LITERATURE REVIEW

2.1 Introduction

The Cu-Ni-Sn spinodal alloys comprising 4-15 wt % Ni and 4-12 wt. % Sn was first developed by Bell Telephone Laboratory, USA in 1970’s to replace the Cu-Be alloys. Most of the Cu-Sn bronze alloys are not heat treatable except for Cu-Be alloys. Cu-Be alloys are strengthened by precipitation hardening mechanism to enhance the strength of the alloys but Cu-Ni-Sn alloys are strengthened by spinodal decomposition to display good mechanical and wear properties compared to that of Cu-Be alloys. Further, these alloys are comparatively less costly and hazardous free. Therefore, Cu-Ni-Sn spinodal alloys are substitute material for Cu-Be alloys in the manufacture of connectors, spring components etc. Studies has been carried out on Cu-Ni-Sn wrought spinodal alloys to evaluate the microstructure, hardness, wear behaviour, yield strength and the studies are discussed below.

2.2 previous studies on Cu-Ni-Sn wrought spinodal alloys

Schwartz and Plewes (1974) investigated the early stage of spinodal decomposition process in Cu-Ni-Sn wrought spinodal alloys to determine the mechanical strength. The objective of this work was to confirm the Cahn’s predictions of increase in the yield strength of Cu-9Ni-6Sn wrought spinodal alloy due to the spinodal decomposition. The Cu-9Ni-6Sn wrought spinodal alloy was prepared by using the induction melting process under inert atmosphere. Further, the alloy was cold rolled, annealed and water quenched. The alloy was then aged at 300°C, 350°C and 400°C and were subjected to X-ray sidebands to determine the wavelength and relative amplitude of the composition fluctuation. Figure 2.1 shows the graph between wavelength (λ) and log time for the foils aged at 300,350 and 400°C. A significant increase in the YS of 80,000 psi (552 MPa) was observed during aging at 400°C. The results of the measurements for isothermal aging at various aging temperatures are shown in the Figure 2.2.
Figure 2.1: Wavelength versus log time for foils aged at different temperature

(Schwartz and Plewes, 1974)

Log Time (Min) (300°C)  Log Time (Min) (350°C)  Log Time (Min) (400°C)

Figure 2.2: YS at 300°C, 350°C and 400°C

(Schwartz and Plewes, 1974)
Schwartz et al. (1974) studied the decomposition behaviour of chill cast Cu-Ni-Sn spinodal alloy using X-ray diffraction and Transmission Electron Microscopy (TEM). The Cu-9Ni-6Sn alloys were made by induction melting under inert atmosphere. Further, the alloys were homogenised at 825°C and subsequently cold worked, annealed and water quenched. The alloys were subjected for aging at 350°C. A presence of side bands on X-ray and electron diffraction patterns and modulated microstructures is observed from Figure 2.3. It is evident from the Figure 2.3 that the supersaturated solid solution decomposes spinodally. The modulated microstructure is observed until 80 hours of aging. It is observed from the Figure 2.4 that further aging of the alloy till 160 hours results in discontinuous precipitate. The YS of the alloy increased upon aging by 75,000 psi (517MPa). A drop in Fracture ductility was observed after 43 minutes aged at 350°C

Figure 2.3: Spinodal microstructures (a) 5 min (b) 40 min (c) 5 hr
(Schwartz et al. 1974)

Figure 2.4: Grain boundary precipitates (a) 80 hr (b) 120 hr (c) 160 hr. aged at 350°C
(Schwartz et al. 1974)
Baburaj et al. (1979) studied the early stages of spinodal decomposition process in Cu-9Ni-6Sn wrought spinodal alloy. Pure Cu, Ni and Sn was melted using an induction furnace to prepare the alloy. The cast alloy was homogenised at 1073 k (800°C) for 50 hours in hydrogen atmosphere. The alloys were then cold rolled and were solutionised at 1098 K (825°C) for 15 minutes and were water quenched. The alloys were subjected for aging at 673 K (400°C) for different periods of time. During aging process, the solid solution decomposes spinodally followed by ordering reaction to produce a meta-stable phase with the DO$_{22}$ structure. Discontinuous reaction originates at the grain boundaries on prolonged aging, which consumes the matrix leaving behind colonies of a pearlite product composed of the equilibrium α and the γ (DO$_{3}$ structure) phases.

Kato and Schwartz (1979) measured the YS value of Cu-10Ni-6Sn wrought spinodal alloy at various temperatures. The specimens were cut from the alloy, solution treated at 1073 K (800°C) under inert argon atmosphere and were water quenched. Specimens were heat treated at 623 K (350°C) for 20 minutes to induce spinodal decomposition. The YS value was found to be high for aged alloy when compared to as-quenched alloy.

