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MAT6040 REPORT

Thixoformability study in wrought aluminium alloys AA3104 and AA5052

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NOTICE

This project “Thixoformability study in wrought aluminium alloys AA3104 and AA5052” was originally conceived as an experimental piece of work, however, due to the Covid-19 situation and the resulting lockdown and its effects it was decided that all projects will be completed without the use of any further experiments or other work that required close contact with others. The format is shown in the above ‘Table of Contents’, and it consists of an analysis of three key publications in the field of research (Thixoforming), an extended Literature Review (building on the review that was submitted as part of the Interim Report) and the preparation of a Review style article on a related area.

Acknowledgements

I would like to express my immense gratitude to Dr Plato Kapranos for his continuous support throughout the elaboration of this project. As an international student, it is not easy to be away from your family and see that even though all the effort your country has been overwhelmed by these difficult times. However, Dr Plato Kapranos was always comprehensive, and his continuous feedback provided me with the necessary confidence to fulfil my main goal.

1 Extended Literature Activity

1.1 Activity 1a Analysis of Key Publications

Three key publications around the theme of generating the appropriate non-dendritic feedstock microstructure for semi-solid processing of alloys will be analysed and comparisons made, highlighting similarities, inconsistencies and disagreements between these articles.

1.1.1 Critical Evaluation of Publication 1: “Efficient refinement of spherical grains by LSPSF rheocasting process.”

This thixotropic feedstock production route, introduced as a promising way for a rheocasting process named Low Superheat Pouring with a Shear Field (LSPSF), generates fine near-spherical grains in short time intervals if the correct processing conditions are used.

Its experimental procedure consists in feeding molten aluminium A356 alloy at low superheat temperature into an inclined barrel which rotates to prevent the formation of a shell on the inner wall and in this way with the temperature just below its liquidus to promote solidification. The metal, which by this time is in a semi-solid state, is collected in a slurry holder, where the temperature can be maintained during a controlled cooling process. The main advantage of this technique is that it can work in a batch or continuous manner [1]. The LSPSF process route is illustrated in Figure 1.

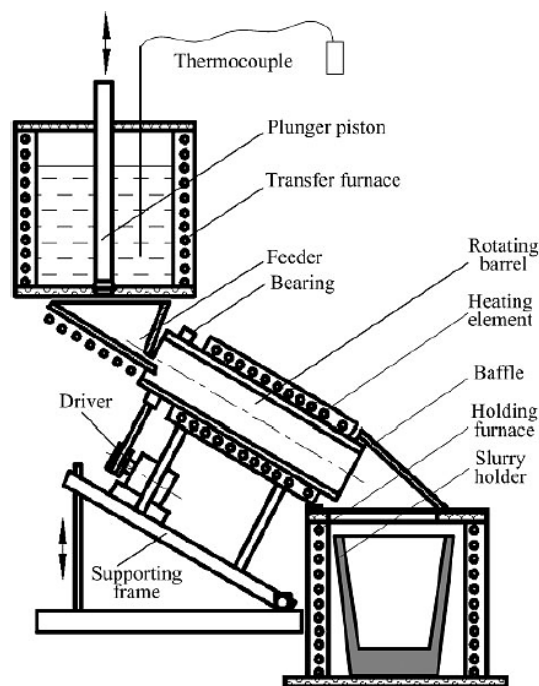


Figure 1 Schematic of system for LSPSF process[1]

In order to obtain the most suitable microstructure for the process, the effects of three parameters were studied: the pouring temperature, the angle of inclination of the rotating barrel and its rotation speed. Firstly, different pouring temperatures were tested while the rotation speed and inclination were kept constant. If high pouring temperatures are used, the microstructure shows rosette-like grains rather than spherical. On the contrary, if the pouring temperature is too low, the molten metal starts solidifying while it flows down the barrel into the slurry holder. Secondly, the rotation speed was varied while the pouring temperature and inclination were fixed. If the speed is less than 60 rpm, rosette-like dendrites are present in the microstructure, while if the speed is higher than 200 rpm, the slurry does not flow down but solidifies in the inner wall of the barrel. As a result, speeds between 90 and 180 rpm show fine and spherical grains. Finally, the inclination angle was used as the changing parameter, and if it were less than 15 °C, the metal would solidify, and a shell will form, while if the angle is in the range between 20 °C to 35 °C, the desired near-spherical microstructure can be achieved. Thus, with all the experiments performed, the parameters chosen as optimal were a pouring temperature between 645-660 °C, an angle of inclination between 20-35 ° and rotating speed between 90-180 rpm [1].

The methodology applied in these experiments is similar to another semi-solid processing feedstock production technique, namely Cooling Slope. The starting point is the molten metal that pours along a slope, which in this case is a rotating barrel and that rotation allows having new contact surfaces to enhance the nucleation in the slurry. Furthermore, although three key parameters were taken into consideration, there are others that can also influence the final microstructure, like the temperature applied to the feeder, the rotating barrel and the slurry holder.

In summary, even though some parameters were not taken in consideration, this novel rheocasting process appears to provide fine near-spherical grains in the microstructure by controlling in an appropriate way three key parameters: pouring temperature, rotation speed and inclination angle of the barrel. Furthermore, this process can be executed in a batch manner with a processing time of 25s. The grains have an average diameter of 65 µm, a shape factor of 0.84 and no presence of entrapped eutectic.

1.1.2 Critical Evaluation of Publication 2: “Grain Renement of Aluminum Alloy Bar by a Modied RAP Process for Semi-Solid Forming.”

The article aims to study a process that uses a modified Recrystallisation and Partial melting (RAP) technique to get a suitable microstructure for semi-solid forming feedstock.

The RAP process begins with the preheating of a 6063-T6 aluminium alloy round bar (ø120 mm x 800 mm), at 300 °C for 90 min. Then, the bar was forged into a stepped shaft with different values of reduction area (%RA), expressed by Eq. 1. After the deformation, specimens from the periphery and centre were extracted to perform a semi-solid isothermal treatment (SSIT) at 630 °C for 10 min. Finally, the samples were quenched to examine the retained microstructure. The steps involved in RAP process can be seen in Figure 2 [2].

$$\%RA = \frac{(A_o - A_f)}{A_o} \times 100 \quad (1)$$

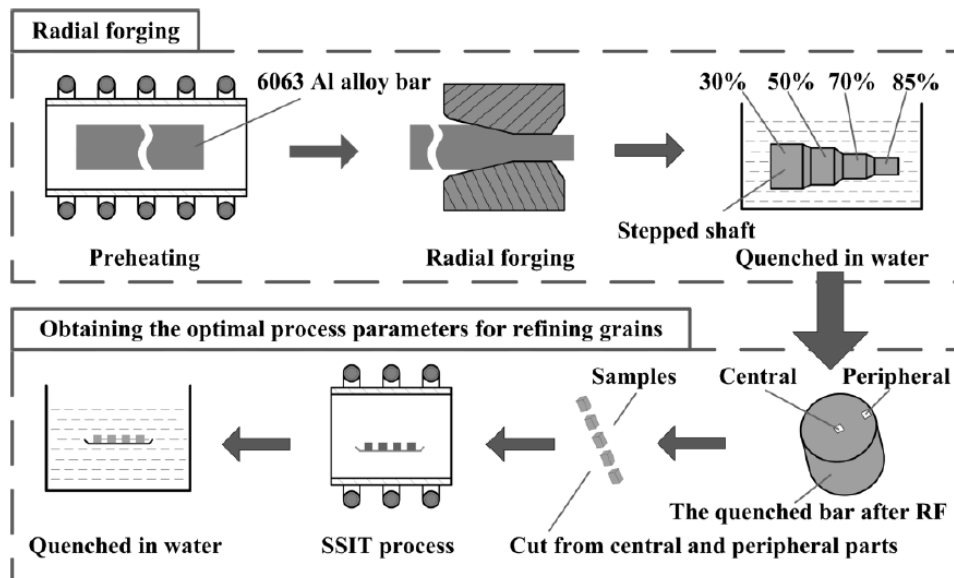


Figure 2 Flowchart of RAP process used [2]

The first specimens assessed had only the SSIT and no previous deformation. The microstructure obtained had coarse grain and a vast difference between the periphery and centre of the part. This microstructure is unsuitable for any semi-solid forming process.

In the other specimens, the deformation applied was radial forging that can be considered as warm working because it was performed after preheating the samples at a temperature between 30% and 50% of melting temperature of aluminium. The values of %RA were 30%, 50%, 70% and 85%, according to Eq. 1. After the deformation, SSIT was performed, and specimens from the peripheral and central part were evaluated [2].

The use of radial forging is an effective way of providing a homogeneous deformation throughout the volume of the billet, but it is not a common technique applied in semi-solid processing. Therefore, for high values of %RA, it is possible to see almost the same microstructure between the peripheral and central parts of the sample. No major difference can be seen after the SSIT in the microstructure, where the grains are fine and more spherical compared to the sample where no deformation was applied.

Applying radial forging, even though, is not a usual method to induce strain energy to the material, is a very useful way to obtain uniform microstructure. In the RAP process, the mechanism to generate the spherical grains is not based on the nucleation of new grains from the molten metal, but in the recovery and recrystallisation stages that occur in the solid metal. Therefore, the first step, annealing, decrease the density of dislocations so the cold work can generate them homogeneously in the whole component. Thus, when the SSIT is applied, recovery and recrystallisation can form new grains uniformly in all the sample. Nevertheless, some parameters

have not been analysed, such as the SSIT temperature and time, that only one value was considered for the tests.

In conclusion, the RAP process can be used to obtain appropriate feedstock microstructures for semi-solid forming. The best results are achieved for higher values of deformation. The optimal parameters are 70% RA and SSIT at 630 °C for 10 min, resulting in shape factors above 0.72 and a grain diameter less than 120 µm (Research has shown that shape factors above 0.6 are appropriate for thixforming).

1.1.3 Critical Evaluation of Publication 3: “Semi-solid process of 2024 wrought aluminum alloy by Strain Induced Melt Activation (SIMA).”

The article aims to produce semi-solid feedstock applying the SIMA technique to obtain finer near-spherical microstructures as compared to other semi-solid feedstock production processes such as Cooling Slope or GISS.

The experimental procedure is very similar to the RAP. It consists of annealing the sample of aluminium alloy 2024 at 420 °C for 3h to reduce the strain energy stored in it. The reduction of energy can be proved by hardness testing of the sample. The decrease in hardness is around 70%. Then, cold work is performed on the part. The percentage reduction of area (% RA) was 40%, which is higher than the critical deformation to induce recovery in the aluminium. The %RA was calculated by the expression shown in Eq. 2 [3].

$$\%RA = \frac{(h_o - h_f)}{h_f} \times 100 \quad (2)$$

Specimens, which are sections of the deformed disk, were heated up to 620 °C for eight different holding times to evaluate which condition provides the best microstructure for a semi-solid forming. In addition, the liquid fraction was measured for the eight holding times to assess their thixoformability [3].

In each section, five points were extracted to assess the uniformity of the process. The microstructure at all locations is almost the same, meaning that the strain energy induced by the compression was uniform and recovery and recrystallisation was successful.

