1.1 Introduction

The conventional casting techniques are well established in processing of Al-Cu based alloys for a long time. However, a typical dendritic structure and macrosegregation give rise to poor mechanical properties and tribological characteristics of alloys. These features are more pronounced in a long freezing range alloys. Consequently, there are continuous efforts in development of semi-solid processing techniques in processing of these alloys. An improvement in quality requirements in critical application of component has been reported in these alloy [Kearney and Elwin, 1990]. The microstructural modification during semi-solid processing has been reported with the work of Kattams and Fleming in early seventies [Kattamis and Flemings, 1967]. These investigators held the hypoeutectic alloy at constant temperature in semi-solid region of the alloy to change the dendritic morphology of the primary phase. Detachment of secondary dendrites subsequent to their necking at the joint followed by their spehroidization resulted in considerable modification in microstructure. However, these processes required considerably long time.Soon after continuous efforts were made in this direction and resulted the evolution of various semi-solid processing techniques. The salient features of these techniques are described in the following sections. The results indicate that a number of variations of the stirring stages leads to continuous improvement in scale of microstructures. Following these features, the typical microstructures of semi-solid processed alloys have been presented and further disussed. The importance of these techniques in processing of long freezing range alloys has been highlighted. The objective of the present investigation is to develop Al-10Cu alloys with superior tribological properties. A section has been added to introduce various type of wear and an understanding of the control processes to reduce the wear rate.

1.2 Semi-solid processing Techniques

Number of techniques are available for casting of alloys following semi-solid processing. Some of important techniques and their characteristics are presented and discussed.

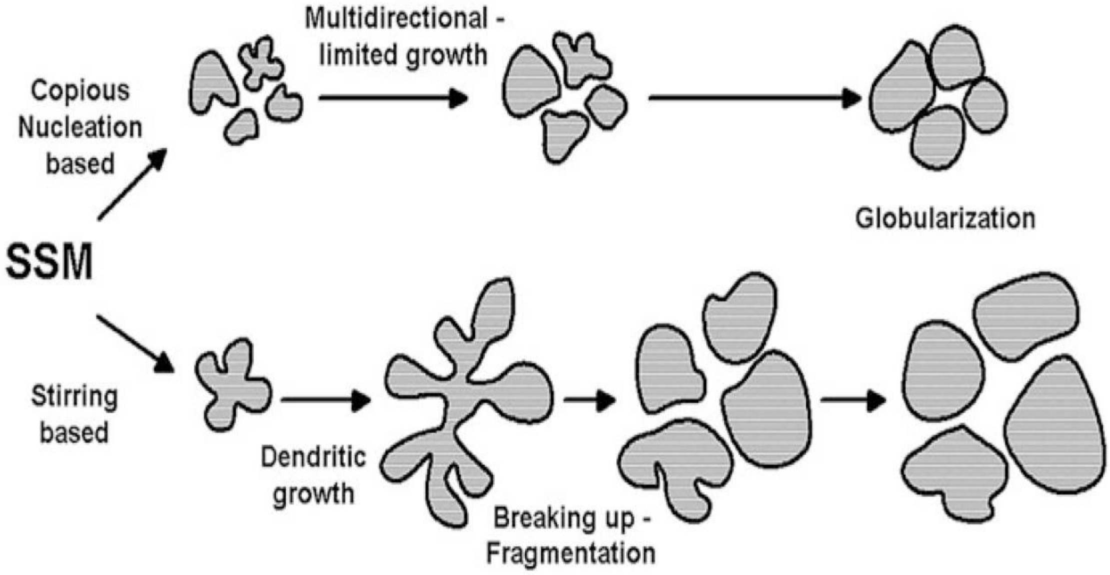


Figure 1.1: Two different mechanisms for rheocasting process. [Nafisi andGhomashchi, 2005]

The semi-solid processing involves fragmentation of dendrites by a number of stirring devices.Eventhough dendrites break up occurs by equilibration of two phases between liquid and solidus of the phase diagram but the kinetics of the process is enhanced by following stirring devices. The concept of dendrites transformation during solidification was proposed by Flemings[Flemings et al. 1991, 1974] , Doherty[Doherty et al. 1984] and further expanded by Hellawell[Hellawellet al. 1996] which can be applicable to semi-solid metal process shown in the fig.1.1. Dendrtes are fragmented by direct(Mechanica stirring) or Indirect (Electromagnetic strirring) during solidification. Dendrite fragments mechanically or by localized dendrite root melting. The dendrite will change to “rosettets and/or “globules”withcontinous shearing of the melt. Particle ripening become dominant with further stirring wihich was controlled by the reduction in interfacial surface energy. Thermally activated mechanisms involves localized undercooling provided in the bulk liquid to crete excessive nucleation analogs to that of the “big bang”theory or “copious nucleation”which was proposed by Ellitot and Chalmers[Elliot et al. 1983, Chalmers et al. 1964].

Excessive nucleation happens if the mean free path between nuclei becomes small. The limited constitutionally super cooled boundary layer and multidirectional heat flow makes the grain to grow slowly which leads the formation of more or less spherical primary phase particles. The advangates of excess nucleation based process are (a) elimination of atleast one step (b) less processing time, (c) better globular morphology of the primary particles.

1.2.1 Rheocasting

This process was started at Massachusetts Institute of Technology, MIT[Flemings et al. 1976] which involves stirring of the metal by the auger paddle, or impellers during solidification for getting the nondendritic microstructure was offered by the stirrers. The necessary shear force required for the formation of non dendritic structure was offered by the stirrers. The semi-solid sluryy directly can be used for producing near net shape compounds by Rheocasting process (Fig. 1.2)(or) feed stock obtained after the complete solidifcation of the slurry can be reheated at a later time to the semi-solid state and can be shaped by injecting into die called thixocasting. The gloubular morphology of the particles in the liquid matrix can be achieved by providing high solidification rates with high shear rates. This process may not be suitable for all commercial applications because of the following (a) low productivity, (b) forming of rosettes, (c) erosion of the stirrers mainly with high melting point and chemically aggressive alloy, (e) contamination of slurry due to oxides and dross. These shortcomings give rised to a new processes like DSF(Direct Slurry Formation[Rice and Mendez, 2001]. Figure 1.3. shows the furnace and mixing configuration of DSF process. Anchor-shaped rotor with vertical shearing rods which are located close to the furnace walls are responsible for scraping the solidifying material and vaccumdrawing liquidAluminium through a tube into the shot sleeve. This process consists three steps. (a) making the semi-solid slurry, (b) maintaining the slurry, (c) transferring the slurry to the die casting machine. Auger and anchor shaped rotors are not only responsible for providing sufficient forces but also help in the homogeneous distribution of the primary particles in the slurry. The slurry will be transported to the diecasting machine with the help of vaccum.

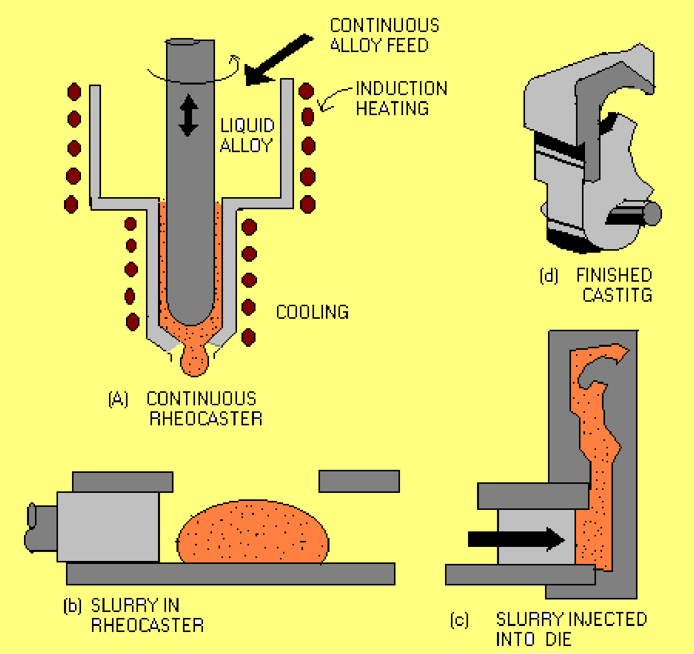


Figure 1.2: Semi-Solid processing by Rheocasting.

