Extrusion, Rolling	- High cost - High residual stresses, buckling, wrinking, cracks during processing - Difficult to achieve the formation of complex shape components

F. Key technologies of SSMF

To success a SSMF process needs the following key technologies:

1. A special pretreatment to the feedstock for having “non-dendritic” or globular microstructures. Dendritic feedstock usually causes defects of “filled” or “non-filled” hot tears in SSMF [20] . Figure 2.12 shows an example of so-called “filled” hot tear.

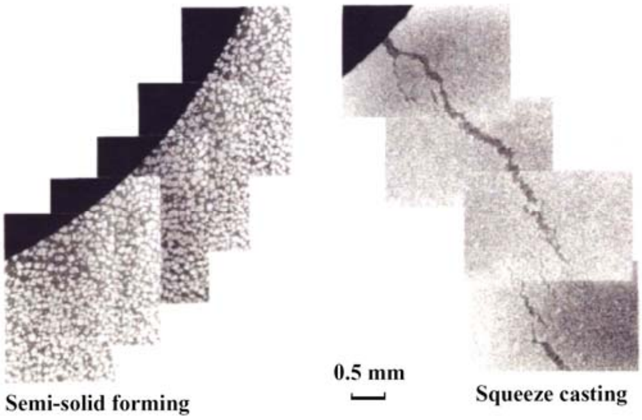


Figure 2.12 Hot tear cracks exist at the corner of a squeeze casting part (right) in magnesium alloy (AZ91). [76]

2. Heating the feedstock precisely to obtain a suitable liquid fraction for semi-solid forming.

Semi-solid temperature ranges of alloy metals are typically narrow. Figure 2.13 shows that liquid fractions of several commercialized aluminum alloys increases with temperature, when the metal is at semi-solid state. From this figure, for example, if an A356 alloy has 44% to 50% of liquid fraction, which range is considered suitable for semi-solid forming, then the A356 alloy should be finally heated to and kept within 575 ^{o}C to 580 ^{o}C. Wrought aluminum alloys such as 2024 and 6082 have even less width of the operation temperature windows.

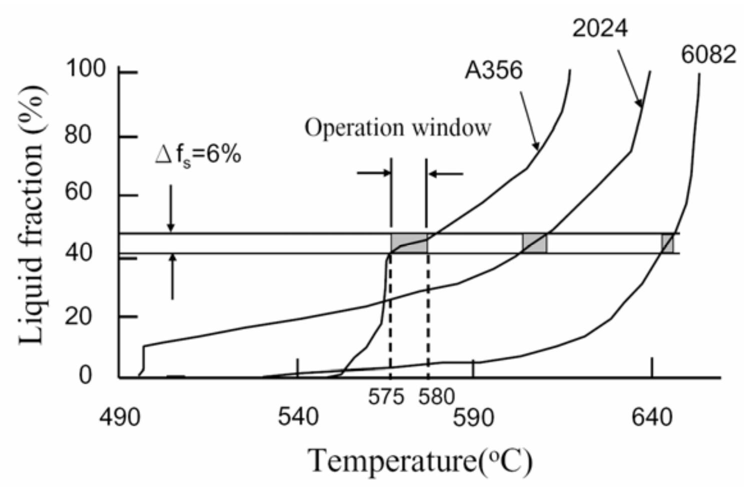


Figure 2.13 Liquid fraction vs. temperature for some aluminum alloys , which shows distinct operation temperature windows within mushy zone for SSMF when liquid fraction is controlled within 44% to50% [77]

3. Eliminating the defect of oxide films during mold feeling

Defects of oxide films in SSMF process results from two major events: oxidization of surface metal during reheating to semi-solid temperature, oxidization of semi-solid metal flow front during feeling of mould cavities. The former is usually prevented by rapid heating process, thus induction heating is preferable in SSMF. The latter effect can be decreased by optimization of the gating system of the SSMF mould.

2.2 Procedures of conventional SSMFs

SSMF processes are conventionally divided into four categories: thixocasting, thixomolding, rheocasting, and rheomolding. Figures 2.14 and 2.15 show the difference in the procedures between the processes with the prefixes of Thixo- and Rheo-. In rheo-process, the semi-solid forming is directly conducted as a melt is cooled down to its semi-solid state. On the other hand, in thixo-process, the semi-solid forming is performed by reheating to semi-solid state of a non-dendritic feedstock that is pre-treated by stirring cast or other special casting routs.

The difference between the routes of -cast and -mold is associated with the injection assembly of the forming apparatus. The former is corresponding to the plunge-sleeve system like those used in conventional die-cast machines. The latter is to the screw-barrel system mold like those in conventional injection molding machines. The four conventional SSMF processes will be detailed as follows.