The deformation of the bar was done as a compression test, so the microstructure will vary depending on the location where the specimen is extracted. There were no images from different locations of the compressed disk to assess the microstructures after deformation. However, in each section obtained, five points were used to evaluate the uniformity of the process. The microstructure at all locations is almost the same, meaning that the strain energy induced by the compression was uniform and recovery and recrystallisation was successful. Unfortunately, only one remelting temperature was tested. Hence, more research should be done to evaluate how temperature influences the final microstructures.

The determination of liquidus and solidus temperature for the aluminium alloy employed was calculated with the cooling curve method. Furthermore, the liquid fraction at 620 °C was calculated by micrography. Differential Scanning Calorimetry could have been used for the determination of both, solidus and liquidus temperature and the liquid fraction at a specific temperature with more precision than the techniques used.

In summary, it is possible to achieve near-spherical microstructures using the SIMA technique. The optimal microstructure was obtained at the holding time of 6 min, having a shape factor is 0.6 for all the holding times, and the average grain diameter is 88.2 μm .

1.1.4 Discussion of all 3 Key papers

As mentioned above, the objective in all three articles is to provide processing methods for generating feedstock with near-spherical grains that are required for semi-solid metal processing. The desired microstructures can be obtained by a number of different techniques such as mechanical or electromagnetic stirring, pouring molten alloys down a cooling slope, or through ultrasonic vibration of molten metal during solidification, as well as many others.

All these methods have advantages and disadvantages associated with each of them, such as the complexity of equipment, high cost, inhomogeneity of the final product or incorporation of unwanted defects and impurities in the feedstock from the solidifying melt. Some techniques developed over the years, such as Low Superheat Pouring with a Shear Field (LSPSF), Strain-Induced Melt Activated (SIMA) and Recrystallisation and Partial Melting (RAP) appear to produce good and consistent quality feedstock and reducing or offsetting some of the disadvantages of other routes.

In all three experiments, the materials employed were aluminium alloys. Table 1 shows the chemical composition of the aluminium alloys used and Table 2 shows the liquidus and solidus temperature for the same aluminium alloys as the range of temperatures define the appropriate heating temperature for the semi-solid processing.

Table 1 Chemical composition of aluminium alloys used

Process	Alloy	Cu	Mg	Mn	Fe	Si	Zn	Ti	Cr	Ni	Pb
LSPSF	A356	0.01	0.35	0.02	0.09	6.9	0.01	0.07	---	---	---
RAP	6063	0.023	0.65	0.018	0.15	---	0.02	<0.1	<0.1	---	---
SIMA	2024	4.368	1.503	0.641	0.238	0.222	0.23	0.009	0.008	0.003	0.007

Table 2 Range of temperatures for SSM processing of aluminium alloys used

Process	Alloy	Liquidus Temperature (°C)	Solidus Temperature (°C)
LSPSF	A356	615	548
RAP	6063	655	615
SIMA	2024	640	490

As it can be seen, one of the aluminium alloys used was A356 which is a cast alloy while the other two are wrought aluminium alloys. The A356 alloy has the highest content of silicon, which is used to improve the fluidity of aluminium. All three aluminium alloys used are heat-treatable alloys, deduced by the presence of elements such as copper, silicon and magnesium in their chemical composition. The 2024 aluminium alloy, contains S phase (Al_2MgCu) as precipitates due to the stoichiometry relation between Cu and Mg [4]. In 6063 and A653 alloys, the main alloying elements are Mg and Si; therefore, the β'' phase is the most important strengthening phase when the alloys are age hardened [5].

The alloys mentioned above are the most used in aluminium thixoforming processes due to their possibility to be age-hardened. Therefore, it is not necessary to focus only on the grain size of the final part as its mechanical properties can be enhanced by ageing treatment. On the contrary, if a non-heat-treatable aluminium alloy is being used, it needs to have fine grain or be work-hardened to present mechanical properties suitable for different applications.

The experimental procedure was different in each case because there were three different processes employed. Two of the techniques involving deformation are similar, but the parameters used, such as how the deformation is performed, the temperatures and time used are different.

The mechanism of nucleation and grain coarsening is also different for the previous processes. LSPSF process, while the slurry flows down the rotating barrel, its temperature decreases due to the constant contact with the inner surface of the barrel. The main difference between LSPSF and other SSM feedstock production processes like mechanical stirring and cooling slope is that in the first one, there is no evidence of entrapped eutectic, which is an indication of pre-existing dendritic structure. Therefore, in LSPSF process, grains are formed due to the direct nucleation from liquid rather than secondary nucleation, which is caused by dendrite fragmentation. Thus, LSPSF enables the creation of numerous grains from the interaction between the inner wall and the slurry that can survive to reach the slurry holder. Hence, the grains start growing into individual grains, resulting in fine grains. The coarsening of grains is limited by the low undercooling and the high density of grains that were formed while the metal flowed down the incline.

In SIMA and RAP processes, the nucleation does not occur in the solidification of the molten metal. On the contrary, the formation of new grains is due to the recovery and recrystallisation that

are driven by the strain energy when the specimen is heated at the semi-solid temperature after it has been deformed.

In the SIMA process, the coarsening of grains is explained by two models. The first one, where smaller grains are absorbed by coarser grains due to the migration of high angle grain boundaries. The second is the Ostwald ripening, which consists of detached smaller grains and their diffusion into the eutectic liquid due to their reduced stability as compared to coarser grains.

In all thixoforming processes, it is crucial to measure the average grain size and shape factor of the microstructures obtained by the different techniques employed. If the microstructure has fine grains, it will provide better mechanical properties, which can be further enhanced by ageing treatments as already discussed. The shape factor offers an indication of the roundness of the grains and the finer and more spherical the grains, the better the flowability behaviour and resulting properties after casting or forging the component in the semi-solid state. The equations used for the calculation of those values are shown in Eq.3 and Eq.4, respectively. Where A is the average area and P is the perimeter of the solid phase.

$$D = 2 * \sqrt{A/\pi} \quad (3)$$

$$F = \frac{4\pi A}{P^2} \quad (4)$$

In the three techniques discussed, the values of grain diameter and shape factors obtained for the optimal microstructure are shown in Table 3.

Table 3 Grain diameter and shape factor obtained by different processes

Process	Alloy	Grain Diameter (µm)	Shape Factor
LSPSF	A356	65	0.84
RAP	6063	< 120	> 0.72
SIMA	2024	88.2	> 0.60

The LSPSF process appears to generate spherical grains due to the temperature gradient near the slurry holder and provides uniform temperature in the semi-solid slurry, making possible to get a homogeneous globular microstructure across the whole volume. In addition, in the RAP process, the size of the recrystallised grain is in an inverse relationship with the percentage of cold work applied to it and there is almost no difference in the microstructure of the peripheral and central parts due to the high rates of deformation used. As already mentioned, the driving force for recovery and recrystallisation comes from the residual strain energy induced by the prior

deformation. Furthermore, the critical size of steady recrystallisation nucleus (R^*) can be defined by Eq. 5.

$$R^* = \frac{2\gamma}{\Delta E_s} \quad (5)$$

Where γ is unit area interface energy and ΔE_s the change of fault energy per unit volume, which increases with the deformation applied. Thus, the higher deformation used, the finer the grain. In addition, after being recrystallised, the grains can reduce their size even more due to the liquid penetration into high angle grain boundaries. This occurs when the specimen is heated to a semi-solid range. There is a fragmentation of grains because the grain boundary energy is more than twice the solid/liquid interfacial energy, leading to a further decrease in the size of the grains.

If the thixoforming feedstock production process requires a deformation route such as the SIMA or RAP routes, this is usually achieved by a reduction of area. It can be achieved by cold working or warm working. According to Eq. 5, the highest deformation should have led to the finest grains. However, in Table 3, it can be seen that SIMA process obtain smaller grains than RAP process. This difference could be because the %RA was not expressed by the same equation for both experiments, as in SIMA it was calculated using heights and in RAP using the areas. Therefore, the %RA values of each method cannot be compared between them, as those values may not resemble the real amount of strain energy in each specimen.

In conclusion, the final values of grain diameter and shape factor are key parameters that have to be taken into consideration when generating feedstock for a thixoforming or rheocasting manufacturing process. Furthermore, each method has its mechanism that defines those parameters. The finer and round grains obtained in the microstructure will provide a laminar die filling and reduce defects such as porosity or segregation and increase the mechanical properties in the final component.

1.2 Activity 1b Expanded background literature review

1.2.1 Brief Introduction to Semi-Solid Metal Processing (SSM)

Semi-solid metal (SSM) processing can be defined as a manufacturing process that consists in producing a slurry formed by near-globular primary particles within a liquid matrix and forming it into complex near net-shape parts that are commercially competitive[6]. The origins of the technology are routed in research carried out at MIT in the early 1970s when a PhD student used a rheometer to measure the viscosity of casting alloy melts at various stages of solidification while assessing their hot tearing sensitivity. A key observation during his experiments was that the resistance of the material to shear tends to decrease if the material was stirred during cooling instead of stirring it after it has been partially solidified [7]. Moreover, the stirring operation resulted in unexpected changes in

microstructure, i.e. from one typical of cast alloys that was obtained without stirring, consisting of dendrites, to one based on spheroidal particles in a liquid matrix [8]. This particular spheroidal microstructure when in the semi-solid state, exhibits thixotropic properties, i.e. it flows like a liquid when sheared, and thickens to a solid if allowed to stand [7]. This thixotropic is both shear and time dependent.

The thixotropic behaviour is based on the globular microstructure in the material. If dendritic microstructures are subjected to shear forces, the liquid present cannot move freely because it is trapped between dendrite arms, which increases the viscosity and on certain cases might result in solid and liquid separation as the liquid is squeezed between the dendrite arms. On the contrary, in spherical microstructures, the viscosity is decreased because the globular particles can move easily past one another, an excellent visual model would be ball bearings in honey, causing the material to flow like a thick liquid[9]. It was quickly realised by the MIT group of researchers that this behaviour could be used in a manufacturing processes that require the filing of a die such as die casting. The first attempts consisted of preparing a slurry with near spheroidal microstructure and injecting it into dies using die casting machines. They observed that the slurry had a smoother laminar flow as compared to a conventional die casting process that uses a melt that had not been prepared to have a non-dendritic microstructure. As a result of this smoother filling of the dies, the resulting near net-shape products exhibited much better mechanical properties than their conventional counterparts [7].

The mechanism of how the dendrites transform into spherical particles is still not completely understood. Some proposed mechanisms take into consideration dendrite arm root melting, dendrite arm fragmentation and growth control mechanisms. Currently, SSM technologies exploit the thixotropic properties to enhance the mechanical properties in the final products. These technologies can be divided into two main categories, those that generate the non-dendritic microstructure in their slurries through controlled solidification from liquid melt, relying on increasing the nucleation rate or starting crystal multiplication in the melt and others that generate the appropriate microstructures in the solid state by inducing strain energy via heavy deformation and then through recrystallisation and partial melting resulting in near spheroidal microstructures [9].