Ichikawa et al. [Ichikawa, 1987] made rheocastings of Al-5mass% Cu and Al-10 mass % Cu by a novel continuous rheoecasting and studied the effect of homogeneous of microstructure on the mechanical properties. The typical grain size in an Al–10 % mass % Cu alloy sheet was 6.9 ± 1.8 µm in the continuous rheocasting process. The grain size of the Al-10Cu alloy is on the order of 100 µm for the conventional rheocasting and

72±26 µm in case of batch –type rheocasting. The ultimate tensile strength of Al-10%Cu alloy sheet was 248 MPa at room temperature ,which was higher compared to UTS off192 MPa in a die-cast Al-10 mass% Cu alloy.

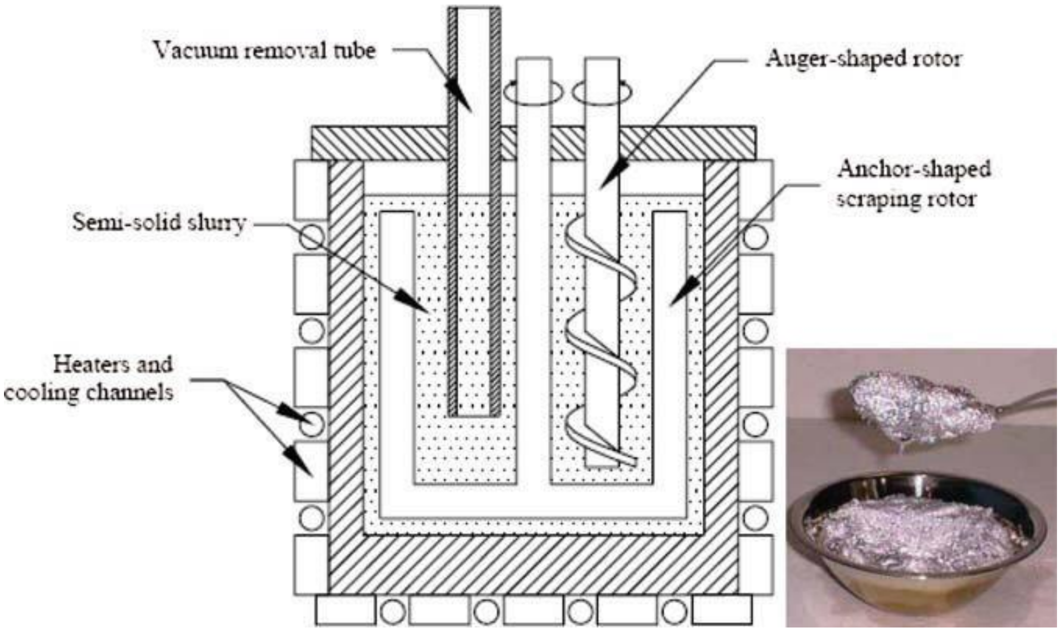


Figure 1.3: Direct Slurry Formation (DSF) process and machine components.

Niroumand et al. [Niroumand, 2000] studied the rheocast microstructure of an Al-10.25wt%Cu alloy shows that the primary features consist of pseudo-particles and pseudo-clusters. The alloy was mechanically stirred at 1000 rpm while being cooled to and kept at a constant temperature of 619 °C for various times before casting. Pseudo-particles were connected in three dimensions and pseudo-cluster was actually a single primary particle. He suggests that the theories based on agglomeration and disagglomeration of particles during roasting be-examined in light of the experimental results.

To overcome the complications encountered with the direct mechanical stirring International Telephone and Telegraph(ITT) in the USA developed the Magneto hydro dynamic(MHD) stirring process. In this process, the rotating electromagnetic fields generates the local shear and causig the dendrietes fragmentation within a continuous casting mould. The advangates of this process include (a) gas entrapment in the slurry is minimized, (b) elimination of centerline segregation, (c) reducing contamination to a minimum, (d) converting columnar structure to equiaxed etc. [Kun, 1984]. The stirring is deep within liquid which has already been filtered and degassed; therefore contamination is almost eliminated. Desired solidified microstructure of nearly about 30µm grain size can be achieved by MHD process and it was the first commercial route for the production of nondendriticthixo billet for decades. The disadvantages of this process includes (a) high production costs, (b) non uniform and non spherical microstructure in the cross section of the cast billet which further increases the production cost when the billet is subjected to thixoforming[Fan, 2002]. Electromagnetic stirring can be achieved by three modes: vertical flow, horizontal flow and helical flow which is a combination of the vertical and horizontal modes as shown in the fig. 1.4. In the horizontal flow mechanical shearing is the main mechanism for dendrite fragmentation because solid particles moves in quasi-isothermal plane. In case of vertical flow mode, thermal processing is dominant than the mechanical shearing because dendrites will be recirculated to the hotter zone of the stirring chamber and partially remelted.

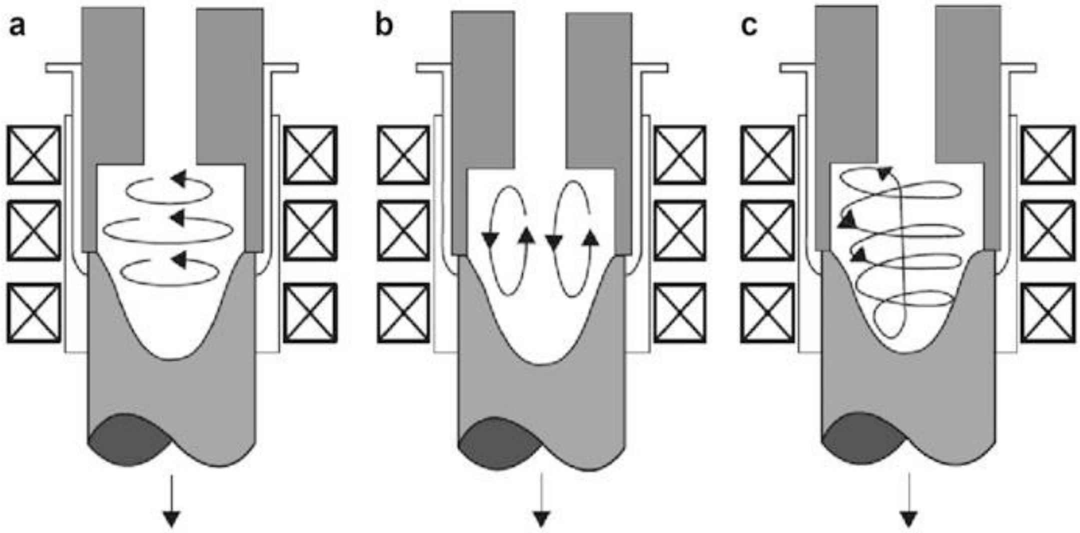


Figure 1.4: Schematic of electromagnetic coils for MHD stirring and solid particle flow pattern in the mushy zone (a) due to rotational inductive coils, (b) due to linear inductive coils, and (c) helicoidal stirring (reproduced from [Niedermaier et al, 1998])

New Rheocasting process (NRC) is one of the slurry-on-demand process was developed by UBE industries Ltd. [Adachi et al. 1996] as shown in Fig. 1.5.

This process involves following steps

1. Preparation of the slightly overheated metal by conventional process
2. Transferring of the metal into a thermally insulated vessel directly (or) with the help the jig(cooling slope method). The amount of superheat and adding the grain refiner depends on the application of the jig. A globular microstructure is achieved by controlled cooling in the semisolid region in the absence of stirring. The alloy is held within the vessel for getting a specific fraction of solid suitable for the subsequent forming process. Finally, in a permanent mold the as-cast SSM billet is pressure formed.