Dtichek and Schwartz (1980) characterised the spinodal decomposition of Cu-10Ni-6Sn wrought spinodal alloy using X-ray diffraction. Using a Jacobian Elliptic function an intensity analysis was performed that varies from a sine wave during the stages of spinodal decomposition towards a square wave for later stages. Tsakalakos and Hilliard formulated a non-linear theory of spinodal decomposition. The theory states that the composition fluctuations were found to increase in amplitude followed by a coarsening regime of near constant amplitude and increasing wavelength. An ordering reaction was found to occur confirming the super lattice reflections observed in selected area electron diffraction index as a DO$_{22}$ structure during the spinodal decomposition process.
Kato et al. (1980) investigated the hardening mechanism by spinodal decomposition in wrought Cu-Ni-Sn spinodal alloys. The author observed an increase in the yield stress of spinodal modulated structure. The dislocation force balance equation was considered for determining the YS of the alloys. The macroscopic yielding is due to the mixed dislocation lying in the positive regions of the internal stress. The YS calculated was found to be proportional to the amplitude of the composition modulation and independent of the wavelength. The calculation of YS in this investigation was found to be in agreement with that of the experimental data extracted from the previous literature.

Quin and Schwartz (1980) investigated the strengthening mechanism by spinodal decomposition on the fatigue behaviour of Cu-10Ni-6Sn wrought spinodal alloy. A YS of 185 MPa was observed for the homogeneous alloy and a YS of 780 MPa was observed for the aged alloy which confirms the spinodal decomposition. The spinodal alloy was found to be harden cyclically for the first few percent of fatigue life and the alloy was found to be soften till failure. Due to the localized demodulation of the composition waves by dislocation motion, the as-quenched alloy was found to be hardened throughout the fatigue life. Figure 2.5 and Figure 2.6 shows the change in stress with the number of cycles during the low cycle fatigue at 0.5% strain and 1% strain.

![Stress vs. Number of Cycles](image)

Figure 2.5: Stress at the 0.5% total strain limit as a function of the number of cycles (Quin and Schwartz 1980)
Theodore J. Lou (1981) investigated the tensile properties like UTS and ductility of Cu-Ni-Sn spinodal alloy processed by cold working and aging. The author found that the alloy possessed superior tensile properties compared to the as-cast and homogenised alloy. The superior properties possessed by the wrought spinodal alloy is due to the spinodal reaction that is taking place as aging is carried out. It is reported by the author that during heat treatment an alpha plus essentially non-lamellar gamma structure develops during the spinodal decomposition. YS was found for the spinodal alloy by the 0.01% offset with a value of 128 Kpsi and an elongation to fracture of 5% was observed for the alloy.

Schellet et al. (1982) carried an investigation on the wear and friction behaviour of Cu-Ni alloy blocks sliding against coated steel rings. The test was conducted at the temperature of 440°C and under argon atmosphere. The sliding speed of 50mm/s was used as the parameter for conducting the test. X-ray diffraction, scanning electron microscopy and energy-dispersive spectroscopy were used for characterising the worn surface and the debris particles. A transfer of ring material was observed since the debris particles were ferromagnetic. The wear rate of the Cu-Ni blocks were determined by the amount of ring material that is transferred. The wear rate of the Cu-Ni blocks were determined by the increasing amount of ring material that is transferred. Further, it was observed that the wear rate of the ring increases as the transfer continues.
**Kratochvil et al. (1984)** studied the property variation of Cu-9Ni-2Sn and Cu-9Ni-5Sn wrought spinodal alloys. The alloys were prepared from pure Cu, Ni and Sn. The alloys were then homogenised at 1073 K (800°C) for 2 hours in argon atmosphere before water quenching. Further, the cold rolled specimens were quenched in water and were aged for 573 K (300°C) and 673 K (400°C) respectively subsequently. Due to the formation of precipitates during the incubation period the yield strength of Cu-9Ni-2Sn alloys was found to increase. The TEM and EDS was used to study the microstructure of the spinodal alloys. It is reported by the authors that the spinodal decomposition takes place during quenching followed by nucleation of the coherent \((\text{Cu}_{x}\text{Ni}_{1-x})_{3}\text{Sn}\) particles. The change of the structure in the sample describes the yield strength of the alloy.