Apart from the well-known methods such as mechanical stirring and cooling slope that have already been discussed in the Interim Report, there are a number of other techniques that can provide excellent non-dendritic microstructures for feedstock that can be used in SSM processes and will be described and discussed below.

1.2.2 Commercial techniques for producing non-dendritic Feedstock for SSM

1.2.2.1 Magnetohydrodynamic stirring (MHD)

Magnetohydrodynamic stirring (MHD) was developed by the International Telephone and Telegraph (ITT) in the USA to solve the inconveniences of batch process and other drawbacks associated with the original mechanical stirring process used by the MIT group at the early attempts of commercialisation [9]. An interesting fact here is that the person who was instrumental in the development of the MHD technique was a University of Sheffield graduate, Dr. Kenneth P. Young who worked as a Post-Doctoral researcher for Professor Merton Flemings at MIT and was employed by ITT after they obtained the patents for SSM from MIT.

The principle of the process is based on the Lorentz force, which appears when a current flows through a conducting body in the presence of a magnetic field. Lorentz force is defined in Eq. 1, where j is the electric current and B the magnetic field.

$$F = j \times B \quad (1)$$

Lorentz forces act over the conductor, and it is rotational. For this scenario, the metal is the conductor, and as it is in a liquid state, it has to move due to the action of the force because it cannot be compensated by a pressure gradient [10]. This phenomenon produces the stirring required for obtaining the spherical microstructure.

With this process, when coupled with a continuous caster, it is possible to produce long lengths of billets of non-dendritic alloys that have uniform consistency and therefore resulting in equally consistent quality and properties of the final products. Furthermore, MHD reduces the number of impurities and gas entrapment in the slurry. Also, the final microstructure has an average grain diameter of usually 30 μm , while the diameter in mechanical stirring is between 100 and 400 μm . For the reasons explained above, MHD became the most used commercial process for the production of non-dendritic feedstock for thixoforming [9].

The rotational flow can be obtained by using three different modes of electromagnetic stirring: vertical, horizontal and helicoidal agitation. In vertical agitation, the sphericity is controlled by thermal processing, while in horizontal agitation it is controlled by mechanical stirring. The helicoidal mode is the combination of both previous styles. Figure 3 shows the different modes of agitation [9].

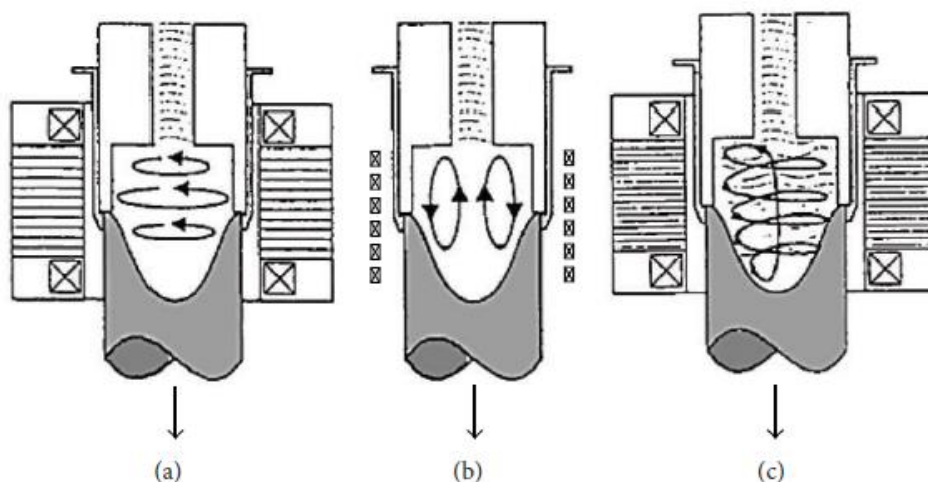


Figure 3 Different flow modes in MHD (a) Horizontal, (b) Vertical and (c) Helicoidally [9]

1.2.2.2 Gas Induced Semi-Solid (GISS) method

This process was developed at the Prince of Songkla University by Dr. Jessada Wanasin who was also a student of Professor Flemings at MIT [11]. The Gas Induced Semi-Solid (GISS) method uses fine inert gas bubbles to generate sturdy convection in the molten metal. Different configurations can be used for introducing the gas bubbles into the molten metal, such as a nozzle or a porous media[12].

The generation of the slurry can be divided into three steps. Firstly, the application of low superheat to maintain the temperature of the system just above the liquidus temperature of the metal, secondly, inject gas bubbles into the molten metal through a diffuser to produce nucleation and stirring, held for the required time to achieve the desired solid fraction, and finally, removal of the diffuser and cooling of the slurry until the desired microstructure and appropriate solid fraction are obtained. Figure 4 shows the processing route of the GISS method [9].

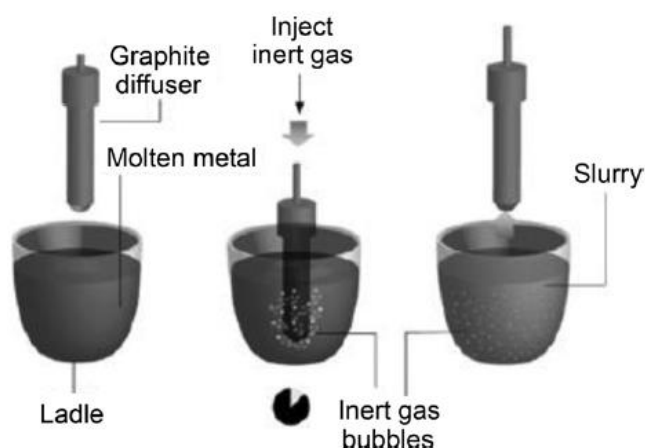


Figure 4 Schematic illustration of GISS process

Nucleation and growth of dendrites start at the surface of the graphite diffuser due to the temperature difference. The gas bubbles throw the dendrites into the melt, which causes their remelting because the surrounding liquid is still superheated. Only a few particles will remain as dendrites, and the process continues for a period of time. This allows the removal of heat and generation of a fine, non-dendritic microstructure [9].

1.2.2.3 Stress-Induced Melt-Activated (SIMA) route

While techniques as mechanical stirring, MHD, Spray Forming are considered liquid state routes that generate non-dendritic feedstock, there are others, such as Stress Induced Melt Activated (SIMA) and Recrystallisation and Partial Melting (RAP) routes that belong in the solid state category [13].

The SIMA process is based on three steps. Firstly, hot working above the recrystallisation temperature, followed by cold work applied to induce more energy into the part and finally, heating of the metal up to a temperature in the semi-solid state between the liquidus and solidus. The application of cold work is a key step in the SIMA process because the stored energy is the driving force for the recovery and recrystallisation that are key factors in controlling the final microstructure. The SIMA process route is shown in Figure 5 [14].

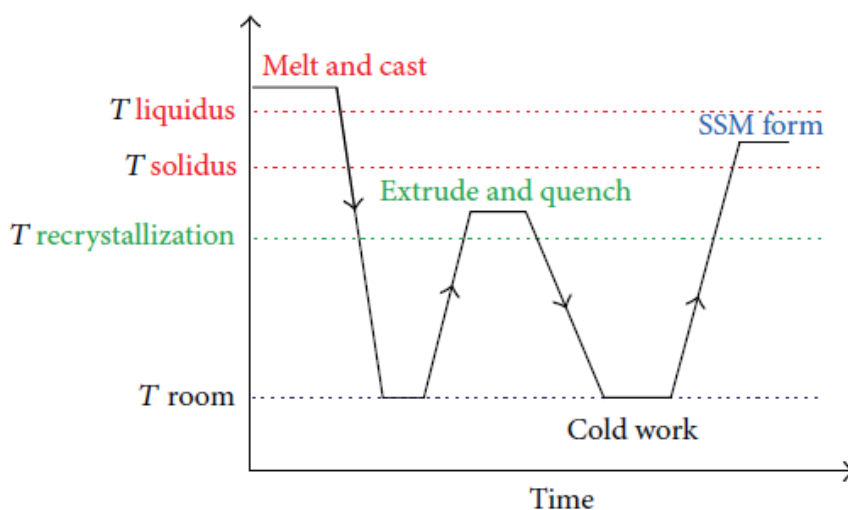


Figure 5 Processing route of SIMA process [9]

After recrystallisation, when heating in the semi-solid state, the high-energy liquid metal generated penetrates the high-angle boundaries of grains generating spherical solid particles in a liquid matrix. Furthermore, the diameter of the particles has a direct relation with the amount of cold work applied to the part. It is possible to obtain grain diameters of 30 μm , making SIMA a technique comparable to MHD as far as quality and feedstock consistency. In addition, SIMA does

not present some of the disadvantages of MHD, such as the heterogeneous composition which leads to an unequal distribution of the liquid phase in the microstructure [9].

1.2.2.4 Recrystallisation and Partial Melting route (RAP)

This technique is similar to the SIMA process described above with the main difference being that in the RAP process the early deformation stage is executed below the recrystallisation temperature. Furthermore, there is no need for the cold working step because since there is no recrystallisation, the energy from the deformation is stored within the material. Figure 6 shows the stages of the RAP process [9]. The microstructural transformation during RAP can be described in three steps. Firstly, while the deformation takes place, the strain energy induced in the material will be accumulated as vacancies and dislocations. Then, at the beginning of the heat treatment, due to the thermal activation, dislocations will be able to climb and cross slip, and vacancies can combine. These changes will reduce the amount of free energy, resulting in recovery and recrystallisation. Finally, when the temperature surpasses the solidus temperature, if the temperature and holding time are the correct ones, the liquid phase will penetrate into the boundaries of the recrystallised grains [15].

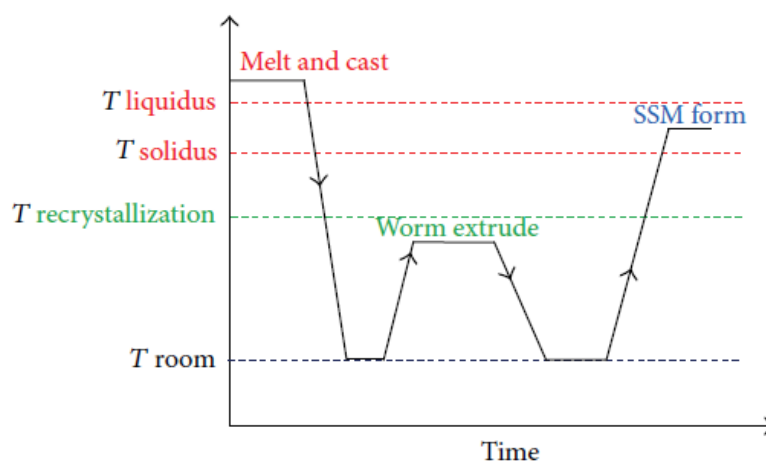


Figure 6 Processing route of RAP process [9]

1.2.2.5 Swirled Enthalpy Equilibrium Device (SEED)

This semi-solid feedstock forming technique was invented in the '90s by Alcan, as a Rheo route with low operating cost and high efficiency [16]. The preparation of the slurry can be divided into three steps. First, the molten metal is poured into a vessel that cools the melt to a solid fraction between 30 and 45%. Then, the vessel is swirled to promote the even distribution of the particles that solidified at the inner wall of the vessel. Some parameters that have to be taken in consideration up to this point are the speed of rotation and the eccentricity of the vessel. In addition,

the vessel has an inner coating to protect it from the erosion during the rotation that can affect the microstructure of the slug [17].