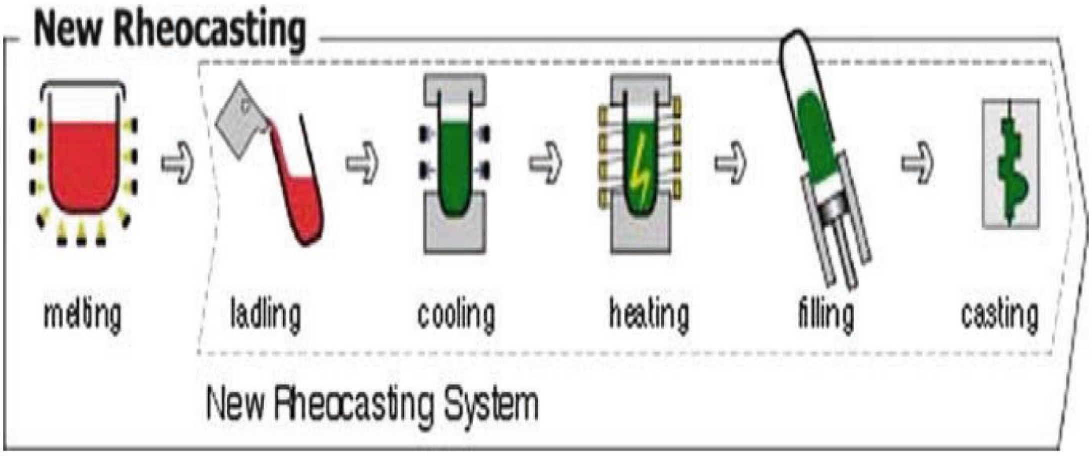


Figure 1.5: Schematic of the new rheo-casting process (NRC) NRC: pouring – controlled cooling –sleeve filling – forming [Kaufmann et al. 2000]

1.2.2The cooling slope process (CSP)

The cooling slope method is one of the populr practice for producing feed stock material for the thixoforming because it eliminates a major elements of the costs in the thixo formed product [Haga and Kapranos, 2002] shown in the fig. 1.6.

The cooling slope process can be divided into three sections.

1. Melting and pouring section:- pouring the melt through a cooling slope with the

required superheat with subsequent solidification in a metal mould.

2. Nucleation section:- While the metal is flowing through the cooling slope plate generates crystal nuclei in the melt.

3. Crystal generating section: The metal obtained from the nucleation is cooled in the metal mould.

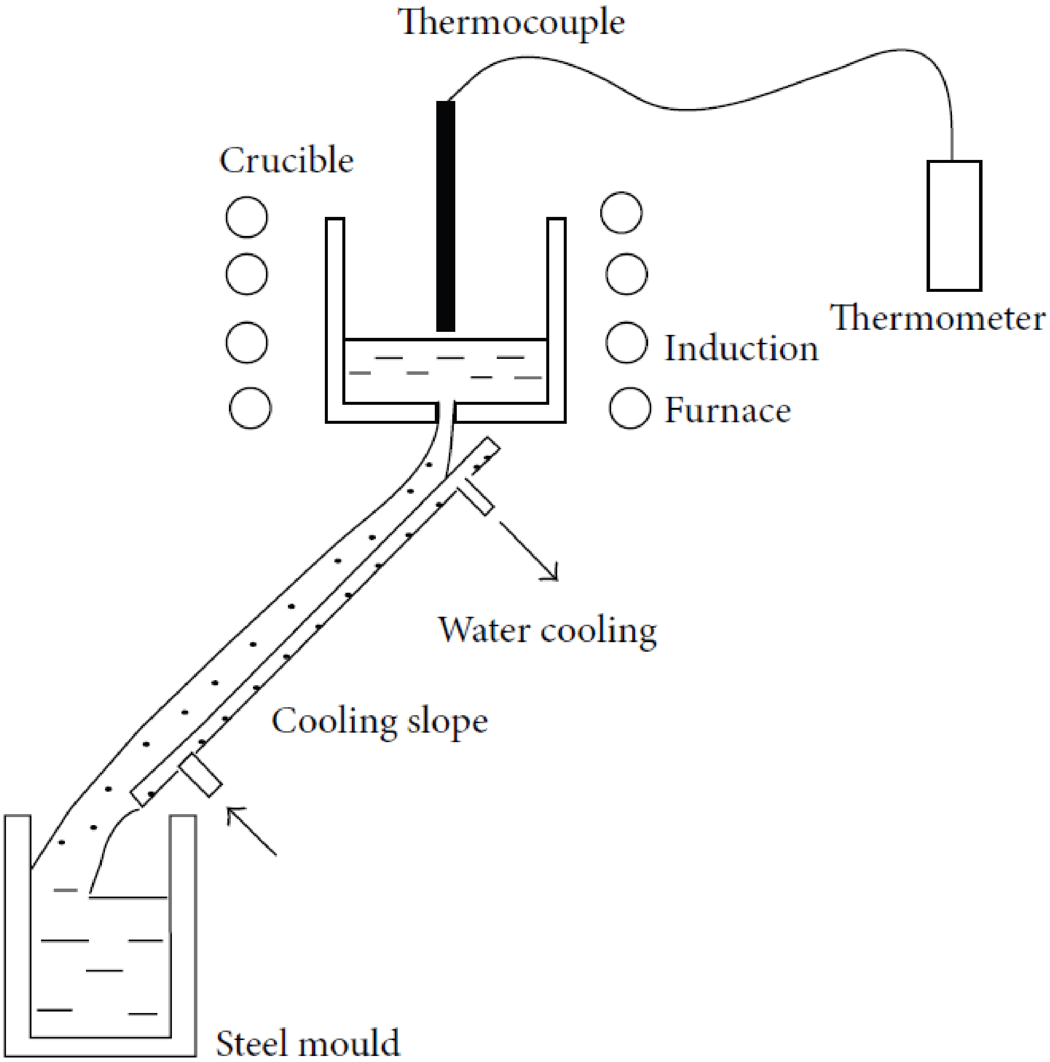


Figure 1.6: Schematic of the Cooling slope process.[Liu et al. 2003]

The refinement of the solid particles within the slurry can be achieved by passing the molten metal through the water/air cooled tube [Uetaniet al. 2006; Grimmiget al. 2006 ; Guo, Yang, 2006] or by cooling slope attached with vibrator[Saffari et al. 2015]. The process variables are (a) length and angle of the cooling slope (b) cooling slope material (c) super heat of the molten metal. Oxide film formation and gas pickup problems should be taken care during commercialization process.

1.2.3Semi-Solid Rheocasting(SSR™ Casting)

Semi-Solid Rheocasting(SSR™ Casting) process was developed at the Massachusetts Institute of Technology(MIT) and proved as the best process to produce fine Semi-solid microstructures with no entrapped liquid. The process consists of following steps shown in the fig. 1.7.

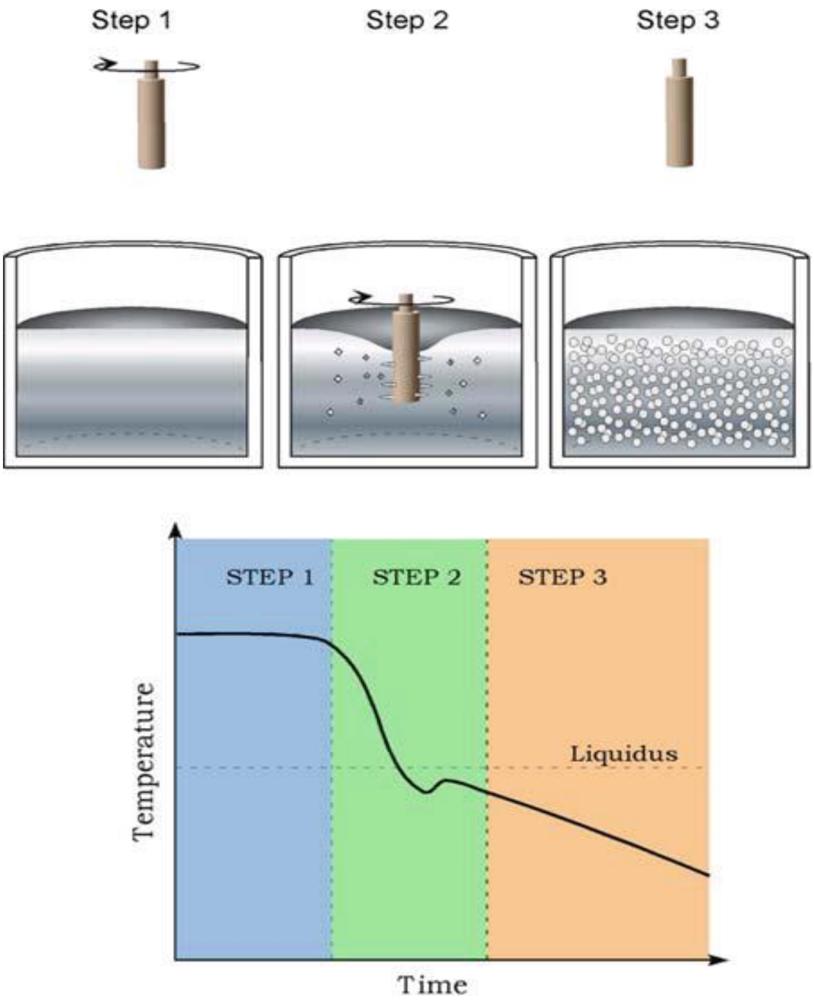


Figure 1.7: Schematic of the SSR process. Molten alloy is held above the liquidus (Step 1), then rapidly cooled and agitated for a controlled duration to a temperature below the liquidus (Step 2) before agitation and cooling ceases (Step 3). [Yurko et al. 2004]

(a) Robot brings the molten metal from the holding furnace contains liquid metal above itsliquidustemperature with the help of coated ceramic crucible to the SSR station.