**Sato et al. (1988)** in their investigation studied the effect of an external stresses on spinodal decomposition of wrought spinodal alloy. The spinodal alloy Cu-10Ni-6Sn, single crystal was processed by means of Bridgeman method in an argon atmosphere. TEM revealed the change in morphology of the alloy by application of the unidirectional stresses in the early stages of stress aging as observed in Figure 2.7. There observed an insignificant change in the morphology of the alloy. At the later stages of the spinodal decomposition the preferential formation of DO\(_{22}\) precipitates are formed. The precipitates observed are of needle shaped with the longitudinal axis along the stress axis has been observed. Upon the appearance of asymmetry in the DO\(_{22}\) spots, directionality has become more notable on every super-lattice and fundamental spot as observed in the Figure 2.8. It can also be observed from Figure 2.8 that the unit cell of DO\(_{22}\) phase takes a tetragonal structure which consists of a double layer FCC.
Figure 2.7: Modulated microstructure stress aged at a) 71 MPa for 600 s b) 216 MPa for 3.6 x \(10^3\) s c) 216 MPa for 3.6 x \(10^4\) s. 
(Sato et al. 1988)

Figure 2.8: (a) Crystallography of a DO\(_{22}\) structure and (b) Schematic view of fundamental and super-lattice diffractions 
(Sato et al., 1988)
Erukhimovich and Prostomolotova (1997) have studied and proposed a new theory of approach to spinodal decomposition in the scalar field. The approach is regarding treating the process as relaxation of the one-time correlation function. The correlation function plays the role of an independent dynamical object which is a unique two point order parameter. The one loop approximation which is actually a zero loop approximation in the proposed approach was sufficient for solving the dynamical equation for the Langevin equation in the correlation function space. This type of approach makes it easy to trace the asymptotic behaviour at long time from the moment of onset of the spinodal decomposition. The values obtained from this study was found to be satisfactory with the studies conducted by various other authors through numerical simulation and corresponding stochastic equations which describes the relaxation of the local order parameters.

Virtanen and Tiainen (1997) studied the effect of nickel content on the age hardening behaviour of Cu-15Ni-8Sn wrought alloys. Alloys used for the investigation were Cu-Ni (2 to 4 wt- %) 7 Sn. The alloys were vacuum cast and cold deformed. Vacuum cast specimens were homogenised and then cold rolled. The cold rolled specimens were subjected to heat treatment at 310°C and 350°C respectively to induce spinodal decomposition. The properties of the alloys were tested by using conductivity measurements and analytical electron microscopy. Hardness values were measured for the spinodal alloy. It was observed that the values of Cu-9Ni-7Sn were found to be similar to that of well-known Cu-9Ni-6Sn spinodal alloy. It was observed that the temperature was found to be an influential factor for the low nickel content alloys. It was also reported that the electrical conductivity for the lower Ni-alloys were not significant compared with the other standard spinodal alloys.

Virtanen et al. (1998) studied the micrograph evolution of Cu-9Ni-6Sn and Cu-6Ni-7Sn. The structure was evaluated using the effect of recrystallization heat treatment. Vacuum and continuous casting techniques were used to prepare the alloys. The continuous cast wires were solution treated in as-cast state and in cold deformed state. Prior to solution heat treatment the vacuum cast alloy were hot rolled and cold deformed. Recrystallization was carried for the cold deformed wire material at 850°C which is close to the solidus temperature of the alloy. The non-cold deformed material was heat treated at a temperature of 850°C for 1 hour. Slow cooling of the alloys resulted in faceted grain boundaries. It was also reported that the (CuNi)3Sn was found as the planar precipitate.
Zhao and Notis (1998) studied the transformation kinetics and micrographs of Cu-15Ni-8Sn alloy. The alloy was prepared by the Amtek Corporation (USA) by powder metallurgy process. The alloys were procured to avoid the severe solute (Sn and Ni) segregation problem during the solidification of the alloy. The authors had formulated a Cu-Ni-Sn ternary diagram based on the data’s available in the literature as shown in Figure 2.9. The alloy was solution treated at 840°C for 3 minutes and was water quenched. Further, the alloy was annealed at different temperature and time and was quenched again in water. The five observation that were reported on the basis of the investigation is a) LI\textsubscript{2} ordered structure b) Spinodal decomposition resulting in ordered structure c) DO\textsubscript{22} ordered structure d) grain boundary and intergranular precipitate γ (DO\textsubscript{3}) precipitate as shown in Figure 2.10 e) discontinuous precipitate as shown in Figure 2.11. It was reported from this study that, below 500°C the spinodal decomposition tends to occur. DO\textsubscript{22} ordered structure occur after spinodal decomposition and LI\textsubscript{2} structure was found to occur after DO\textsubscript{22} ordering. It was observed from the micrograph that the discontinuous precipitates was found to occur at the later stages of the spinodal decomposition. Thus, it is clear from the above observation that the spinodal decomposition tends to occur before the process of ordering. It also provides the information that regarding the existence of both DO\textsubscript{22} and LI\textsubscript{2} long range order (LRO) structures in the spinodal alloy.