The second step consists in opening a valve at the bottom of the vessel to pour some remaining liquid. The time can vary depending on the parameters used before, and usually, the drained liquid is around 20%. Finally, the slug is taken out of the vessel and by this stage, it has thixotropic properties. Figure 7 describes the steps of the SEED process [17].

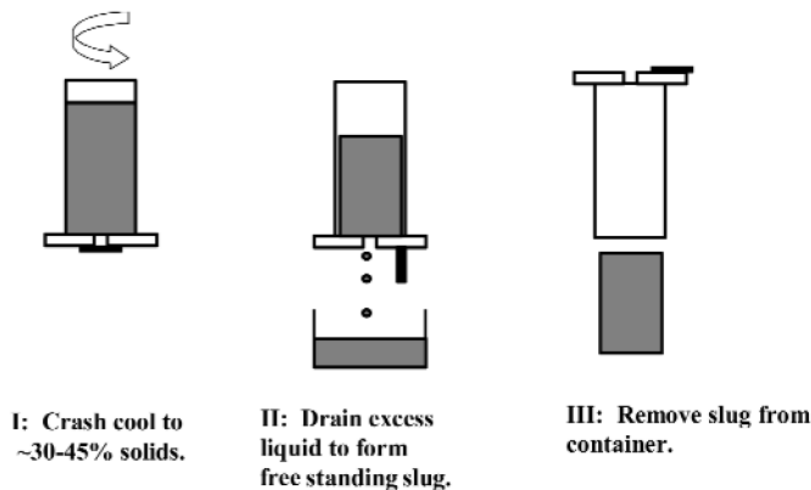


Figure 7 Schematic illustration in SEED process [17]

A simpler version of the process has now been developed that does not take into consideration the second step, because by optimising the parameters used, the draining effects are compensated and this configuration is currently industrially applied [18].

1.2.2.6 Rheometal - Rapid Slurry Formation (RSF) route

This process developed by Rheometal is also known as Rapid Slurry Formation (RSF) route. The process is based on the enthalpy exchange between alloy systems that have different enthalpies but the same chemical composition [19]. Usually, the two systems are one solid and one liquid and are mixed by a stirring operation to form a new alloy system that has the required enthalpy and solid fraction. Rheometal process has a relevant difference compared to other SSM processes because it does not require an outer cooling or precise temperature control for the slurry preparation [20].

The Rheometal procedure consists of pouring liquid metal into an insulated container, then a solid metal alloy, usually in the form of a bar of the same composition, is submerged into the melt and the stirring operation starts. The piece of solid metal is relatively cold and therefore has lower enthalpy than the liquid metal. Therefore, it absorbs heat from the molten metal as it starts to melt, generating a new alloy system with the desired enthalpy. Due to its function, the solid metal is also called Enthalpy Exchange Material (EEM). Figure 8 shows the steps of the Rheometal (RSF) process [20].

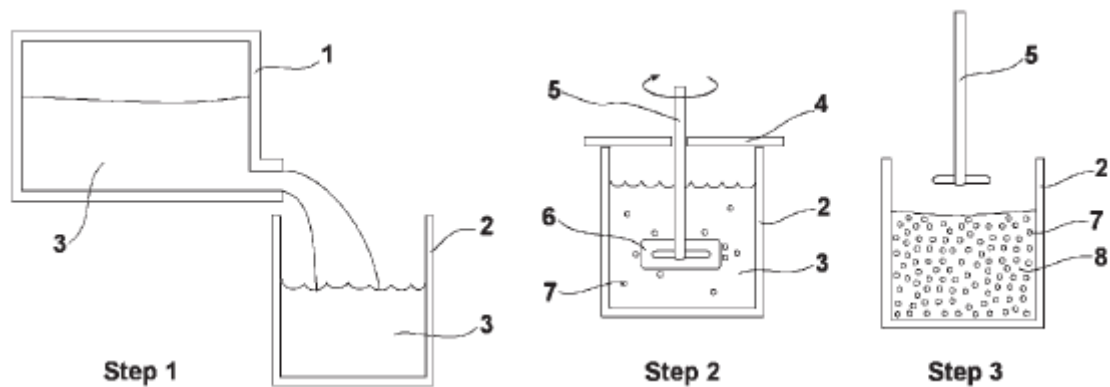


Figure 8 Schematic diagram of Rheometal (RSF) process [20]

The solid fraction of the slurry is defined by the temperature employed, the composition of solid and liquid metal and the added percentage of the EEM. Some equations can be used for the calculation of the volume or mass ratio between the molten metal and the EEM, if the solid fraction of the slurry is given [21].

1.2.2.7 Semi-Solid Rheocasting (SSR)

The first developed rheocasting process at MIT used mechanical stirring to generate the non-dendritic microstructure when the liquid was cooled. Moreover, low superheat temperature has been used to encourage the formation of fine, equiaxed dendrites that will grow into a non-dendritic microstructure. Nevertheless, the original Semisolid Rheocasting (SSR) work performed at MIT proved that the key factors that influence the creation of non-dendritic microstructures are the combination of rapid cooling and convection while the alloy is cooled through the liquidus. Furthermore, agitation is not necessary after a small fraction of solid had formed [22].

To control the cooling and convection of the process, a copper rod can be used to produce the non-dendritic microstructure by distributing the particles that solidified at the surface of the rod throughout the volume acting as nuclei seeds [23]. Amazingly, if the metal temperature is below liquidus temperature, stirring has no impact on the final microstructure [22].

The SSR procedure can be explained in three steps. First, the molten metal is put into a vessel at a temperature slightly above its liquidus. Then, the copper rod is submerged into the melt, and starts the stirring movement. This initiates the solidification on the surface of the rod and decrease of the temperature below the liquidus. Finally, the rod is retired, and the solid fraction present starts to increase in the cooling slurry. Figure 6 shows the process of SSR [9]. Figure 9 shows the three steps of SSR process.

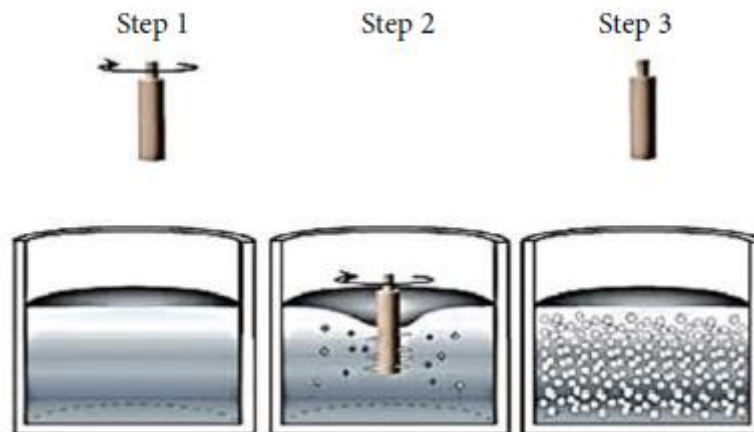


Figure 9 Steps in the SSR process [9]

1.2.3 Current Market applications

Semi-solid processes have been applied over the past forty years to industrial applications, although they are still not very common among manufacturing processes. In the second half of the 1990s, for instance, SSM forming represented around 1% of the market in the US, and the sales are far lower when compared to other conventional processes such as casting and forging. Hence, there is a market that can be exploited using the characteristics that products obtained by SSM can provide [24]. In the US, Thixomat Inc. focused on producing magnesium products in electronic and automotive applications. On the other hand, in Europe, more specifically in Italy, Stampal SpA focused on aluminium products for the automotive market [24]. For example, alongside Stampal SpA, Fiat started investing for the fabrication of parts that will be used for some car models [6]. Nevertheless, in spite of some successful commercial attempts, the interest in SSM processing was relegated to R&D, and its commercial possibilities started to fade [24].

One of the reasons the viability of SSM processes decreased was due to the inability of recycling the feedstock left after being processed, as the MHD route that was the main method of generating the feedstock required manufacturers to pay a high premium, as well as having to send back to the producers their scrap for reprocessing. Nonetheless, in recent years, the interest in SSM processes has increased because new processes such as SSR and GISS can be recycled in situ. Even though there are some efforts from the US and Europe, China appears to be the one responsible behind the revival of SSM processes [24].

The communication market has played a vital role in the revival and redevelopment of SSM processes. A Chinese company, together with a Chinese university, started to research in die optimisation, slurry preparation and delivery for Rheo-HDPC methods to produce parts for mobile phones manufacturers. Moreover, with the forthcoming of the 5G era, components have a complex structure and are usually made of aluminium because they require high thermal conductivity and good mechanical properties. Rheometal parts fulfil the requirements because they have proven that

they can provide better thermal and electrical properties than components manufactured by casting [25]. While in Europe, marine and heavy-duty auto parts applications have reduced costs by minimising the soldering and providing fatigue performance [24]. In addition, in Thailand, research is being done in the GISS technique, aiming to integrate the slurry maker with the die-casting machine to obtain a continuous production that can have many industrial applications [26].

The future trends for the SSM processes are related to the slurry technology and high melting point alloys. For the first one, the aim is to reduce the cost of conventional die castings processes, increase productivity and improve the quality of final products. Furthermore, high melting point alloys have always been taken into consideration in research during the last 30 years. This has allowed complex steel components to be made at a reduced cost compared to conventional forgings. In Europe, for instance, several companies have consolidated these activities to commercialise the thixoforming of high melting point alloys [6].

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2 Specific Project Activity – Review Article



Type of the Paper (Review)

The development of Semi-Solid Metal (SSM) processing from inception to date

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Abstract: Semi-Solid Metal (SSM) processing of alloys and composites has its origins in research work carried out at MIT in the early 1970s. However, the process has been in and out of commercial favour over the past 50 years or so. The first years of the technique were focused on research work, which tried to expand its possible applications. After 20 years, the automotive market decided to take advantage of it and started its commercialisation, focusing on aluminium alloys, mostly in Europe. Unfortunately, the technology could not hold its position due to the high price required for its feedstock, relegating it to R&D once more. During this period, it became possible to develop new methods to overcome those problems making its resurgence feasible in recent years. Europe and mainly China have put renewed efforts behind SSM processing looking for a process that can fit in with the demands of current technologies, so it might be that SSM processing has finally found a market where it can fulfil its potential. This paper will review the various stages of its development over the past five decades, outlining the successes, missed opportunities and what can be expected in the future years.