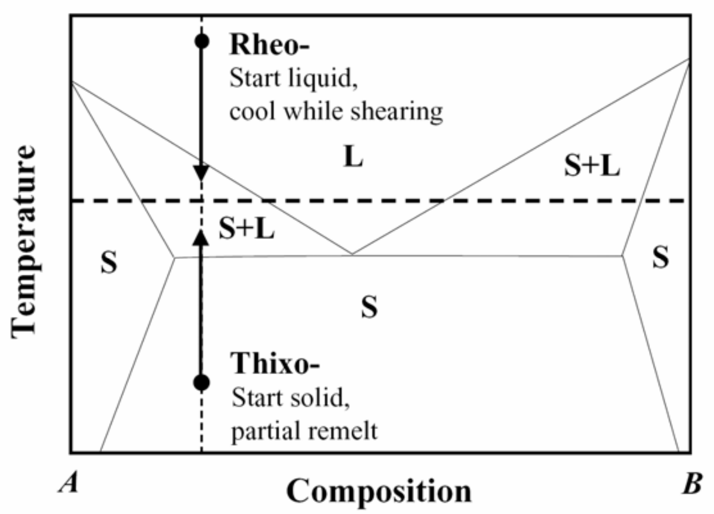
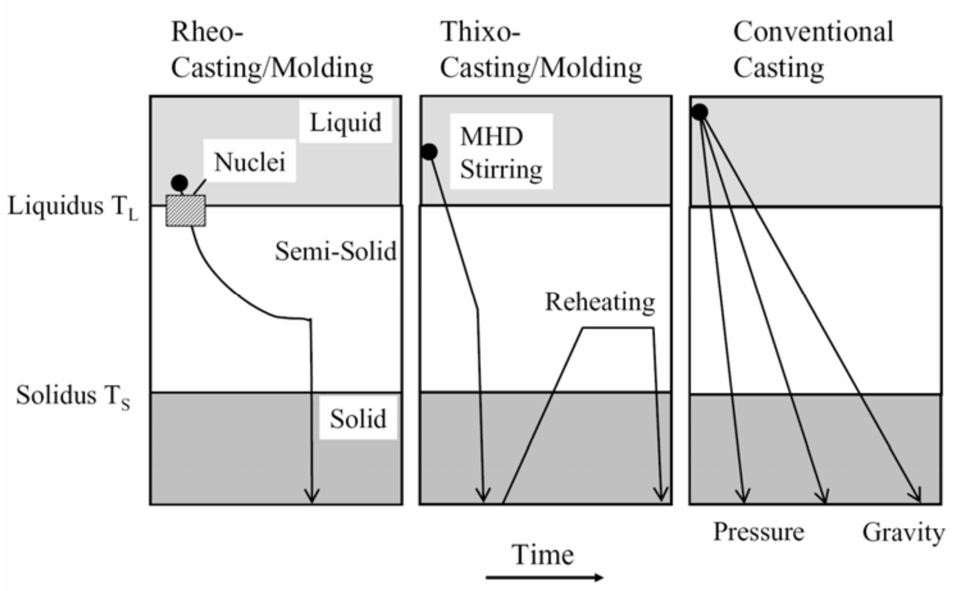


Figure 2.14 Eutectic binary phase diagram, showing mushy zone temperature in (S+L) (solid and liquid and the comparison between rheo- and thixo- semisolid processes . [27]



(b)

Figure 2.15　Cooling curves of metals in various shaping processes, showing the comparison between rheo- and thixo- semisolid processes. [76]

A. Thixocasting

Thixocasting is a semi-solid forming process that forms metal components by injecting semisolid materials into the mold using a die-casting machine. Amount the aforementioned four SSMF routes, today thixocasting is the most popular method for semi-solid forming of aluminum alloys.

Figure 2.16 draws the procedures of the conventional thixocasting. Basically, the procedures are divided into two major parts: the procedures for fabrication of SSMF non-dentritic billets, which need be done before the semi-solid formation procedures.

The non-dendritc billets are fabricated by many methods; however, MHD stirring is now only commercialized. The non-dendritic billets can be purchased from SSMF billet casting plants. The SSMF billets often have the microstructure that comprises nondendritic solid grains that are surrounded by a eutectic phase with a lower melting point than the solid particles. During reheating stage, the eutectic phases melt first and remaining solid, in the form of spherical metal particles, gives a semi-solid “mush” which can be shaped into the desired part.