(b) A rotating graphite rod is inserted into the liquid metal to cool the melt rapidly for a short time(5-20 seconds). During the stirring , small solid fraction(about 5%) is formed.

(c) The graphite rod is removed so that semi-solid metal is cooled without stirring to form a solid fraction of about 15-20%. The particles generated in stage 2 grow and change to globular form solid particles distributed in the liquid.

(d) The semi-solid alloy is poured into the shot chamber of the die casting machine once the pre deformed solid fraction is achieved and where it is injected into the die.

1.2.4Stain Induced Melt Activation (SIMA) Process

This process, originally developed by young [younget al. 1983]. This process involves following steps: (a) Hot working followed by cold deformation to induce residual plastic strain in the billet. (b) reheating the cold worked billet to a semi-solid temperature to produce the globular structure. (c) Thixoforming the billet in its solid state shown in the figure 1.8. Plastic deformation induces high angle grain boundaries and recrystallisation when the billet is reheated to semi-solid temperature these will be wetted by the liquid metal and resulting in a fine and globular microstructure.

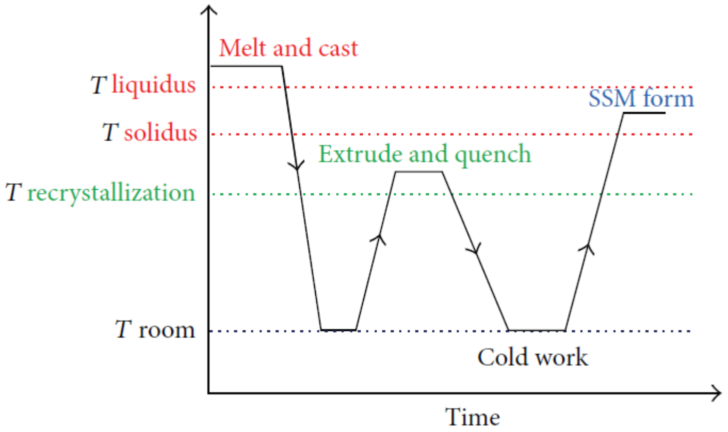


Figure 1.8: Schematic illustration of the stages of the SIMA process[young et al. 1982].

Kirkwookd and co-workers [Boyedet al. 1988; KirkwoodandKapranos, 1989] introduced warm working at below the recrystallisation temperature instead of cold working for achieving the maximum strain hardening. The process parameters are (a) amount of plastic deformation (b) semi-solid reheating temperature (c) soaking time during semi-solid region. By optimizing the process parameters one can achieve uniform distribution of fine, globular primary solid particles in the matrix. The smaller size and fine globular particles can be achieved with greater amount of cold working [Loue, Sue´ry, 1995].The primary particle size can be achieved as small as 30 µm and this process is a potential competitor to the MHD process [Kirkwoodet al. 1992]

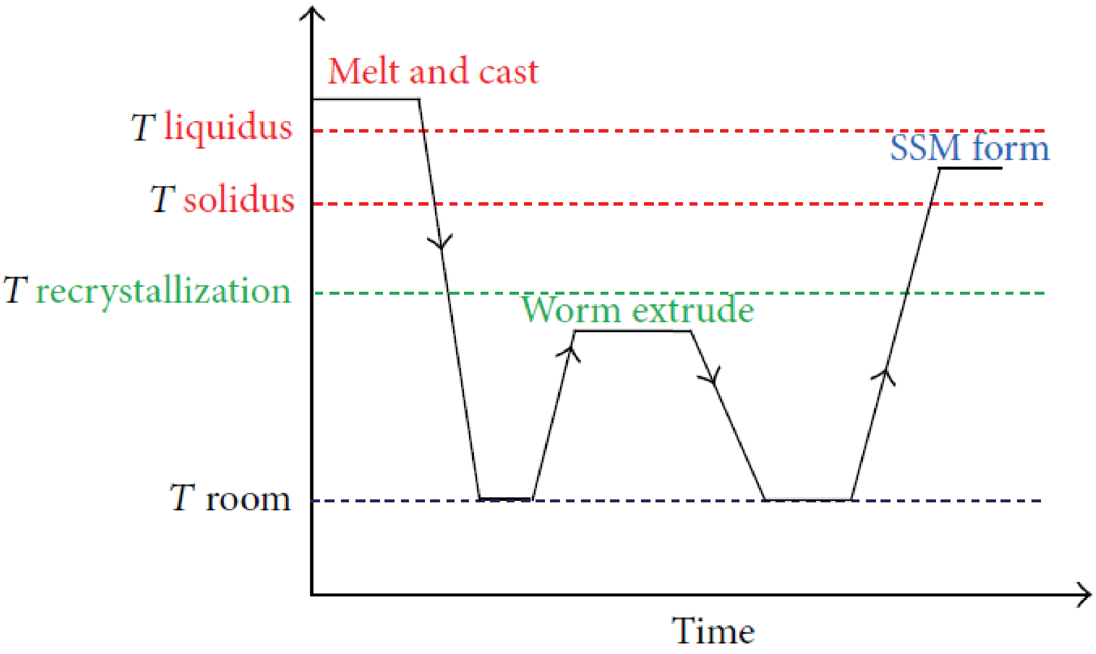


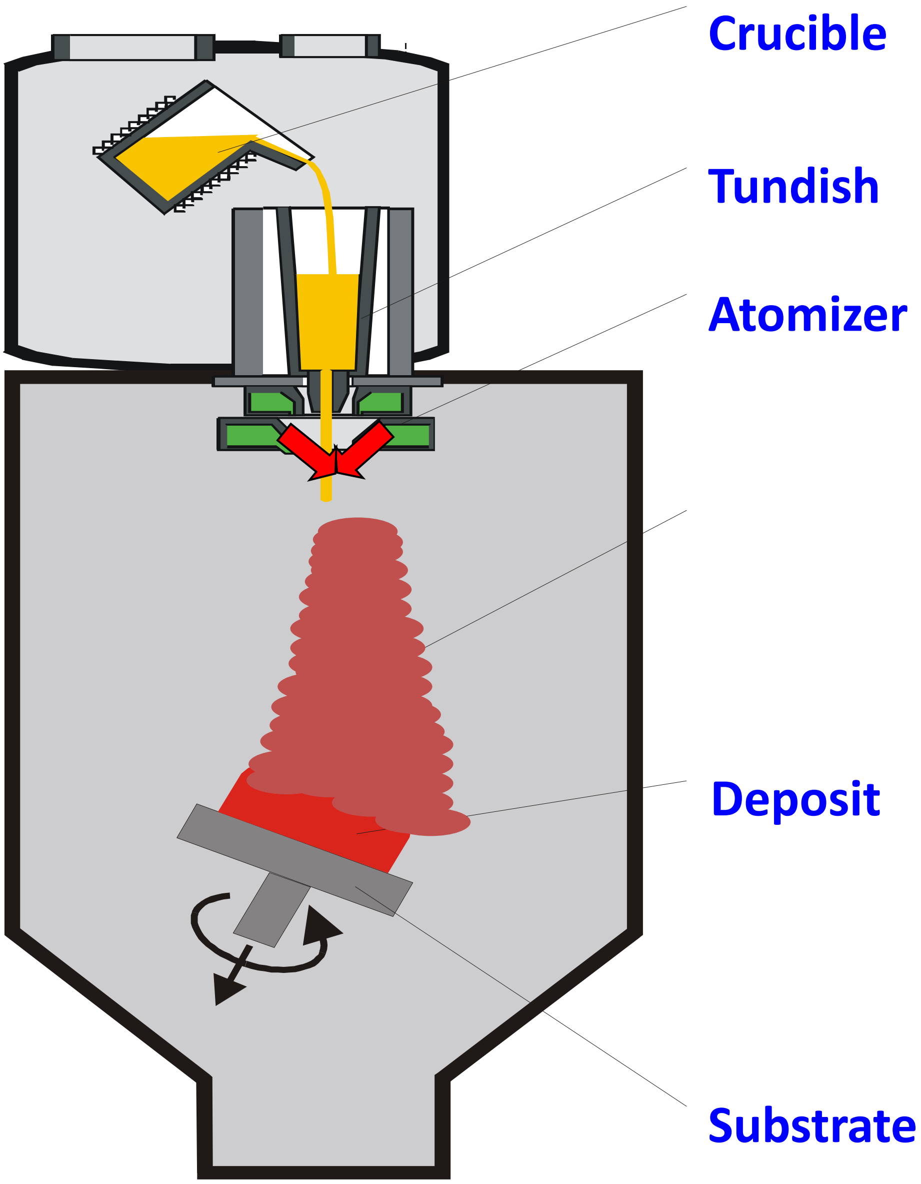
Figure 1.9: Process stages of the RAP method.[Kirkwood et al. 1992]