Keywords: Semi-solid processing; thixoforming; rheocasting; non-dendritic microstructures

1. Introduction

SSM processing is a manufacturing route that covers the different existing techniques that imply working materials in their semi-solid state[1]. This technology consists of process them by taking advantage of its spherical microstructure which provides its characteristically thixotropic state. Therefore, the material thins and flows when sheared, and thickens when it is allowed to stand[2]. This metal forming route was patented by Spencer when he was a PhD student under the supervision of Prof. Flemings in the early 1970s[3].

SSM processing caused expectation because it was a novel manufacturing process that could be exploited in new different ways. The money invested in the development and better understanding of the technology and three international conferences focused on the topic proved the awareness created by the potential advantages of SSM processing. However, despite all the effort done in the early years, there were some problems that needed to be solved. For instance, the existing techniques for producing the spherical microstructure did not take out the full potential of the technology, and the full comprehension of the rheology of the slurries was not achieved yet[4]. To overcome these problems, research continued on the feedstock production and many methods were developed such as SEED, GISS. These techniques helped to reduce the cost in the production of feedstock, and allowed to recycle the scrap in-situ, generating substantial savings[1].

Currently, SSM processing has found a market in telecom and automotive industry thanks to all the components required for the implementation of 5G network and the goal of fabricating lightweight vehicles to reduce the emissions, respectively. However, the path that SSM processing followed has not been easy [5]. There have been periods where it was successfully commercialised, and even though it looked like it was able to find a niche, it returned to the labs trying to find a better way to improve.

Therefore, this paper presents a review of the development of SSM processing throughout its almost 50 years of history. Since its creation in the early 1970s up to these days, and finalising with what can the industry expect of it and which directions could help to improve the importance of it. In addition, some of the more relevant events related to SSM processing of each decade will be exposed, such as the invention of techniques for the production of the non-dendritic microstructure and companies which tried to take full advantage of the process.

2. 1970s: The beginning

The phenomenon of semi-solid processing can be traced to 1923 when Schalek and Szegvari found that aqueous iron oxide gels could turn liquid through soft shaking and obtaining a liquefied gel that could hardly be distinguished from the original sol [6]. Nevertheless, the milestone for SSM processing can be considered the research carried out by Spencer and Flemings at MIT in 1972. They observed that for the same value of solid volume fraction, the shear stress required to initiate shear was three orders of magnitude lower for samples that were stirred during solidification. Moreover, the rheological behaviour of partially solidified sheared Sn – 15% Pb alloy had properties characteristic of thixotropic slurries, which lead the researchers to conclude that such slurries had possible applications in casting processes and new other methodologies that could be developed [7]. Figure 1 shows the microstructure of the Sn-15wt% Pb alloy after being continuously sheared and cooled to 0.60 volume fraction solid and quenched in water [8].

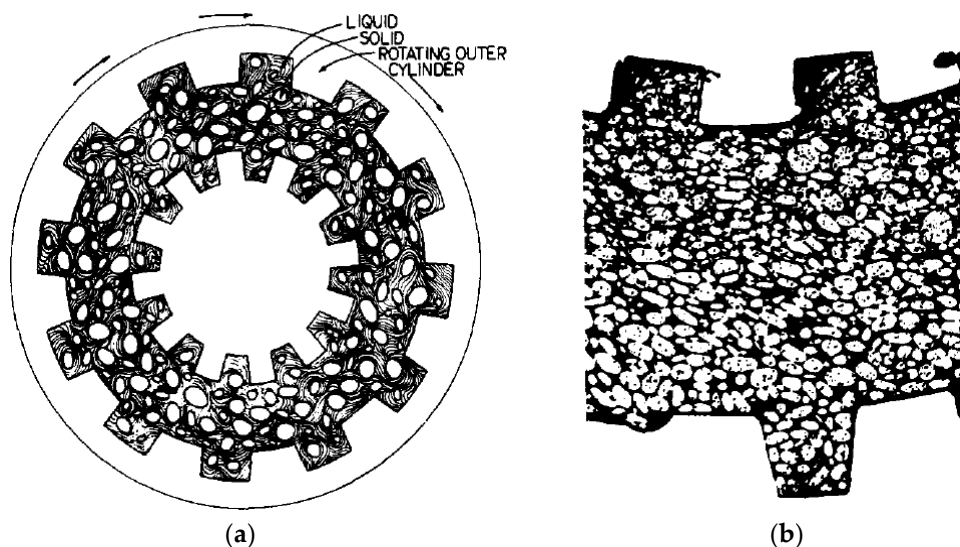


Figure 1. Microstructure of Sn-15wt% Pb alloy partially solidified after being continuously sheared. (a) Schematic illustration from the top view of the concentric cylinders of a Coutte Viscometer; (b) Microstructure of 0.6 solid volume fraction after being sheared and water quenched [8].

The basic and important terminology relating to semi-solid forming was established during this period of time. For instance, the process of cooling the molten metal to a semi-solid state, processing it to have a non-dendritic microstructure, and finally casting it into a particular shape was called Rheocasting. In addition, rheocast metal could be cast in batches to obtain non-dendritic specimens when cooled to room temperature. These could be later reheated to the semi-solid state to achieve slurries with thixotropic behaviour that is fed under pressure into a die through a die-casting or similar processing route. This alternative route was termed Thixocasting [9].

The main characteristic of the microstructure shown in Figure 1 is the presence of "non-dendritic" particles in the slurry before quenching. From the experiments conducted, it was observed that there are no preferred shear planes in fluids, while in dendritic solids there are preferred shear paths. Therefore, from a rheological point of view, the rheocast metal is a liquid slurry that can be given a viscosity value. If the solid volume fraction is low, the viscosity is low, and this increases with the increase of volume fraction solid. For fraction solid values of 0.50, the viscosity is similar to heavy machine oils and as such, this semi-solid material could be employed in forming processes like die casting [8].

These techniques extended the possibilities related to forming processes as some of them developed techniques where although the temperature of the metals was over their solidus temperature they appeared to be more like casting processes due to their thixotropic behaviour. However, that mushy thixotropic state of metals offered a number of new possibilities, such as a notable decrease in the working forces required, obtaining higher reduction and working rates, better flow characteristics into closed dies, and with the help of cooling devices the usage of processes like direct rolling and extrusion in the semi-solid state also became possible. For instance, for a Pb-Sn alloy at a solid fraction of 85%, it was possible to achieve a 99.94% reduction in an extrusion process, and still obtain good mechanical properties [10].

At this time research clarified as to how the flow behaviour of the liquid phase around the grain boundaries influenced the deformation of the material by proposing that the liquid component of the slurry present around the grain boundaries decreased the bonding forces between the grains, hence, when the material is subjected to an external force, grains can easily move, rotate and pass each other. It was also reported that in some aluminium, copper and lead alloys when the solid fraction was reduced from 100% to 80%, flow stresses decreased to around a fifth [11].

The first possible applications of rheocasting and thixoforming were also envisioned during this decade. It was suggested that both techniques could be applied to all alloy metals as long as they exhibited a reasonable freezing range that would offer an appropriate processing window. Nevertheless, each metal alloy presents disadvantages together with the advantages expected by the processing of semi-solid slurries. For example, the low melting point aluminium alloys are easily amenable to the production of good quality castings and enhanced die lives, while attempting to shape superalloys or steels that present good flow characteristics and appropriate processing windows comes with the challenges of shorter die life as well as other problems associated with their higher melting points resulting in additional costs. Rheocasting and thixoforming offer potential solutions as they do employ lower temperatures than traditional casting [12].

Prof. Merton Flemings continued the early work in semi-solid metal processing and established a number of the early patents. He introduced a process for forming continuous slurries in the semi-solid state that consisted in having the molten metal in a zone where it is vigorously agitated and then cooled resulting in degenerate dendrites and on reheating achieves a non-dendritic microstructure. Furthermore, Flemings suggested a method for semi-solid forming ferrous metal compositions. Metals up to 85 wt% Fe could degenerate their dendrites if robust agitation was performed because it prevented the creation of interconnected dendritic networks. In addition, to prevent the oxidation and possible clogging of the output, a protective gas blanket was used just after the agitation zone [13].

The MIT researchers were quick to recognise the benefits of semi-solid metal processing and also, as their early attempts showed, the main drawback to full commercialisation, i.e. the need for a consistent quality non-dendritic slurry making technique.

This early research work made throughout this decade brought semi-solid metal processes into the attention of companies that were always on the lookout for new innovative techniques for near net-shape manufacturing that can be exploited than the ones been used at the time.

3. 1980s: R & D and early commercialisation attempts

The early research had shown that near spherical microstructures necessary for SSM processing of alloys was primarily controlled by four independent parameters: shear rate, stirring time, cooling rate and volume fraction of the solid particles. It was also reported that the size of the solid particles decreased as the shear rate increased and that for larger volume fraction solid the particles present in the microstructure were also

larger. Moreover, the sphericity of particles found in the microstructure can be increased if the solid volume fraction, stirring time and shear rate are also increased [14].

The next phase of semi-solid processing research showed more emphasis to finding possible methods in making SSM a continuous process and expanding the variety of alloys that could be used. Flemings and his group at MIT studied how strain-rates and deformation influenced the behaviour of semi-solid dendritic Sn-Pb alloys in a compression process. The research was performed because they wanted to assess if there were a group of particular conditions that could deform the semi-solid dendritic alloy homogeneously. They found that at low velocity ranges, the alloy presented high amount of segregation in the liquid phase while it was being compressed, and this effect increased with deformation of the specimen. On the other hand, at high-velocity ranges, the alloys showed a uniform behaviour while deformed. They suggested that at low velocity intervals, deformation can be used as a refining process, while at high velocity ranges, it can be used as an efficient forming process. Figure 2 shows two different microstructures for the same strain rate but two strain percentages[15].

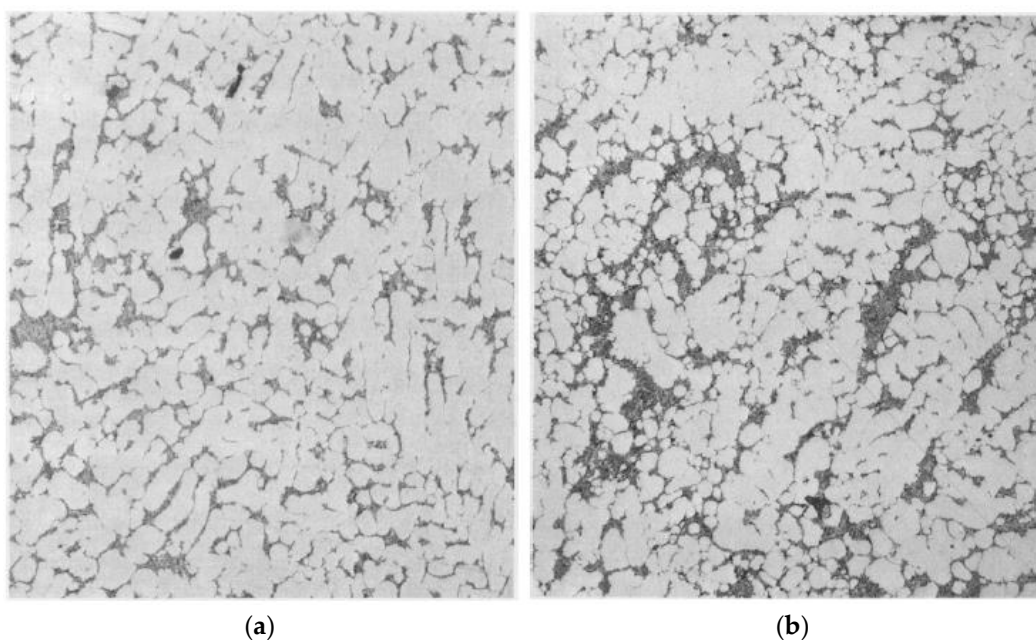


Figure 2. Microstructure after dendrite fragmentation during the compression of Sn-15wt% Pb at $1.33 \times 10^{-2} \text{ s}^{-1}$. Both magnifications are 119.75X (a) Image taken at a strain of 0.36; (b) Image taken at a strain of 0.87 [15].