![Figure 2.9: An isopleth at 15 wt% Ni for the Cu-Ni-Sn ternary phase diagram.](Zhao and Notis 1998)
Antonov and Popov (1999) carried an investigation and proposed a model for the kinetics of spinodal decomposition at high diffusion rates which is described by the hyperbolic equation. It has been reported the formation of new phases in the investigation. The formation of new phases are described by using the zero-radius non-linear potential.

Deyong et al. (1999) studied the mechanical properties and microstructure of conventionally processed and rapidly solidified Cu-Ni-Sn alloys. The alloys which are used for the investigation were Cu-10Ni x Sn where x varies from 6 wt-% to 12 wt-% and Cu-15Ni-8Sn. Induction furnace was used for melting the alloys. An inert argon atmosphere was used for melting the alloys. The cast ingots were then homogenised at 825°C for 50 hr under argon atmosphere in order to prevent oxidation. The homogenised samples were then quenched in
Further, the samples for testing were prepared from the continuous casting process which were homogenised. Another set of homogenised specimens were produced from melt spinning to form rapidly solidified material. It is observed from the investigation that the results were found to be chemically homogeneous materials important to mechanical strengthening. A micro crystalline structure was observed as a resultant microstructure. It was observed from the microstructure that no Sn segregation was found in the conventionally cast alloys. It is also evident from the microstructure that there was a micro-segregation of Sn in the form of $\gamma$-precipitates as shown in Figure 2.12 These $\gamma$-precipitates were found at the grain boundaries of the rapidly solidified ribbons. The age-hardening effect of the rapidly solidified alloy was found to be similar to that of their conventional counter-part which results in the increase in Ni and Sn content of the alloy. The hardness was found to increase with increase in Ni content due to the alloy hardening of the matrix. It was concluded from the study that the rapidly solidified specimens possess higher mechanical properties and hardness compared to conventionally cast alloys. It is been reported from Figure 2.13 that Cu-15Ni-8Sn offers better strength compared to other spinodal alloys. It is reported from the study that the maximum hardness for the alloy obtained with increase in Sn content reveals that Sn contribute to the spinodal decomposition process.

Figure 2.12: Higher magnification of ribbon microstructure showing $\gamma$ precipitates at grain boundaries (substrate side; Cu-10Ni-10Sn)

(Deyong et al. 1999)
Sofonea and Mecke (1999) studied the microstructural characterisation of kinetics in spinodal decomposition. In this investigation Mirikowski function was used to measure the morphological changes that is occurred in time variation in homogeneous phase during spinodal decomposition. The function provide characteristic length scale L of pattern in a computationally inexpensive way. Scaling behaviour of the content is studied by this function. The function also allows to study the shape and connectivity of the spatial structures and to cross over from the early stages of decomposition and to the later stage of domain growth.

Kirkaldy (2000) have studied the ternary spinodal decomposition by Gunzburg-Landau treatment. It is reported from the investigation that the Gunzburg-Landau treatment accords with the irreversible thermodynamics with the experimental and computational modelling. Since the two 2 x 2 coefficient matrices was not be able to bring to the diagonal. This modification treatment was motivated by the Bragg-Willaiams thermodynamics. Gunzburg-Landau which is a time-dependant function suggested by Goryachev, the corresponding matrices are proportionate.

Liu (2000) studied the spinodal decomposition of fine grained binary spinodal alloys. The kinetics of slow grain growth and spinodal decomposition was investigated by implementing the Monte-Carlo method. Where a coupled algorithm of Q-state and spin-exchange using model operates. The energy that is developed in the grain boundaries is described by imposing
a potts spin lattice on the Ising crystal. A simulation was carried out where the size of the grain was comparable with the spinodal length on the order of magnitude. It is observed that the grain boundaries of low energy in the spinodal alloys enhance the solute diffusion. Whereas the alloys having grain boundaries of higher energy hinders the solute diffusion. The kinetics of spinodal decomposition is modulated by grain growth.

Maier-Paape et al. (2000) studied the spinodal/ ordering process for multi-component Can–Hilliard. The initial stages of phase separation process in the multi-component Can-Hilliard system was condensed through spinodal decomposition. The system was developed with the recent works of Maer-Pappe and Wanner. In this research the authors had established an existence of certain dominating subspaces which determines the behaviour of most solutions originating near a spatially homogeneous state. It is observed from the investigation that depending on the initial concentration of the alloy components several distinct phenomenon can be observed. If the initial concentration of the three components are almost equal, the dominating subspace would consists of 2 copies of finite-dimensional subspace from the binary alloy case. For the other concentration only one copy of the binary dominating subspace determines the behaviour of the alloy. The initial coupling of the concentration in the spinodal alloy which is observed in the initial separation process can be observed in the latter stages.