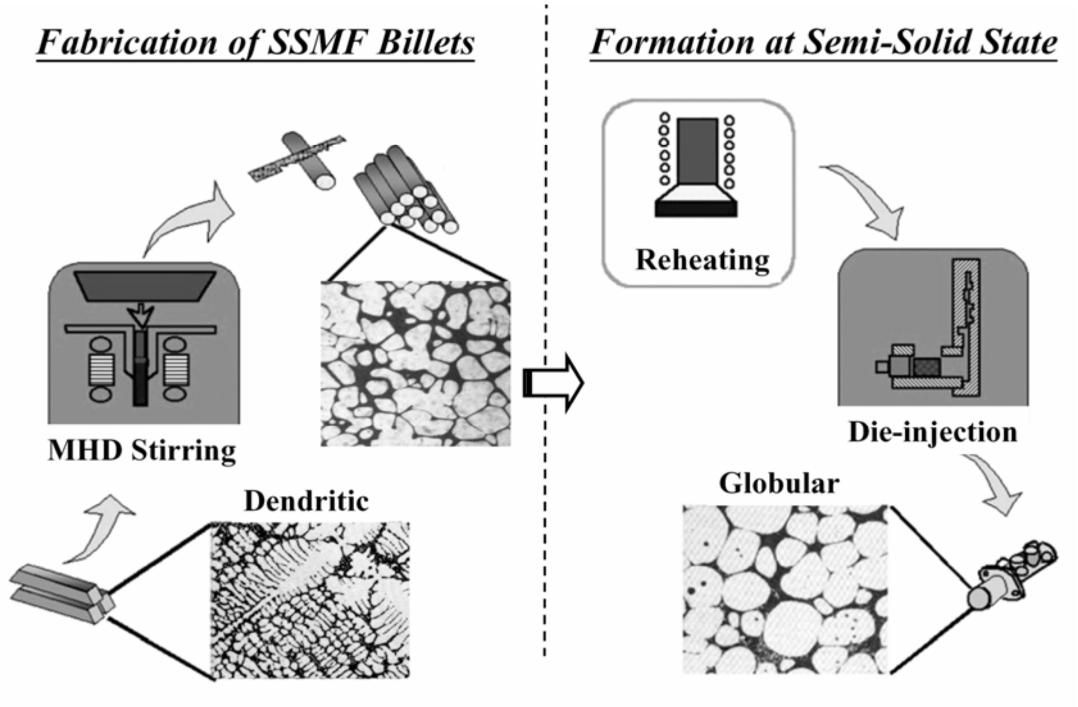


Figure 2.16 Procedures of conventional thixocasting.

B. Rheocasting

Rheocasting is a "slurry-on-demand" SSMF process, in which non-dendritic slurry is produced when it is just needed to be shaped. Rheocasting is first proposed by Flemings *et al.* in early 1970's. In Flemings' method, the non-dendritic slurry was fabricated by continuously mechanically stirring a cooling liquid metal until the melt is approximated of 50% solid, then it is injected into a mold cavity. However, this approach causes the stirrer to be damaged by the melt; hence, it is not practicable.

In 1998, UBE Ltd, Japan, developed a new rheocasting (NRC) process and patented it. Figure schematically shows the NRC process, as is shown in Fig.2.17. A slightly overheated melt liquid metal is poured into specially designed steel crucibles. In the crucibles, semi-solid slurry is formed by controlled cooling until a special microstructure is formed. By controlling the slurry temperature, a stable skeleton of the solid phase is formed within a few minutes after pouring. The solid-like slug is then heated by induction heating to homogenize the slug temperature before being transferred into the sleeve of the vertical SQC machine, where it is cast into its final shape. So far, the NRC process has been evaluated by processing aluminum and magnesium alloys.

NRC offers a significant cost advantage over thixocasting, since it does not need to purchase the non-dendritic billets and reheat them, besides the failed parts, the runners and biscuits can be recycled immediately.

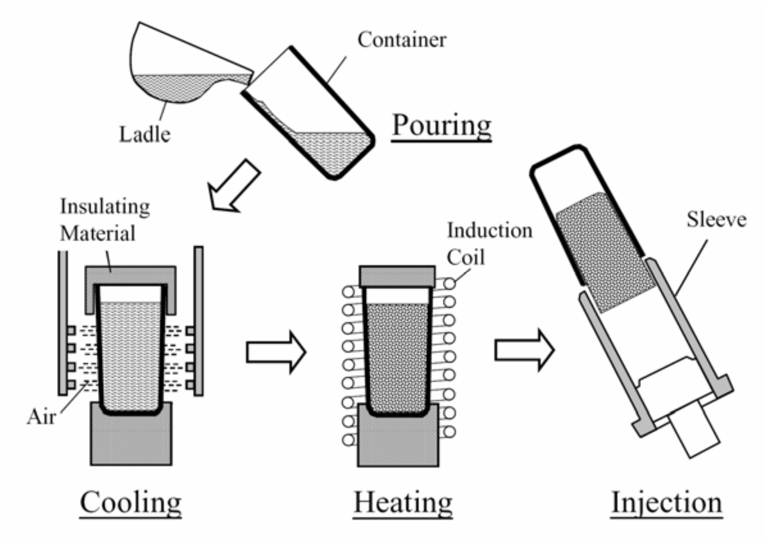


Figure 2.17 Procedures of New Rheo-Casting (NRC) process (UBA, Japan) [76].

C. Thixomolding

Thixomolding was invented by Dow Chemical, USA, in early 1988. Dow Chemical patented this technology in 1991 in USA Patent No. 5,040,589, and trademarked it as Thixomolding®. In this period, Dow Chemical established a new company called Thixomat.

Figure 2.18 schematically shows the apparatus of Thixomolding ®. Magnesium solid chips are charged in a feed stock container that is set upon a barrel-screw assembly. The chips slips into a barrel and are forced forward to a mold by a rotating screw. As are screwing stirred, the chips are heated to a semi-solid state, and then injected into a mold cavity by a shot system.

Nowadays, Thixomolding® has well-developed and commercialized in mass production of magnesium alloy parts applied in computer and automobile industries. However, the technique can not adopted for aluminum alloy, because aluminum melt often reacts with the barrel and screw and cause significant damage of this injection assembly, especially during vigorously agitating.