Another technique proposed at the time for generating microstructures of near globular particles is based on the use of powder metallurgy. Its procedure is based on premixing and compaction of different powders. The first step consists in mixing the powders with a liquid. For this research, Al-50 wt% Mg and industrial methylated spirits were used as powders and liquid, respectively. Then, the mix is melted and compacted to prevent porosity. This step is nominated consolidation, followed by a heat treatment performed to generate the desired solute distribution. The grain diameters obtained from this process range from 10 to 200 μm , and the solid volume fraction can be accurately determined. Finally, it was found that using the correct parameters as powders, compositions and consolidation conditions, the technique can be used in industrial applications [16].

Al-Pb alloys had an interest in the automobile industry due to their lower cost compared to tin-based alloys. Nevertheless, the main problem with this alloy is the wide miscibility gap of Al and Pb in the molten state. Hence, it was almost impossible to distribute the lead homogeneously into the aluminium using conventional casting techniques. The procedure consisted of mixing the vacuum-melted Al-Pb alloys with a stirring bar at low speed during cooling. Then, when solidification started, the stirring speed had to increase to obtain the spherical microstructure desired for rheocasting applications. The microstructure showed

irregular lead-rich phases located between the particles generated by the fragmentation of aluminium dendrites which are uniformly dispersed throughout the ingot [17].

Some research was conducted in Al-Cu alloys involving different percentages of copper with the goal to decrease its grain size. In this work, the refinement was performed via a rheocasting technique during the cooling of the alloy at different rotation speeds of the stirring bar. The generation of fine spherical grains was achieved in three alloys containing 10 wt%, 24 wt% and 30 wt% of copper when speeds in excess of 20 s⁻¹ were used. Table 1 shows the resulting grain sizes at different rotation speeds. Moreover, the addition of grain refiners such as Ti or B reduced even more, the grain size of the ingots [18].

Table 1. Grain size of different Al-Cu alloys under different rotation speeds [18]

	33 s ⁻¹	50 s ⁻¹	67 s ⁻¹
Al – 10%Cu	101 ± 31	98 ± 34	90 ± 29
Al – 24%Cu	87 ± 28	75 ± 30	61 ± 32
Al – 30%Cu	54 ± 19	52 ± 21	46 ± 14

At the beginning of the 1980s, the patents created by Flemings and his collaborators were bought by the International Telephone and Telegraph (ITT) Company in USA as they tried to take advantage of what this novel technology could provide them for many of their products [19]. Together with investing in the MIT patents, they also employed Kenneth Young, one of the collaborators of Flemings who was familiar with the technology. Ken Young was an ex-University of Sheffield, department of Metallurgy graduate and has played a pivotal role in the commercialisation of the SSM process.

4. 1990s: First full commercialisation of SSM processing

The first two decades of SSM processing were a transition from its inception and laboratory research to a process that grew fast, even though it had a reasonably short commercial life, in the early 1990s. However, in a sector governed by casting processes, thixocasting, for instance, only represented nearly 1% of the total market. Hence, it needed to overcome the challenge of becoming economically competitive [20].

The automobile industry played a key role in the early commercial development of SSM processing during these years. Many factors were taken into consideration at the moment of choosing which material should be used because they have to fulfil the requirements of design, engineering, production and supply. In addition the environmental impact of transportation dictated that weight reductions and the associated reductions in fuel usage were imperative and therefore the introduction of light alloys into transport vehicles became a priority in achieving the desired weight reductions [21]. For instance, in Europe, the emphasis was placed on recycling and environmental topics and in Japan due to additions as air conditioning and anti-lock brakes they wanted to maintain the overall weight of cars. Hence, many car manufacturers started looking for light alloys like aluminium and magnesium and new technologies to reduce the cost of producing the components [22]. As already stated above, key to the commercial success of SSM processing was the establishment of a route that could guarantee consistent good quality non-dendritic microstructure feedstock. Ken Young using his expertise from the years of research at MIT and metallurgical background knowledge with his colleagues at International Telephone and Telegraph (ITT) in the USA established the first version of a Magnetohydrodynamic stirring process (MHD) that generated long lengths of consistent quality of non-dendritic alloys. The MHD process breaks down the dendritic structure via localised shearing of a melt through the use of rotating electromagnetic fields. As the process is contained in a mould and the sheared melt is cast in a continuous format, the resulting slurry, which is appropriately degassed and filtered, results in long lengths of consistent good quality feedstock material of small average grain size of around 30 μm. The consistency of quality, the reduced segregation and the low porosity content established the MHD method of non-dendritic feedstock production as the main method for the full commercialisation of thixoforming [18]. However, there were two main drawbacks that created implications for the future of commercial applications using this feedstock production methodology, namely the fact that there were only one or two main producers and therefore they could

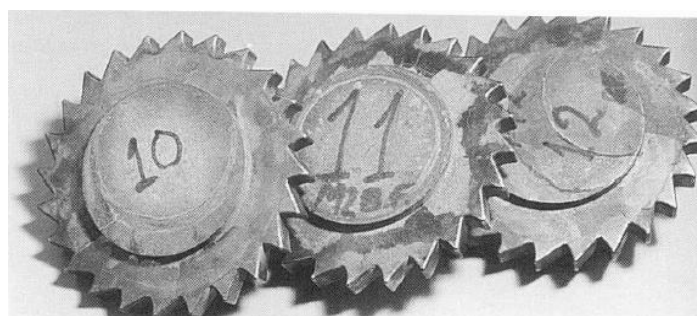
command a premium for their feedstock and secondly the users of MHD feedstock had to send back their scrap back to the producers in order to have them re-made into non-dendritic feedstock.

Thixoforming at the time appeared as an innovative manufacturing process that could meet the new demands of the transportation sector through near net-shape of light alloys and composites. In Europe, around 40 SSM manufacturing cells were installed. Some companies that used to provide aluminium feedstock for electromagnetic stirring also were established in Europe, and some of them produced feedstock for their consumption like Alusuisse-Lonza in Switzerland [23]. Using their feedstock, Buhler in their die casting foundry fabricated the suspension control arm for Porsche's Boxster [22].

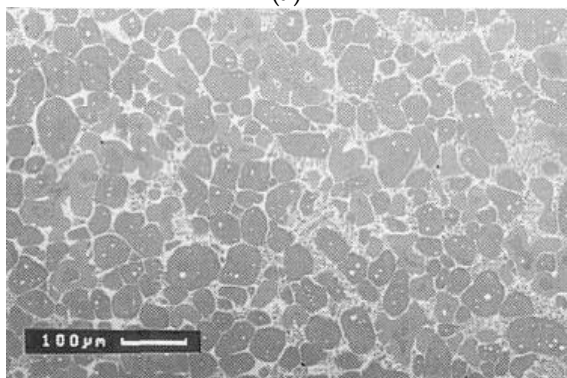
In 1994, in Japan, a company started using thixocasting for its production of wheels made of aluminium, and in 1996 the production of Mg alloys castings started. Furthermore, during these years, numerous SSM processes appeared in Japan. For instance, RHEO-TECHNOLOGY, LTD. developed techniques which employed electromagnetic force, and Hitachi Metals, LTD that adopted a cold crucible method to stir semi-solid alloys in die casting shot sleeve. Furthermore, methods for producing slurry without stirring were also developed. They were based in the simultaneous nucleation of grains and restricting their growth due to the interference between them, providing fine grains [24].

SSM processing also had a market for small components. For instance, golf putters were made using aluminium 357 alloys; automotive pulleys were made from metal matrix composites materials because their wear resistance could even be improved if fly-ash was used in a 30% volume content [25].

Although SSM processing focused mostly in light alloys and copper, it also was considered as a possible manufacturing process for alloys as tool steels and superalloys. For instance, the M2 tool steel was selected to be thixoforged. The feedstock was produced by two different techniques, Recrystallisation and Partial Melting (RAP) and Spray Forming. The thixoforging of toothed cogwheels was possible when the RAP feedstock was used as it can be seen in Figure 3. The components had high accuracy in their geometry and achieved a hardness of 810 HV after being tempered [26].



(a)



(b)

Figure 3. Thixoforged toothed cog wheels made from M2 tool steel (a) Top view from the whole component; (b) Microstructure of the component [26].

Apart from SSM processing, another alternative method tried to achieve commercial attention during these years. It was named semi-liquid process. It started producing around 9,000 automotive fuel rails per day in Italy and Brazil since the early 1990s. This process uses convection ovens to heat SSM slugs to induce

low volume fraction solid and enhance the flow into complex thin-wall geometries. A critical consideration for this process is that it relies on a particularly prepared billet, that has already been conditioned to generate the desired microstructure for SSM processes [27].

At this time, an Italian manufacturing company, Stampal S.p.A., under the guidance of their enterprising CEO Gianluigi Chiarmetta made a number of automotive parts for Alfa Romeo, Fiat, VW and other automotive producers as it is shown in Figure 4. In the main they used MHD material provided by the French company Pechiney but due to the additional costs of having to send their scrap back to France for reprocessing the commercial viability of their thixoforming operation became doubtful. They added different ways of sourcing their non-dendritic feedstock but although their products achieved great performance standards as far as properties go, their commercial viability suffered on the cost side and eventually Stampal was sold to a Dutch manufacturer and slowly stopped their thixoforming activities [14].



Figure 4. Components produced by Stampal S.p.A for multiple automotive brands (a) Engine suspensions mounts made from aluminium alloy A357 for Fiat; (b) Steering knuckle made from aluminium alloy A357 for Alfa Romeo [28].

As it has been explained lines above, the main problem in the commercialisation of SSM processing was the feedstock. There were not a variety of thixo-typical alloys that could take full advantage of the process. The most common alloys were aluminium alloys A356 and A357, with round bar feedstock of only two sizes, 3" and 6" diameters. Furthermore, a source for a continuous quality feedstock was necessary because even the slightly difference in microstructure influence in the process. This could also tackle the problem in adjusting the feedstock price and make it similar to other processes in the market [23]. Another possibility to make thixoforming a more appealing technology was to make the feedstock recyclable and avoiding sending the reject material to the provider. The "slurry on demand" process tried to overcome this difficulty by eliminating the requirement for special raw material and enable on-site recycling in liquid metal. It consists of transforming the liquid metal into a semi-solid slurry using electromagnetic or mechanical stirring. Then, the slurry had to be transferred to the shot sleeve of the casting machine. "Slurry on demand" allowed to eliminate the more expensive MHD feedstock billets required for SSM processing and solved the recycling issue because scrap could be returned to the melting furnace in situ [27].