. Recrystallization and partial melting (RAP)process is similar to SIMA process, but the prior deformation occurs below the recystallization temperature called cold working shown in the figure 1.9. The fine and non dendritic microstructure obtained by the fragmentation due to the high energy liquid metal flow through high-angle grain boundaries. Kirkwood and co-worker has replaced the cold working deformation step with warm working to get maximum strain hardening [Kirkwood andKapranos, 1989].

The main processing parameters which affect the microstructure in the semi-solid state are (a) heating time (b) reheating temperature and (c) amount of plastic deformation [Kirkwood ,Sellars, 1992]

1.2.5Spray Casting (Osprey Process)

Spray casting (Osprey process) is a non agitation process which produces feedstock for thixo forming, especially for high temperature alloys (steels and super alloys), schematic diagram is shown in the fig. 1.10. In this process the molten metal is directed through a nozzle which results in atomization of the liquid stream into different micrometer sized droplets which experiences the cooling rate in the order of $10^3 Ks^{-1}$. The small size droplets solidify during the atomization, large droplets remain fully liquid and intermediate size becomes semi-solid.The droplets are interacted with substrate and solidified to form a shaped casting. The second stage droplets impinge, consolidate and solidify on the substrate for getting homogenous structure. Semi-solid with high solid fraction will fragment and liquid and semi-solid droplets of high liquid fraction splat on impact. A portion of the solid grains will remelt and resolidifies slowly. The resultant microstructure consists very fine equiaxed grains[Abramovet al. 1998]. A number of variants of spray casting process are available to produce near-net shape product . The centrifugal spray casting has created considerable interest due to its abiity to cast into a ring shape perform of different diameters. The shape control of the perform coupled with characteristics rapidly solidified microstructure are considered to be a major benefits of the process. Billet, ring and plate shapes can be manufactured by spray forming process as shown in fig. 1.10.


Crucible
Tundish
Atomizer
Deposit
Substrate

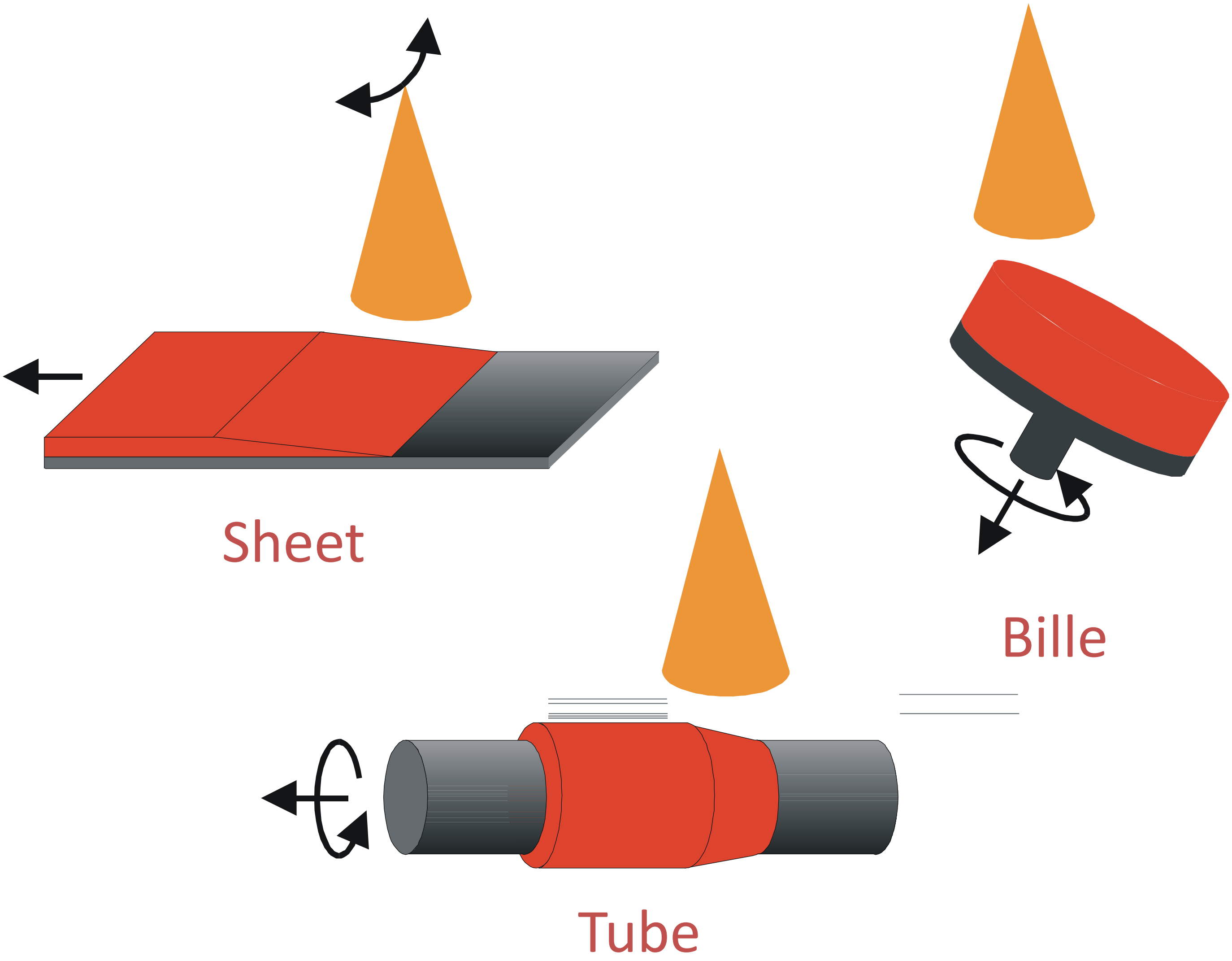


Figure 1.10: Schematic illustration of the experimental setup of spray forming.

1.2.6 Thixocasting

Thixoforming is a near net shape forming process from a semi-solid nondendritic alloy slug within a metal die. If the component shaping is performed in a closed die, it is called thixocasting while if the component shape is performed in an open die, it is referred as thixoforging. [Atkinson, 2005 and Ogris, 2002]. This process conists two stages, namely reheating and forming. In reheating stage fine-grained equiaxed microstructure solid billet is partially remelted to a semi-solid state by induction heating. In forming stage the billet is injected into the die of the cold chamber high pressure die casting mahine as shown in the figure 1.11. Most of the alloys currently used are not optimised for semi-solid processing. A small change in the temperature may cause large difference in solid fraction of the alloy. So uniform heating heating of the slug is very important. The billets manufacted by MHD process are not fully homogenised with repect to both chemical compostion and structure. Gates and risers cannot be recycled[Poddar, 2008].