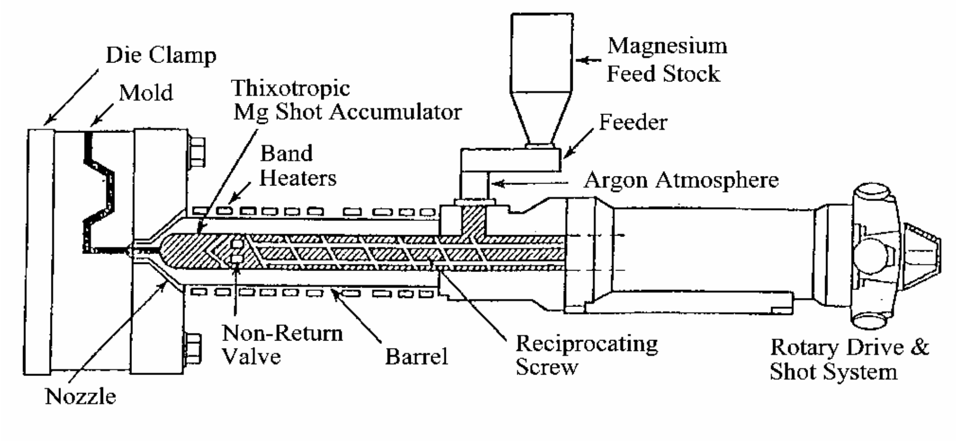


Figure 2.18 Schematic diagram of Thixomolding ® apparatus invented by Dow Chemical [78].

D. Rheomolding

In 1992, K. K. Wang and his co-workers proposed a new method and apparatus for the injection molding of semi-solid materials (SSM). Figure 2.19 depicts the injection system of the rheomolding apparatus. This invention was patented by Cornell Research Foundation, Inc., in 1996 (USA Patent No.5,501,266).

In this process (called "Rheomolding"), a superheated liquid magnesium alloy is cooled into the semi-solid state in the barrel of a special vertical injection-molding machine. The growing dendrites of the solid phase are broken into small and nearly spherical particles by the shearing force generated by the screw and barrel. Finally, the semi-solid slurry is injected into a mold cavity through a nozzle tip.

Although the rheomolding process is more economical than Rheomolding®, it is still not commercialized due to the difficulty to control a suitable semi-solid temperature and to avoid the melt from leakage through the gap between screw and barrel. .

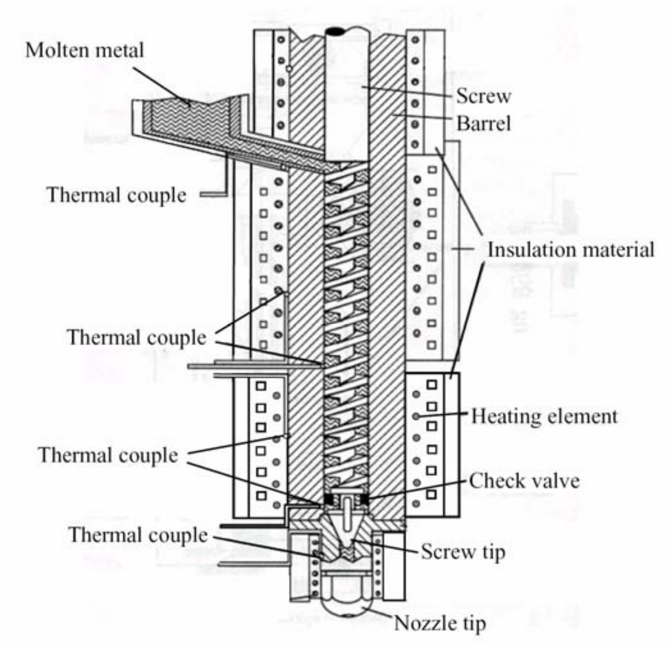


Figure 2.19 Schematic diagram of the srew-barrel injection system of a rheomolding machine invented by Cornell Research Fundation. [29]

2.3 Applications of SSMF

SSM processing of aluminum for automotive applications started in the early 1990’s. The process is now being practiced around the world. Figure 2.20 demonstrates the examples of the commercialized SSMF products. For example, fuel rails (Fig. 2.20 e) are the large volume automotive part in production today and as critical components in fuel injection systems, must be pressure tight.

SSMF fabricated parts are of very high quality, being pressure tight and exhibiting excellent structural integrity. Besides, the improved mechanical integrity allows components to have smaller cross-sections and the replacement of steel with aluminum for safety critical components such as suspension components for cars. In the transportation industry’s request for weight reduction, SSMF therefore offers a considerable advantage over other processes. Figure demonstrates some of the SSMF automotive parts.

In Fig. 2.20, most the parts are fabricated using alloys A356 (Al-7%Si-0.3%Mg) and A357 (Al-7%Si-0.5%Mg), and are fabricated by either thixocasting or rheocasting.

However, currently, neither of these two SSMF processes can successfully fabricate hypereutectic Al-Si-X alloys containing very fine Si particles, even, recently, SSM billets in 390 (Al-17%Si-Cu-Mg) alloys have been introduced as well. This inability results from the fact that the semi-solid feedstock used in the two processes is typically fabricated using the IM method, while the alloy melt solidifies slowly, making it difficult to refine the microstructure. Therefore, a variety of technical challenges remains for SSM casting to continue to gain increased use in a broader range of applications.