5. 2000s: Back to R&D

Despite all the attempts to commercialise SSM processing, the process was not able to consolidate its market share in Europe. However, companies like Vforge in USA successfully continued using SSM commercially by targeting the correct markets, but more widely unfortunately, SSM returned to the R&D state [1]. The reason behind this event was that the viability of the process became unsustainable due to the high cost of the premium put on MHD feedstock. Furthermore, there was no possibility to recycle the MHD scrap left by the process but it was necessary to send it to the feedstock provider for reprocessing and that involved more expenses[1].

SSM processing kept being focused in light alloys due to the importance they had in the automotive industry as opposed to high melting point alloys [29]. Nevertheless, steel components were also used in this sector, but that was restricted to only conventional casting technologies. Therefore, thixoforming appeared as a possible alternative to generate elements which take the advantages of casting techniques and achieving the requirements for mechanical properties. With the new millennium, a European consortium formed by "THIXOCOMP" and COST 541 "THIXOSTEEL", worked along RWTH Aachen to overcome the difficulties of SSM processing of steel and try to exploit it [30].

When research work was performed in alloys with high melting point, more specifically on steels, it showed a disadvantage due to the narrow gap between the solidus and liquidus temperature in low carbon steels and low alloy steels. Hence, most part of the research was performed in high carbon, high alloy steels that, unfortunately, are the most difficult to work using traditional techniques. The use of differential thermal analysis (DTA) to measure the liquid volume fraction of alloys to recognise if they were suitable for thixoforming, was adapted for steels. For instance, the solidus and liquidus temperatures should be as low as possible, but their gap has to be the largest possible [31]. However, it has to be taken into consideration that the usual technique for measuring the liquid volume fraction is quantitative metallography because thermal analysis is not suitable for metallurgical operations. Another challenge present in the SSM processing of steel was the die development [32]. Due to the high temperatures and the process itself, the die needs to be wear-resistant, therefore, many possible solutions were investigated, like the use of oxide PVD coatings, PACVD alumina films and ceramic inserts [31].

In this decade, a simple feedstock processing method, named cooling slope, characterised by the fact it does not require any expensive equipment, became a quick way of non-dendritic feedstock generation for R&D work [33]. The presence of globular grains in the microstructure is explained by the crystal separation theory, which states that crystals nucleate at the surface of the plate. Then, due to the movement caused by gravity, nuclei formed are removed from the surface and distribute in the slurry, ensuring its fine size [3]. In addition, the output of the process can be synchronised with the production of the ingot, improving the efficiency of the whole process [33]. Figure 5 shows a schematic of the cooling slope process.

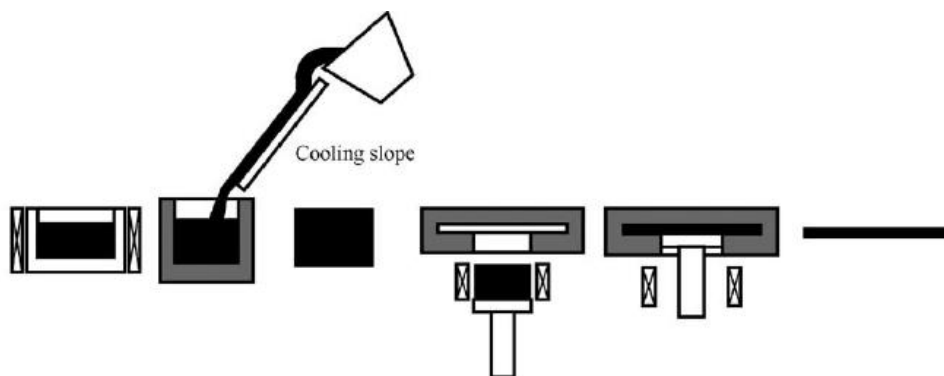


Figure 5. Schematic illustration of the cooling slope method for generation of non-dendritic microstructure [33].

This technique managed to achieve good results at the moment of producing the feedstock for SSM processing of steel with high carbon content. For instance, in a particular steel with 1.49 wt% C, apart from obtaining the globular microstructure, it reduced the grain size from 520 μm to 200 μm at low solid volume fractions. Moreover, the grain size could decrease even more if the fraction solid had increased. Furthermore, there was an improvement in the results of tensile strength and hardness for the specimens obtained by SSM processing compared to casting [34]. The Cooling slope process can also be used in cast iron samples. It was found that a microstructure with globular precipitates can be achieved mostly in hypoeutectic carbon iron and high-chromium iron, and this can have beneficial effects on the mechanical properties. However, more tests should be performed to corroborate the theory [35].

Another technique developed during these years was the gas-induced semi-solid process (GISS). This technique also does not depend on stirring the molten metal to fragment the dendrites and obtain the

globular microstructure. GISSCO, Co. Ltd. was employing GISS processing to fabricate commercial parts like automotive rotor covers [36]. Figure 6 shows the final microstructure of two different aluminium alloys obtained by GISS process.

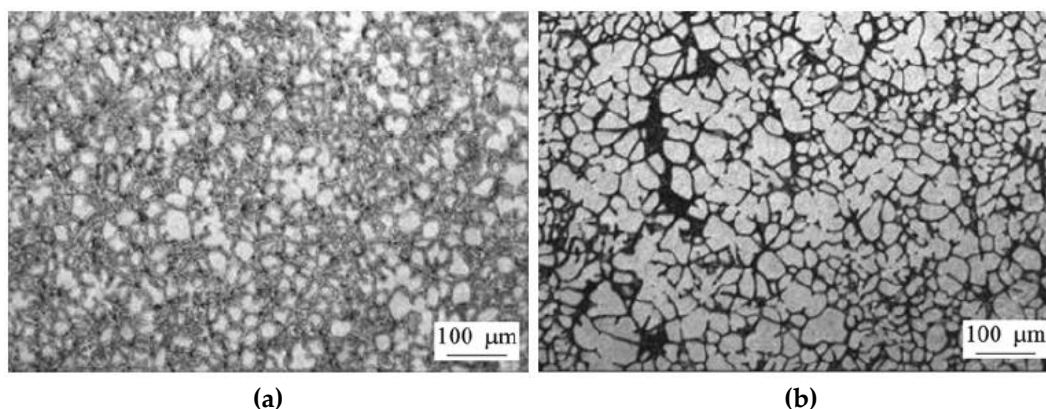


Figure 6. Microstructure of two of the most used aluminium alloys (a) Aluminium alloy AA5052; (b) Aluminium alloy AA6061 [36].

Some research continued being done with light alloys, for instance, a route using thermomechanical processing for obtaining the desired globular microstructure in the $AlSi_8Cu_3F$ aluminium alloy where a billet is heated to different temperatures around 450 °C and then extruded. Previously, it was necessary to reshape the as-received ingot and inoculate it according to standard commercial practice, then, heat the billets to a semi-solid temperature for some time and finally, quench them to assess their microstructure [37]. Thixoforming was also used in high performance aluminium alloy like AA7075. The feedstock was produced utilising the RAP route, and one variable of the experiment was the number of steps during heating. The best results occurred with three-step heating, achieving an average yield strength of 477 MPa, while the wrought material had 505 MPa. In elongation, there is a more significant difference, 3.0% and 11% for thixoformed and wrought metal, respectively. The elongation could be improved by reducing the defects through die design [38].

6. 2010s: Revival of SSM

By 2009, the production capacity of SAG (Slazburger Aluminium AG) was around 400,000 pieces per year. Their production was based on structural applications, where requirements like strength, ductility and weldability needed to be fulfilled. Unfortunately, the economic crisis in 2009 caused a problematic time for casting processes because it was difficult to gain profit from them due to the huge production capacities released in the foundry industry [39].

In 2010, even though the production in Austria was reduced, it regained its capacity steadily until 2018. Nevertheless, the economic crisis made notorious the weakest point of SSM processing, the high cost related to the feedstock due to the limited number of suppliers and the incapacity of the process to recycle their scrap. Therefore, research was performed looking for a method to industrialise rheocasting, and it made possible the implementation of two rheocasting cells at Fueltech AB in Sweden, which is a SAG subsidiary. These cells produce three different parts for Volvo trucks. This example was followed by SAG Austria, and they industrialise rheocasting in 2017 [39].

SSM processing of steel saw relevant developments during these years. The current conditions for semi-solid forging (SSF) are around the solidus temperature, implying small content of the liquid phase; while in the beginning, the solid volume fractions were around 70 – 80%. The usage of low liquid volume fraction detailed before stopped the attempts of using coatings or ceramic inserts for the dies. It was possible to obtain sound parts employing slurries containing a small amount of liquid while having low die wear. For instance, after producing 3500 parts via SSF, employing conventional tool steel for hot working, the damaged on the dies was similar to the one used in hot forging dies. Unfortunately, despite being able to produce complex components, having near-net-shape capability and reducing costs, SSF has

not been able to penetrate in the market because the same equipment required for SSF is needed in the conventional hot forging process. Therefore, companies will continue using the process they have been using for the last years instead of adapting to a novel one that provides similar mechanical properties [40].

On the contrary, light alloys, especially aluminium saw a growing interest in SSM processes, mainly in those methods that overcame the problem of not being able to recycle their scrap in situ, like GISS and SEED [1]. Is in this scenario, that the GISS technique has been used for many applications like prosthetic adaptors made from aluminium, where low porosities and high strength is required. Another application of GISS can be found in low-cost armour plates, where the requirement is to stop 7.62 mm ball rounds under the standard NIJ Level III. For this application, a metal matrix composite was used, the metal was the aluminium alloy 7075-T8, and the composite was silicon-carbide (SiC) [41].

On the other hand, rheocasting has seen a notable expansion on the products that can be fabricated with this technique. The drivers behind this resurgence are Europe and China. In Europe, the applications are towards automotive and marine sectors, while in China the trend is focused on the telecom industry. The automotive industry widely used the SSM process named Rheometal. The aim of this sector was the design of fatigue resistant parts. Therefore, for being able to improve the fatigue-resistant of components, it was mandatory to reduce the internal porosity. Rheometal allowed this by optimising the casting parameters like die temperature and slurry solid fraction. Furthermore, the process has adapted for handling large shot weights because the applications of the process are in the range of 12 – 27kg [5]. Figure 7 shows multiple automotive components made by rheocasting.