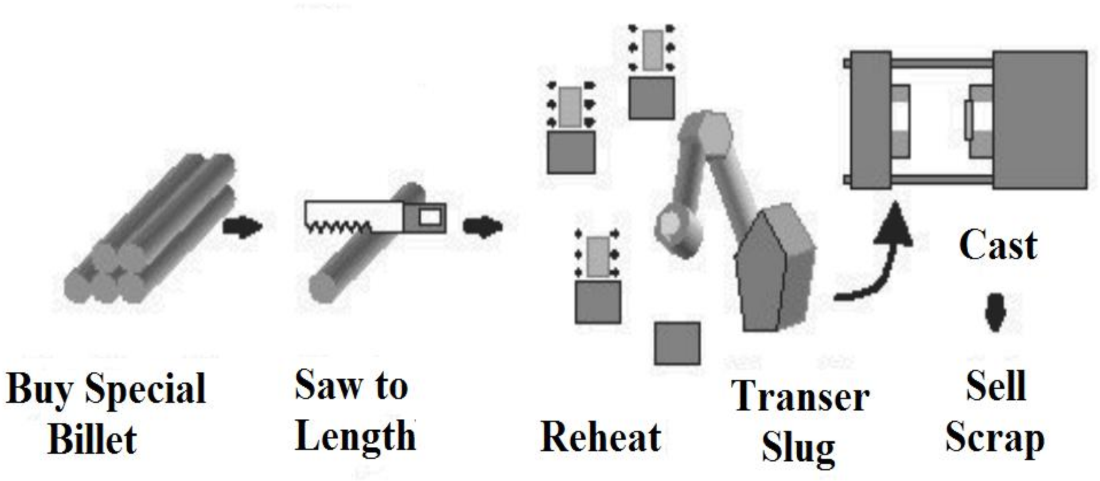


Figure 1.11: Schematic diagram of Thixocasting process

1.2.7Thixomolding

Thixomoulding offers an alternative to conventional magnesium die casting and produces many internal, external communication, laptop computer covers, handheld power tool components. The magnesium alloy chips(around 2to 5mm) are fed into a heated barrel of an injection moulding system where they are partially melted and changed into semi-solid slurry(f_s 0.05 -0.3 max) rotting and translational movements. Finally the slurry is injected into a mould cavity.

MHD has got its popularity to produce large quantities of consistently good repeatable quality globular microstructures suitable for commericial industrial application as compared to other techniques but scrap is not recyclable in situ. Mechanical stirring and cooling slope are simple techniques, but oxidation and gas porosity has to be taken care in the commercial applications. Spray casting produces high value quality products for critical application, but most expensive. SSR is the combination of stirring and near liquidus casting. Low cost, fully recyclable and gives better properties than conventional casting routes but cannot achieve the properties obtained in the MHD route. UBE New Rheocasting process can recycle the nondendritic scrap material insitu but its commercialization is costly. The Cooling slope method is simple but defects and inclusion problems made this process unsuitable for critical applications.

1.3 Microstructures of Semi-solid processed Alloys

1.3.1 Dendrite Fragmentation Mechanism

The microstructure evolution during semi-solid processing has been investigated by earlier investigators [Doherty et al. 1984, Vogel and Cantor, 1979, Flemings, 1974 and Hellawell, 1996]. It has been reported that the dendrite necking detachment and spherodization depend on the temperature of processing and stresses employed. These are presented in section that follows:

Several mechanisms have been proposed to explain the conversion mechanisms from dendritic to globular morphology by several researchers. These include

(a) Dendrite arm fragmentation[Doherty et al. 1984, Vogel and Cantor, 1979]

(b) dendrite arm root remelting[Flemings, 1974, Hellawell, 1996]

(c)Growth control mechanisms.

Dendrites arms have plasticity so that they bend plastically under shearing force generated by melt stirring. This plastic bending introduces large mis orientations inside the dendrite arms to form geometrically necessary dislocations. Such dislocations rearrange themselves and form grain boundaries. Any grain boundary with misorientation ,greater than 20° contains an energy that is twice the solid/liquid interfacial energy which leads to wetting the grain boundaries cause the wetting of the grain boundaries with liquid metal. Finally resulting the separation of dendrite arms[Vogel et al. 1979, Doherty, 1984]. Hellawell [Hellawell, 1996] suggested that secondary dendrite arms detaches at their roots because of remelting rather than breaking off[Flemings, 1974 and Figueredo, 2001] due to the solute enrichment and thermosolutalconvecton which is produced by solidification. This yields, grain multiplication[Flemings et al. 2004].

1.3.2 Micro/Macro structural Analysis

Uniform distribution of fine and spherical solid particles in the liquid matrix is the ideal microstructure for semisolid metal slurry. The solid fraction is very important because it changes the slurry viscosity. If the solid fraction is high, it may create in die filling and if the solid fraction causes insufficient viscosity and turbulence in turn create die filling problems. The mechanical properties of castings can be improved by a better understanding of rheological behavior.

The solidification characteristics of metal and alloys can be found by the DSC(Differential Scanning Calorimetry) and cooling curve analysis (CCA). DSC technique is more accurate than the cooling curve analysis of metal and alloys.

While solidification we can see dendritic solidification near the mould wall. Dendritic structure grown in some portions or in all portions depends on the process parameters and solidification conditions.

The Semi-solid microstructure primary particle is supposed to be single globule probably interconnected to other globules called pseudo-globule and can be seen in the optical micrograph. This can be observed in the rheocasting through mechanical or electromagnetic stirring. Dendrites breaks by mechanical fragmentation [Flemings, 1974] or by dendrite root melting mechanisms[Apaydinet al. 1980] cramped dendrites are formed branches plastically bend instead of disintegration.

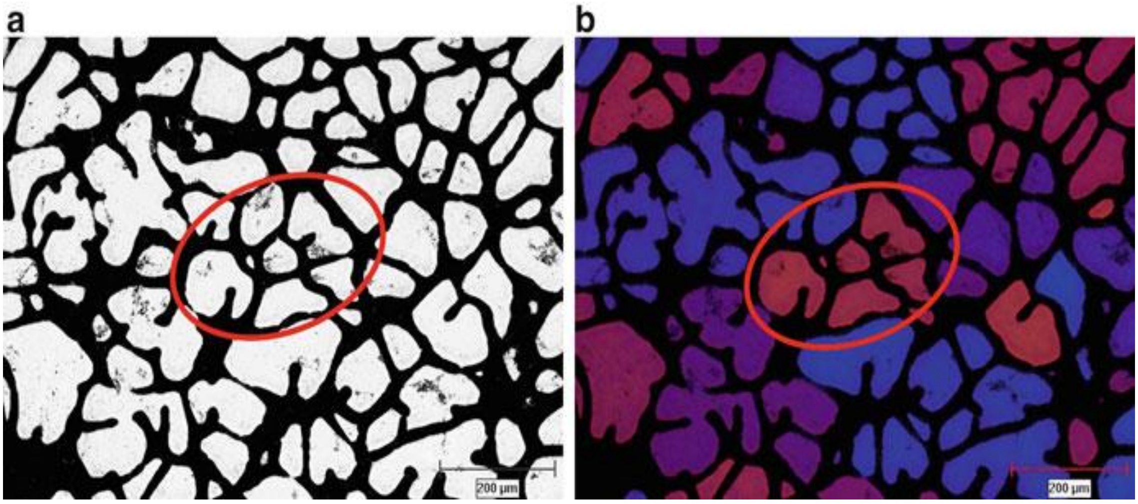


Figure 1.12: Formation of cramped dendrite: (a) bright field illumination, (b) polarized light, A356 alloy quenched at 598 °C.

Sometimes due to insufficient applied shear force branches cannot disintegrate and bend which in turn for the cramped dendirtes. Cramped dendrite may be the origin for pseudo-gloubles which can be seen in the fig. 1.12. These particles have the same colour and contrast so we can conclude that these are not formed by the agglomeration of spherical particles.