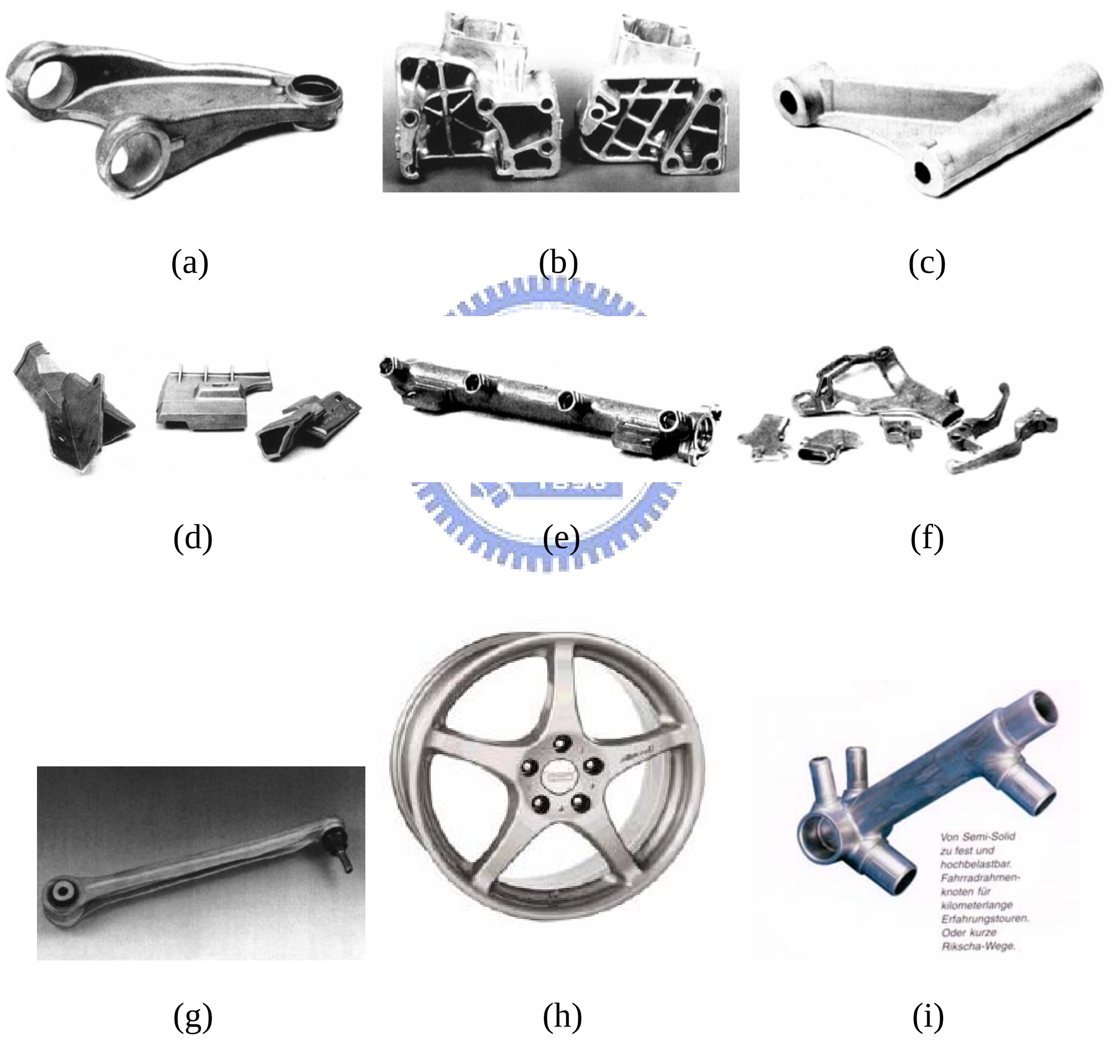


Figure 2.20 Applications of SSMF.

(a) Front triangle (b) engine brackets (c) bracket component (d) vantime nodes (e) fuel rail (f) snowmobile and mountain bike part (g) car suspension arm (h) wheel and (i) bicycle joint

CHAPTER 3 A NOVEL CONCEPT OF SEMI-SOLID FORMING OF HYPEREUTECTIC AL-SI-X BY POWDER THIXOCASTING

3.1 Motivation

This Chapter will present the earliest design concept for a novel SSMF process that involves traditional PM routes to achieve net-shape forming of high-performance hypereutectic Al-Si-X alloys. In addition, the novel process is introduced herein as powder thixocasting.

The prior arts that involve processing of metal powders in semi-solid state and the resemblance between powder thixocasting and powder forging are also described in this Chapter. These descriptions are helpful to understand the conducted experiments that describes in following Chapters.

3.2 Hypereutectic Al-Si-X alloys

Hypereutectic Al-Si-X alloys have good wear resistance due to the plenty of Si particles. Besides, these alloys also have the advantages including high strength, low thermal expansion and together with excellent castability and reduced density. They are usually used in the applications where good wear behavior is necessary, such as connecting rods, cylinder liners, pistons, engine block, oil pump gear wheels and air conditioner compressors, etc.

A. Binary Al-Si phase diagram

Hypereutectic Al-Si-X alloys, the aluminum alloy that contains more than 12% Si, have high volume of primary and eutectic Si particles dispersed in an aluminum alloy matrix. A390 (Al-17%Si-4%Cu) is the most common used among the commercialized hypereutectic Al-Si-X alloys.