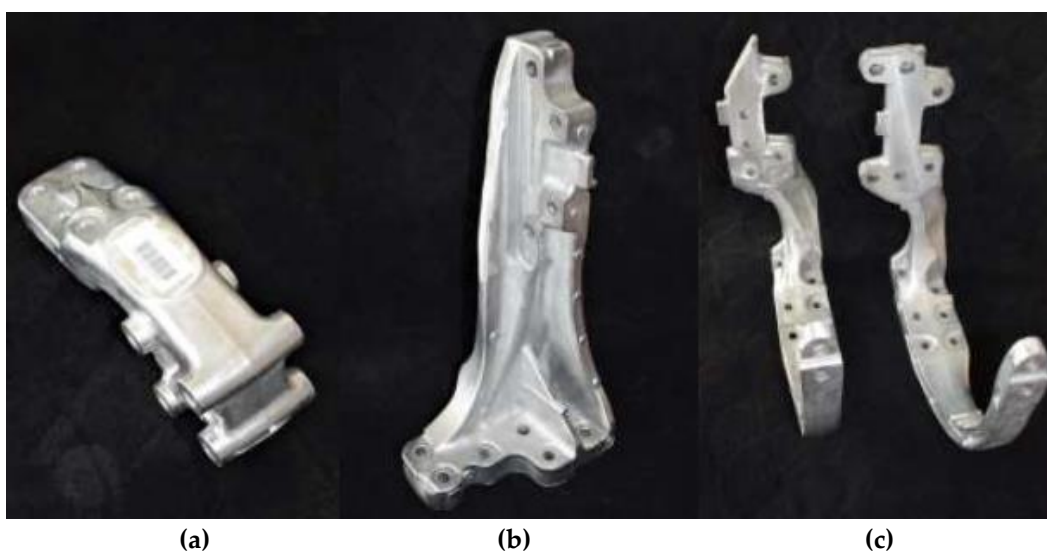


Figure 7. Automotive components made by SAG Fueltech Sweden AB and Volvo Trucks AB using rheocasting (a) CAB mount; (b) Muffler bracket; (c) Muffler bracket [5].

Moreover, rheocasting techniques used to employ high solid volume fractions, around 40 – 60%. Nonetheless, the current solid volume fraction has shifted to low values, 10 – 30% due to the minor requirements for the machines. Therefore, the quality of aluminium components manufactured by die casting was improved by using semi-solid casting. Contrary to conventional die castings, rheocasting products do not eliminate but reduce the porosity of the parts. The use of premium semi-solid feedstock is not essential because the low solid volume fraction castings employ the same turbulent die filling conditions of conventional die casting. Hence, the advantage of semi-solid casting over traditional casting is the simplicity of the process used to make the slurry and keep the low cost of equipment [41].

A relevant field of application of rheocasting is the electronics sector. The production is focused on the elaboration of radio frequency filters, which are components with complex geometries. Moreover, the current development of the 5G network has increased the sizes and complexity of the parts. Hence, high pressure die casting (HDPC) process will have difficulties filling the geometry, and defects will be induced.

On the other hand, rheocasting enables lower final intensification pressures, making possible the fabrication of the component [5].

Other SSM process, and probably the most successful over the last years, has been thixomoulding. It was developed by Thixomat and is mainly used for the fabrication of magnesium alloy castings. The most used alloys for thixomoulding are AZ91D, AM-60 and AM-50. The components manufactured under this process are used in a wide range of markets like automotive and electronics. The aim of used thixomoulding was to provide precision to critical dimensions, alignment for numerous components, and dimensional stability [42]. Figure 8 shows various components made by thixomoulding.

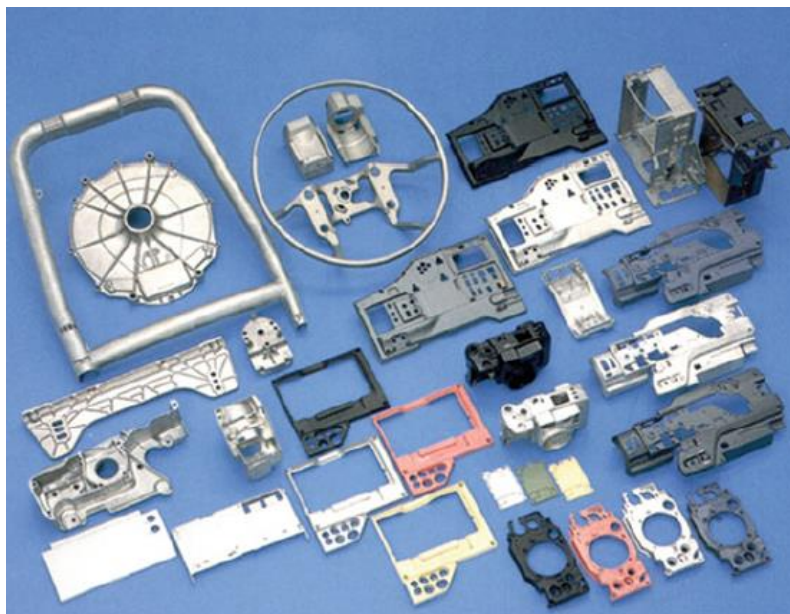


Figure 8. Multiple components of magnesium alloys manufactured by thixomoulding process [42].

Furthermore, apart from the previous applications, research continues with the purpose of expanding the field for SSM processing. For instance, the aluminium alloy A201 is a commercial alloy due to its high mechanical properties and good formability. However, this alloy presents difficulties when it comes to casting due to numerous reasons like poor fluidity, cracking and hot tears. Therefore, one possibility was to assess if thixofforming was a valid processing route for the A201 alloys. The feedstock was cast using the cooling slope method, and the results obtained for tensile strength were similar to the as-cast route, and the elongation showed an improvement of nearly 50% [43].

7. 2020s: Where next?

Unfortunately, this year the whole world has suffered the effects caused by the pandemic due to Covid-19, and the field of SSM processing has not been the exception. Fortunately, the outbreak will delay but not stop the research that the Austrian Foundry Research Institute and Comptech AB have been performing on rheocasting, aiming to establish tolerance limits and identifying possible compositions of engineering alloys that can be suitable for the process [44].

Moreover, another parameter to take into consideration is the huge development that additive manufacturing (AM) has had in the last years. AM is a manufacturing process able to fabricate complex structures reducing their cost, lead times and achieving lightweight. For instance, recent studies have developed methods to overcome the problem of manufacturing aluminium via AM due to the difficulties associated with laser melting [45].

Back in 2000, Flemings said that the future for SSM processing was going to be focused on light alloys like magnesium and aluminium, and to some extent, composites using those metals as the matrix. He also announced that the process would have a niche in the automotive and electronic market. Moreover, he declared efforts will be made in the production of the slurry from the liquid, and that better and more

economical processing routes will be found [46]. Time only proved him right. The most used alloys in SSM processing are the both he mentioned. China and Europe, the drivers of the resurgence of SSM processing during the last decade, has focused mainly in the electronic and automotive sector. China did it due to the production required for implementing the 5G network, and Europe did it looking for greener processes and recyclable materials.

In addition, Flemings said that for the further development of SSM processing, three research directions were key: to have a better understanding of the mechanism of the rheocast structure generation, the application of numerical modelling for the SSM production and finally, the design of engineering alloys specifically for SSM processing [46]. Currently, it is possible to say that there is a wider comprehension of the generation of rheocast structure. How parameters such as the solid fraction, stirring speed influence on the microstructure of the feedstock [47]. Numerical modelling has been employed for the last years in SSM processing. Nevertheless, part of the work has been based on rheological data obtained in steady state experiments, which is a phenomenon that does not happen in reality. Hence, other methods like the one developed by Rouff and coworkers, which considers micro-modelling between the spherical particles and the surrounding "active zone" has to be considered [48]. Even though this method may look complicated, it has been proved that research on that field can be done [49]. Furthermore, up to this date, it has not been possible the design of tailored alloys for exploiting the full potential of SSM processing. Casting and wrought alloys continue been used for SSM processing purposes. However, designing an alloy specifically tailored for SSM processing is one challenge that should be tackled. Alloys being able to form the correct percentage of liquid during partial melting, and being susceptible to heat treatment are properties that will boost the expansion of the technique [4].

Therefore, what can we expect for SSM processing for the future years? Even though it is not possible to predict how much time the current situation will last, the future of SSM processing looks promising. Most of the time SSM processing has indeed been in the R&D level, but nowadays some techniques have reduced the cost for premium feedstock, and the most crucial aspect is that SSM processing can fulfil the requirements for current technologies in the automotive and telecom sector as it has been exposed before. For instance, 5G equipment and electric vehicles demand better cooling systems to maintain batteries and reduce the heat from electric motors. These components require a thermal conductivity higher than 180 W/mK and using semi-solid casting with HPDC process as a viable option regarding the manufacturing cost and to meet the requirements for thermal conductivity. Furthermore, it was forecast that the number of installations would have an increase in 2019, involving an rise in machining, development and sells related to rheocasting, like Volvo Car Corporation that had a keen interest in SSM casting for their next generation of lightweight components [50]. Figure 9 shows components made by rheocasting process.



Figure 9. Components manufactured by Comptech Rheocasting (a) Part for the aviation industry with increased elongation; (b) Thin and weldable heat sinks [50].

8. Conclusions

In summary, the lifetime of SSM processing has been divided into five stages to highlight the development of the technology during the years from its creation in 1972 to the present, and its possible future development.

During the 1970s, the discovery of the possibilities carried out by forming materials in their semi-solid state caused expectation in the field. Flemings worked in different methods to generate the desired non-dendritic microstructure and patented some of them. In these years, the materials used for this technology were aluminium and copper based alloys; however, all of them had disadvantages due to the brief research performed in SSM processing.

In the 1980s, research highlighted the fact that the globular microstructure required was controlled by mainly four parameters: shear rate, stirring time, cooling rate and the solid fraction present in the slurry. The aluminium alloys started to position as the primary alloy for this process, as they lead the research performed in these years. Furthermore, at the beginning of the decade, the patents of Flemings were bought by a company which tried to innovate using the technology.

The first big step of SSM processing occurred in the 1990s. Ken Young, one of Flemings' collaborators, successfully developed the MHD, a technique that allowed availability of consistent good quality feedstock material. This permitted large industries in the automotive sector to consider SSM for their production. Big brands as Porsche, Alfa Romeo and Volkswagen manufactured some components using this technology.

In the 2000s, due to the elevated price of the feedstock for MHD, companies quit from using SSM processing. Hence, it caused the return of the technology to the R&D status, in search of less expensive methods that could generate the desired non-dendritic microstructure. This allowed the creation of methods like cooling slope and GISS that made cheap source of non-dendritic feedstock available.

Although SSM processing had returned to R&D level, the 2010s saw once again its resurgence. The coincidence of two events made possible its revival; firstly, the recently developed technologies that allowed the cost reduction of feedstock production and secondly, the requirements of the 5G network in China and the resurgent automotive sectors in Europe and China.

The future cannot be predicted, but due to the market share that SSM currently possesses, SSM processing is fulfilling finally its commercial potential. However, it is necessary to continue looking for better options of feedstock production and try to eliminate the few disadvantages of the process, such as wide alloy ranges that can exploit the full potential of it.

It has been almost 50 years since the possibilities of SSM processing were discovered in the labs of the MIT, so the technology cannot be considered as 'novel' anymore; however, despite the time that has passed, in recent years, SSM processing has been able to find markets for its products and can look forward to continue its further expansion.

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