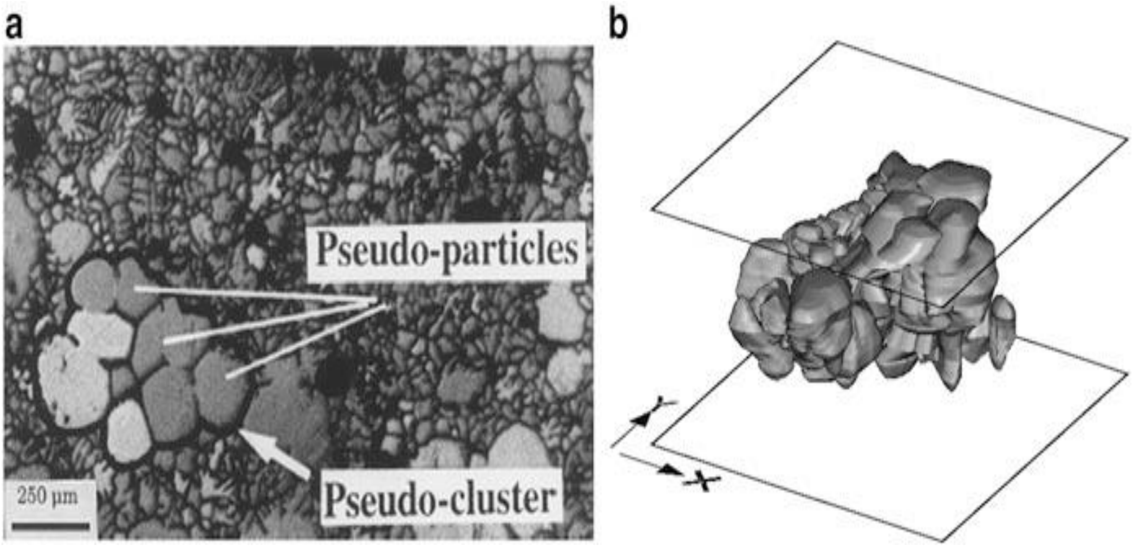


Figure 1.13: Definition of pseudo-particles and pseudo-clusters, (b) CAD generated view of a 3D rendered pseudo-cluster.[Niroumand and Xia, 2000]

Niroumand et al. studied that Al-10.25% Cu alloy produced by mechanical stirring and his serial sectioning polished surface showed that microstructure of slurry contains pseudo-particles/clusters [Niroumand and Xia, 2000]. Process of agglomeration of small globule particles was identified as single primary grains by many researchers but the majority of these particles were interconnected form underneath (3D) three dimensionally pseudo-cluster and resulting 3D model of the sample shows the complex structure can be seen in Figure 1.13.X-ray microtomography was carried out for Al-15.8%Cu alloy sample which was held at 555°C for 80 min and proposed two coarsening mechanisms.

First mechanism: - small globule was progressively dissolved, which can be seen in the Figure 1.14(a) like Ostwald ripening mechanism but neighbors coarsening was not large enough so cannot seen by the naked eye.

Second Mechanism:- The figure 1.14(b) shows that the globules are in equal sizes. While necking between particle 1 and 2 is increasing, but necking between particle 2 and

3 remain stable. The particle radii decrease slowly as neck diameter between particles increased and finally formed into a single particle[Limodinet al. 2009].

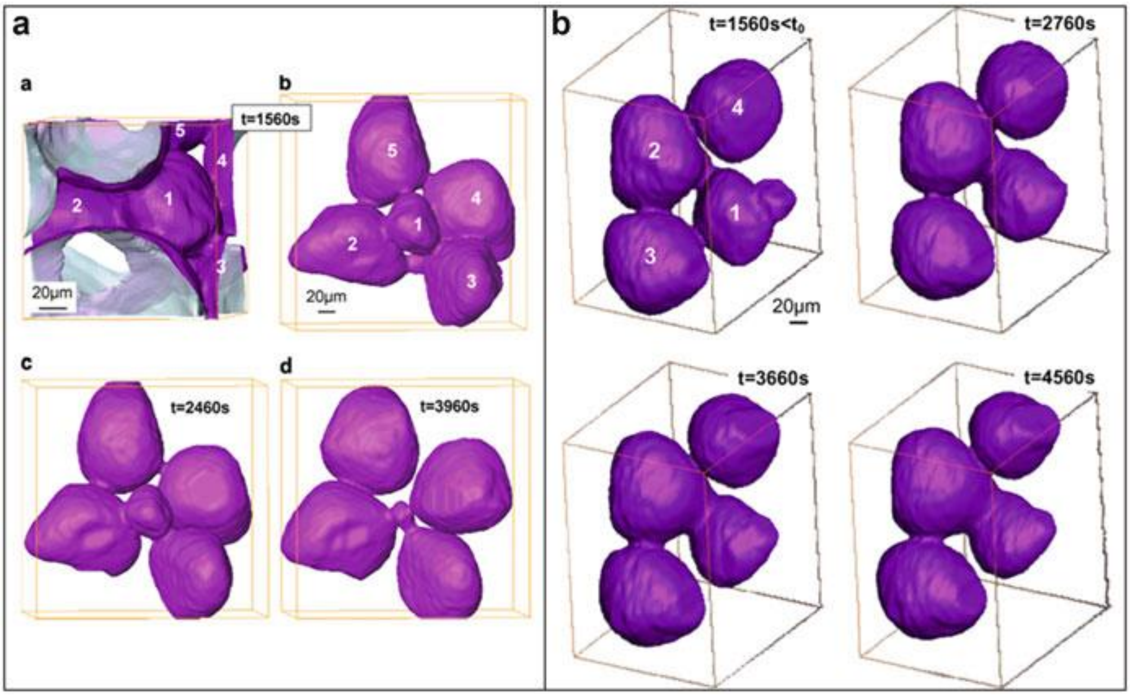


Figure 1.14:X-ray microtomography of Al–15.8%Cu held at 555°C for 80 min, (a) globules with various sizes, visible dissolution of globule 1 over time, (b) globule with equal size, coalescence toward formation of a single particle [Limodinet al. 2009]

1.4 Wear chatacteristics of Semi-Solid Processed Alloys

The wear of a material has been reported to occur depending on its microstructural features. The grain size and precipitate distribution in wrought alloys and dendrite arm spacing and degree of macrosegregation in cast alloys typically influence the wear rate. Different wear behavior are brought out in the following section.

1.4.1 Adhesive Wear

Adhesive Wear is wear which occurs due to the relative motion, sliding motion between the mating surfaces under the influence of load. Machined surface looks exactly flat but it contains hard asperities when observed on a microscopic scale. When two surfaces are brought close proximity only at a few points the surface may touch and adhere strongly to each other due to which asperity junctions will be formed.The elastic and plastic deformation of the softer material among the two materials in contact occurs . The reason for this deformation isdue to high pressure exerted on very small contact area.The tangential force, shear this softer junction when the strength of the junction exceeds more than the shearstrength of the material. The spetsleading to Adhesive Wear is shown in figure 1.15

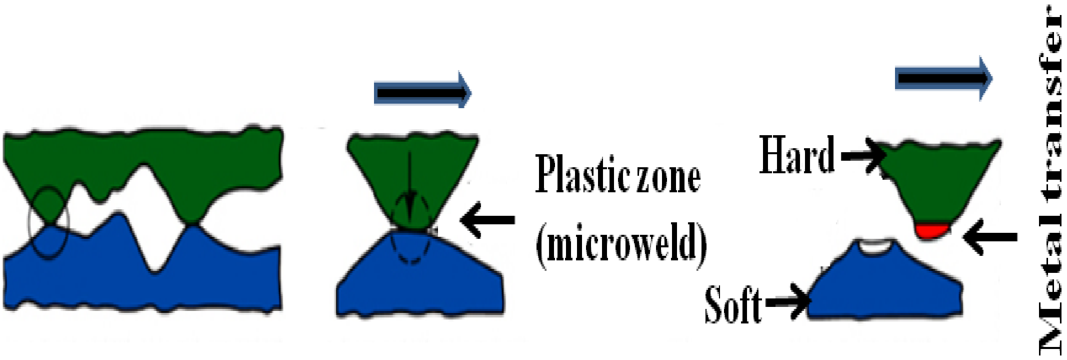


Figure 1.15:Steps leading to Adhesive Wear[Stokes, 2005]

The adhesive wear depends upon physical and chemical factors such as material properties, chemical atmosphere , applied load , sliding velocity etc.The reasons for the adhesive wear are contact asperities deformation, development of adhesive junctions , removal of protective oxide surface films etc.Cold welding, scoring, seizing may; cause due to adhesive wear. Adhesive wear can be minimized by applying lubrication, selecting the harder materials and application of lower load.As adhesive wear occurs due to the shearing of friction junction these can be classified into two.Mild wear occurs wen shearing occurs in the interface itself and severe wear occurs a little distance within the softer metal

1.4.2 Abrasive Wear

Abrasive Wear occurs when a harder material is rubbing against a softer material leaves hard particles called debris between the two surfaces. Based on the severity of wear it can be called scratching, gouging orscoring. In Abrasive Wear initially the material isdisplaced and form ridges along the grooves called ploughing. Further the separated material derisor small chips called cutting. Due to this cuttingaction if the material is removed from the face it results in a localized fracture in the material called fragmentation.