Figure 3.1 depicts the simple binary Al-Si phase diagram, indicating a eutectic point at 12.6%Si and 577°C. The solubility of Si in α-aluminum reaches a maximum 1.65% at the eutectic temperature, whereas there is almost no solubility of aluminum in

Si. If Si <12.6% (i.e. for hypoeutectic Al-Si alloys), the alloys consist of primary α-Al grains dispersed in an matrix of the eutectic α+β. If Si >12.6% (i.e. for hypereutectic Al-Si alloys), the alloys consist of primary β-Si grains dispersed in an matrix of the eutectic α+β.

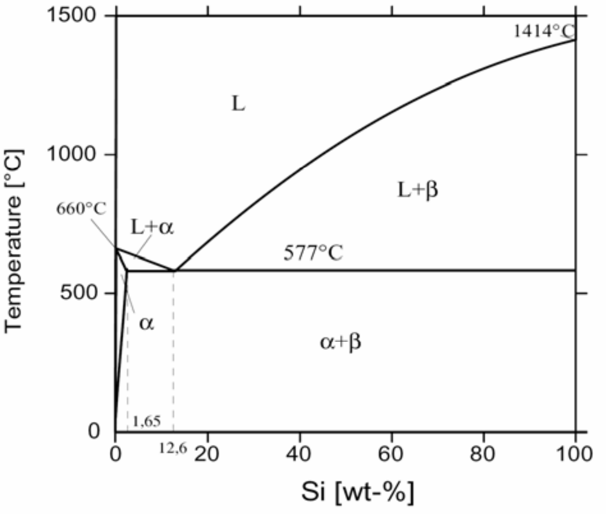


Figure 3.1 Binary phase diagram of Al-Si alloy [27]

B. Problems in net-shape forming of hypereutectic Al-Si-X alloys

Near net-shape forming of hypereutectic Al-Si-X alloys with fine microstructure is still difficult, although these materials have been commercially used for many years. Among the net-shape forming methods, the techniques of ingot metallurgy (IM) and powder metallurgy (PM) are the two most popular routes for processing hypereutectic Al-Si-X alloys. However, IM components always contain large primary silicon (Si) particulates, despite the use of modification of Si. Large and extremely hard Si particles may reduce tool life during machining and significantly reduce alloy mechanical strength. Besides, the IM components often contain macro-segregated Si particles, owing to the fact that silicon particles are slightly lighter than aluminum melts and tend to float.

On the other hand, PM processes can produce hypereutectic Al-Si-X components with fine and uniformly distributed Si particles, However, conventional sintering processes are very difficult to effectively consolidate hypereutectic Al-Si-X powder because of the presence of oxides on surface of the powder particles. During last two decades, techniques for powder forging or powder extrusion have been developed to effectively consolidate the hypereutectic Al-Si-X alloy powder. These methods are successful to produce compressor scrolls and other bulk materials of the hypereutectic Al-Si-X alloy. However, these processes are still difficult to achieve net-shape formation of complex components, due to the poor formability of the powder preforms when they were processed at solid states.

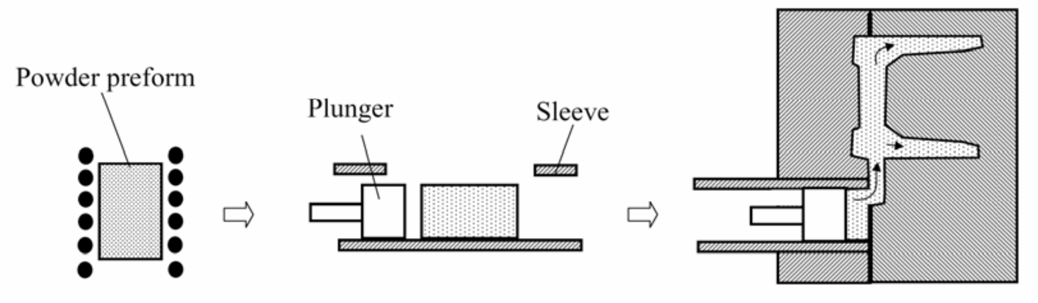
3.3 What is Powder Thixocasting

Our earliest design concept of powder thixocasting was based on how to apply SSMF technique in traditional PM technology. Although many processes that combine techniques of SSMF and PM have been proposed [35-44], the method that can directly achieve net-shape forming were limited, except for the Rheomolding ® as described in Chapter 2.

This dissertation proposes a new approach and introduced it as Powder Thixocasting to highlight its advantages in the facilitation of net-shape forming and to distinguish from other process that combines SSMF and PM.

Briefly, powder thixocasting is a process that combines conventional techniques of powder metallurgy and thixocasting process. Figure 3.2 schematically depicts the new process. Prealloyed rapid solidified powders were firstly consolidated into cylindrical preforms, which act as the non-dendritic feedstock for thixocasting. This powder preform feedstock differs from the casting ingot billets for conventional thixocasting, as is describe in Chapter 2.

Powder thixocasting can be considered as a new technique that expands SSMF to traditional PM. When fabricating aluminum alloys, commercialized SSMF processes can be divided into two categories, thixocasting and rheocasting, according to the initial state of the feedstock used for SSMF. In former, the feedstock is a solid; whereas, in later it is a liquid. However, all these commercialized SSMF processes are narrowed down in ingot metallurgy (IM) routes and still does not be expanded to PM routes. On the other hand, traditional PM processes are typically processed metal powder at its solid state, such as powder forging and sintering. Some PM processes that associate with partial liquid phase, such as liquid phase sintering. However, in liquid phase sintering the liquid is only utilized to promote sintering but not be utilized to facilitate the deformation of powder preform.



(a) (b) (c)

Figure 3.2 Schematic diagram of the powder thixocasting process

(a) heat a pre-alloyed powder preform into semi-solid state using a induction coil, (b) transfer the heated preform to a sleeve, and (c) inject the semi-solid preform into a mold cavity using a plunger of a high-pressure die casting machine.

3.4 Prior Arts of Metal Forming that Combining PM and SSMF

The followings present the prior arts of semi-solid forming processes that involve PM technique.

A. Consolidation of Mixed Powders as Synthetic Slurry (COMPASS)

In 1986, R.M.K Young and co-workers [38] first presented the idea of combining the semi-solid and powder processes, termed consolidation of mixed powders as synthetic slurry (COMPASS). Young et al. prepared the “non-dendritic” feedstock by heating a mixture of powders with different melting points. For example, an Al-Mg semi-solid alloy was fabricated by compressing a mixture of a globular aluminum powder and a solute-rich Al-50% Mg alloy powder, as shown in Fig. 3.3. In subsequent heating of the mixture, the solute-rich powder, which generally has a low melting temperature, would melt first to wet the globular powder, forming “non-dendritic” metal slurries. This idea to preparing “non-dendritic” semisolid slurry through a mixture of powders is successfully applied in Rheomolding ® process, a process similar to plastic injection molding as is described in Chapter 2.

Among the net-shape forming methods, Rheomolding ® is the most successful process nowadays in that semi-solid powders are processed. However, Rheomolding ® is only commercialized for fabricating magnesium components with complex shape [29], and it still can not be used for aluminum alloys.

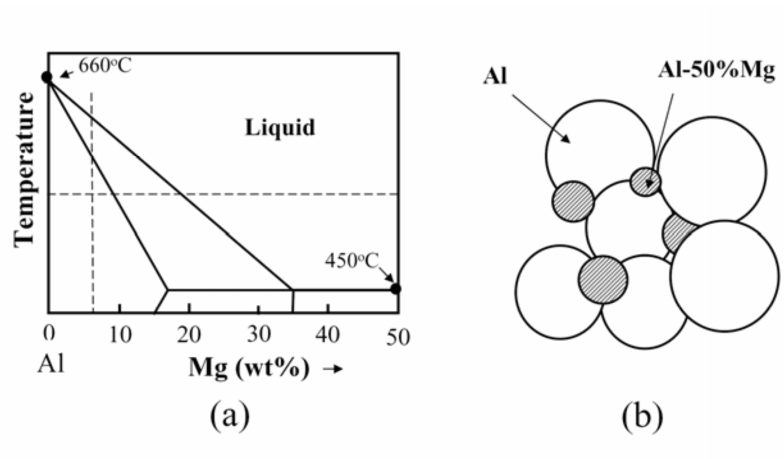


Figure 3.3 Schematic diagram of COMPASS (Consolidation of Mixed Powders as Synthetic Slurry) [26]

(a) A simplified Al-Mg phase diagram, showing the melting points of Al and Al-50%Mg, (b) a mixture of the two powders.

B. Semi-Solid Powder Densification (SSPD)

In 1998, C.-Y.A. *Tsao et al [41]* proposed a method called Semi-solid Powder Densification (SSPD) to fabricate self-lubricating aluminum/SiC/graphite hybrid composites. Figure 3.4 show the apparatus of SSPD. A mixture of aluminum alloy, SiC and graphite powders was put inside a mold and compressed at semi-solid state using the upper and lower ram. Although this process overcomes the wetting obstacle between aluminum melt and graphite or ceramic particles, it still has problems such as detrimental effect of aluminum powder surface oxide on the consolidating strength.

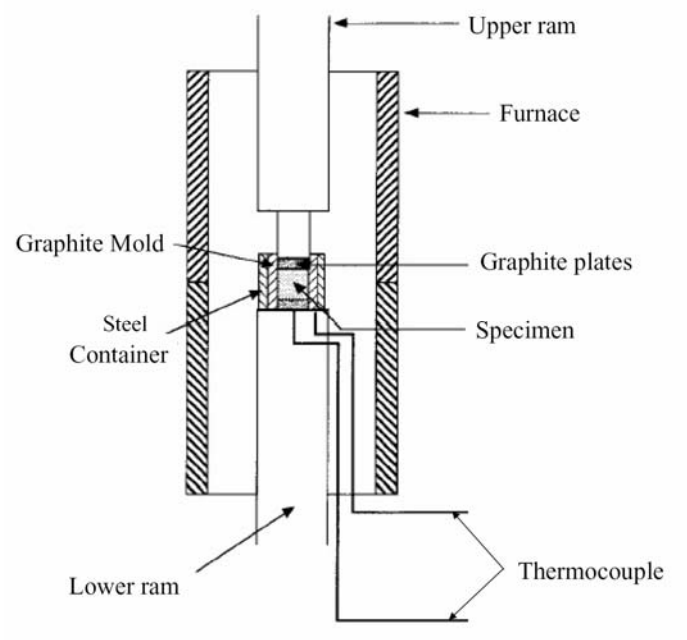


Figure 3.4 Schematic diagram of SSPD (Semi-Solid Powder Densification) process.[41]