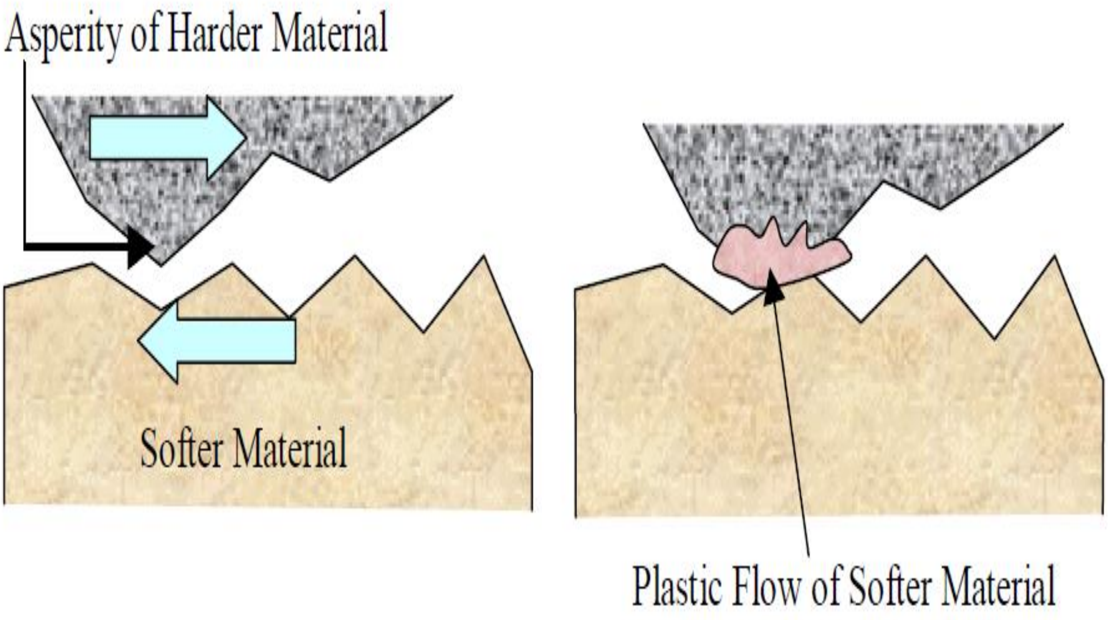


Figure 1.16: Abrasion in the microscale. [Stokes,2005]

Abrasive wear can be divided into two types. Two body abrasion and three body abrasion.Two body abrasion occurs when one surface is harder than the other rubbing surface. The harder material asperities penetrates into the softer material causes plastic deformation under the application of normal load. Here the material removes by the action of both micro-ploughing and micro-cutting.Examples: grinding, cutting and machining.

In three body abrasionhard loose particles roll between two softer surfaces and removes material form one or both the surfaces. For example, oxide forms on the surface of the material forms wear debris causes further damage by abrasion. The abrasion in the microscale and schematic wear phenomenon are shown in figure 1.16 & 1.17 respectively.

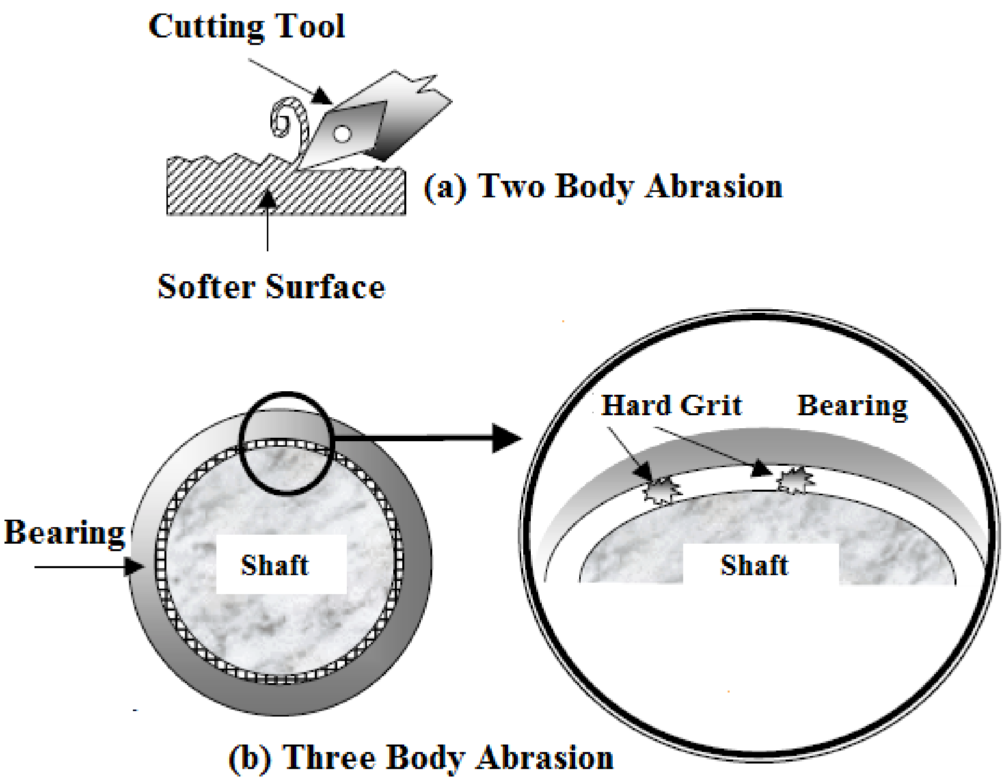


Figure 1.17: Schematic of abrasive Wear Phenomena. [Stokes,2005]

1.4.3 Corrosive Wear

When metal surfaces are not sliding under the corrosive atmosphere, oxide film forms and protects from further corrosion. But if they are subjected to sliding then oxide film breaks and corrosion proceeds. Corrosive wear is caused due to the combined effect of chemical and mechanical action. Corrosion wear also occurs if the design is not proper and moisture removal process is not properly done.However, Erosive weartype occurs in the industries impingement of solid or liquid particle cause removal of the material from the surface due to the repeated deformation and cutting action.

1.4.4 Surface Fatigue Wear

Removal of the particle from the surface due to cyclic loading surface Fatigue Wear. When two surfaces are sliding across each other micro-cracks generates below the surface because maximum shear stress at the subsurface and propagate to the surface finally causes failure of the component (Fig. 1.18).

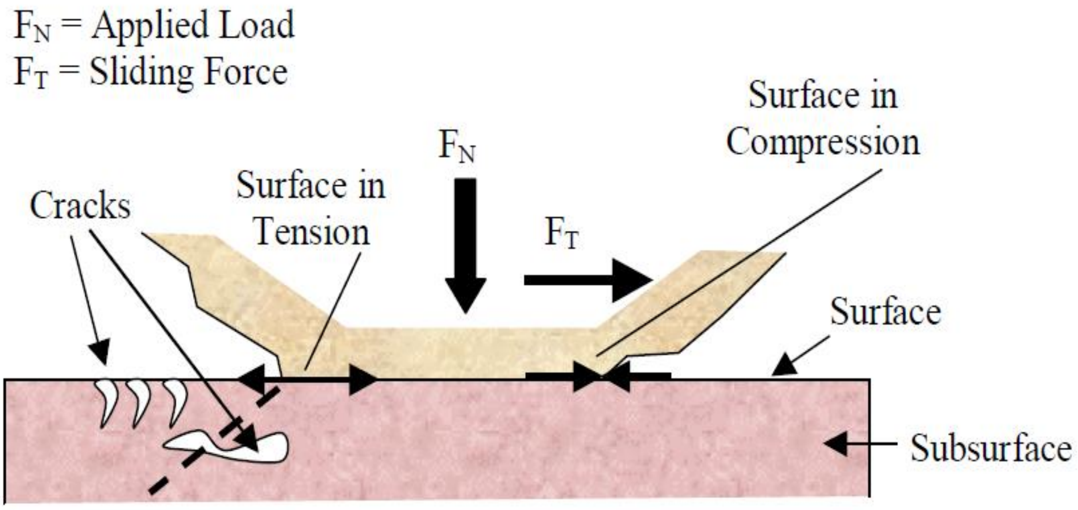


Figure 1.18: Schematic of fatigue wear, due to the formation of surface and subsurface cracks

1.4.5 Cavitation

Generally it occurs in fluid handling machines. Eg. Marine propellers, dams slipway and all other hydraulic turbines[Bhusan and Gutpa 1991]. When a solid and liquid are in relative motion the liquid become unstable and forms bubbles getting burst against the surface of the solid causes some failure known as cavitaion failure.