C. Semi-Solid Powder Extrusion

Aluminum matrix composites (AMC) can be fabricated by semi-solid powder extrusion [42]. A mixture of aluminum alloy and ceramic powders were uniform mixed, and then through procedures including cold pressing, degassing in vacuum, sealing and then semi-solid extrusion. The deformation force of semi-solid extrusion is only 1/5-1/3 times that for fully solid extrusion. This process produces AMCs of high mechanical properties. However, it still lacks for net-shape forming of complex components.

D. Thixocasting using Spray forming Billets

Recently, P.J. Ward [35,36] has proposed a method combining techniques of thixocasting and spray forming process In conventional thixocasting, the non-dendrite feedstock used is fabricated by IM routes; whereas, in method of P.J. Ward, the feedstock is made by spray-forming process followed by extrusion.

The method succeeded in net-shape forming of hypereutectic Al-Si-Cu alloys with integrity and fine microstructures. However, it also has many drawbacks, including the low yield of spray forming of around 60% to 80% due to over spraying [35,36], and increased costs due to greater required investment in spray forming equipment.

3.5 Powder Thixocasting vs. Powder Forging

Indeed, powder thixocasting is very similar to powder forging, except that the former processes metal powders in their semi-solid states, while the latter in solid state, described as follows.

A. Powder forging

Powder forging, also called sinter forging, was originally developed in the 1970s, and it speeds up the production rate of traditional PM parts. For instance, nowadays it successes in mass production of fully dense PM steel parts, such as the connecting rod used in automobile engines. Figure 3.5 shows the procedure of powder forging. In this process, a powder blank is pressed to a simple shape halfway between that of a forging billet and the required finished part. This compact, referred to as a preform, is sintered and then hot forged to finished size and shape in a closed die.

The amount of deformation involved is sufficient to give a final density very closely approaching that of the solid metal, and consequently, the mechanical properties are comparable with those of material forged from wrought bar.

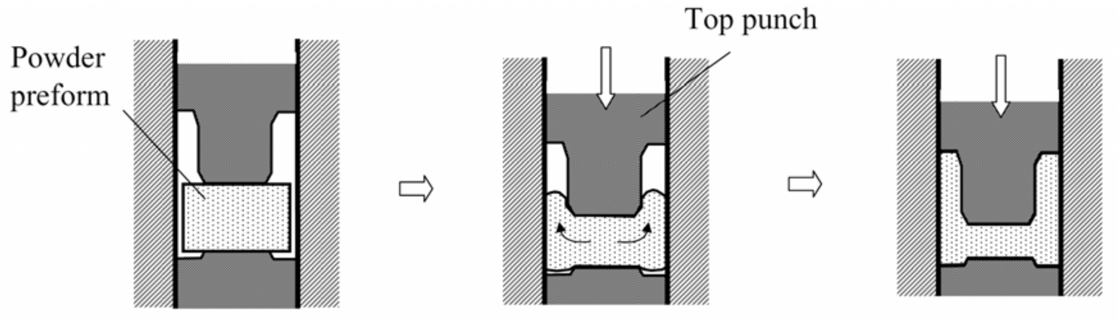


Figure 3.5 Schematic drawing of powder forging process

B. Prospects of powder thixocasting

The main advantage of powder thixocasting over powder forging is its feasibility for net-shape forming of very complex shape components, since powder is more easily deformed in semi-solid state than in solid state.

Since gas-atomized powders have fine microstructures and near spherical morphology, powder preforms therefore should have the thixotropic microstructures that is suitable for thixocasting. However, some issues still exist for this novel process. Firstly, the advantage of PM in fine structures will be inevitably degraded because of the high processing temperature during semi-solid forming. Therefore, powder thixocasting is considered not suitable in producing precipitated-hardened or strain hardened high strength alloys. It is more suitable in producing the alloys strengthen by incorporating with ceramic or thermally stabilized intermetallic particulates. Building on the ideas in COMPASS and P.J. Ward's experiments outlined above, it was considered possible to thixocast powder preforms, rather than spray formed billets, to net-shape a hypereutectic Al-Si-X alloy. That is why Al-Si-X alloys were selected in this thesis, and a series of experiments were conducted to realize the aforementioned concept, which will be detailed in Chapter 4.

An additional advantage is the dimensional consistency achievable in consequence of the accurate metering of the quantity of powder used. Indeed they may be superior in some respects because of the freedom of the sinter forged part from directionality, the greater homogeneity as regards composition, and a finer microstructure, as well as the absence of internal discontinuities resulting from ingot defects that are possible in forgings made from cast metal.

Powder thixocasting was expected to expand the fabrication concept in the PM industry. It is believed to be a highly promising means of combining pressure-assisted consolidation in conventional powder metallurgy (PM) with newly developed semi-solid casting. This new method should be able to carry out net-shape forming of various materials except the hypereutectic Al-Si alloys, including metal matrix composites and metal alloys with precipitates stabilized at high temperature.