Zakharov (2002) studied the spinodal decomposition and diffusion kinetics in quasi-equilibrium solid solutions. Within the local equilibrium approximation the atomic mobilities of the component were developed in a hierarchical manner. The evolution of the solid solutions were treated at the hydrodynamic stage. The equation describing the evolution of the distribution of “fast” component in the quasi-equilibrium solid solutions at the arbitrary stages of the transformation are derived within the generalised lattice model accounting for the specific volume of the components by using the “fast” and “slow” components of diffusion and the method of contracted descriptions.

Ramnarayan and Abinandanan (2003) studied the spinodal decomposition in a polycrystalline material. The authors used a phase mode to study the decomposition in the material in which the grain size is of same order of magnitude as the character decomposition wavelength. In the theory of phase models, every grain (i) has an order parameters in their model associated with it. The value of unity inside the $i^{th}$ grain decreases smoothly through the
grain boundary region to zero outside the grain. The microstructural examination of a symmetric alloy of composition, c= 0-5 shows that the evolution depends on the differences in the grain boundary energies that are A- rich and B-rich phases. The interior of the grain size is filled with the β-phase if the grain size is small. It is also observed that by the authors that if the grain size is large the microstructure exhibits an A- rich grain boundary followed by a B-rich layer, the grain interior exhibits a spinodally decomposed microstructure. Further, during the spinodally decomposed process the grain growth is suppressed completely.

**Shukla and Mohanty (2003)** studied the homogeneous nucleation for a 1st order Quark-hadron phase transition. It is observed that the beginning of hadronization a significant supercooling is necessary. It is also observed that the spinodal decomposition process competes with the nucleation process that provide an alternate mechanism for the phase conversion.

**Zhang et al. (2003)** had investigated the metal spray forming technology and its metallurgical application. The tool that is used in the investigation was designed to create a spray used in the investigation. The nitrogen gas of atomising pressure of 2 MPa was used in this investigation. When the rotating speed was 10 rpm the molecular atomisation and copper deposition were performed. Spinodal structure, meta – stable phase and discontinuous precipitates were observed in the aging treatment of spray formed Cu-15Ni-8Sn wrought spinodal alloy.

**Dobrestov et al. (2004)** studied the stochastic description of phase separation near the spinodal curve of wrought alloys. The statistical methods developed earlier for non-equilibrium alloys were applied to describe the phase separation near the spinodal curve. It is observed that the size of equilibrium regions which is found using simulations was found to be the important parameters of the simulations. A significant changes was observed in this study where the nucleation is evolved to spinodal decomposition under the variation of concentration and temperature across the spinodal curve. The difference of the supersaturated parameters determines the scale of evolution.
Liu and Gao (2004) proposed a method called Differential cluster variation method (DCVM) for the analysis of spinodal decomposition in alloys. It is observed that in this method, a lattice symmetry operations in the presence of an infinitesimal composition are utilised to bring down the connection equation. The equation are found to deduce for the correlation function and to reduce the variable in the analysis of the cluster variation. The application of this method is made to calculate the gradient energy coefficient in the Caln-Hilliard free energy function. The analysis is carried out to evaluate the wavelength formation in the spinodal decomposition of Al-Li alloys.

Straffelini et al. (2005) studied the dry sliding wear behaviour of 2 Cu-Be alloys against AISI M2 stainless steel as the counterface material under dry sliding condition. The hardness and the thermal conductivity of the first alloy was found to be 390HV and 106 W/mK. Whereas, the hardness value for the second alloy was found to be 270 HV and the thermal conductivity was found to be quite higher compared to the first alloy which was found to be 208W/mK. A metallic in nature was observed for the alloy in the lower loads. Lower wear rate was reported for the first alloy. Whereas, the wear rate value for the second alloy was found to decrease. It was observed that as the applied load was increased, a transition in the wear mechanism from metallic wear to tribo-oxidative wear was observed. The results were interpreted in terms of tribological behaviour which is formed during the sliding on the surface of Cu-Be alloy specimens.

Kuksin et al. (2007) investigated the spinodal decomposition and phase diagram of Lennard-Jones system in meta-stable state. The molecular dynamics method was used to treat the meta-stable states of Lennard-Jones system. This was treated at different temperatures and pressures including negative pressure region. Analysis of the crystal and the liquid was made on the basis of relative position of the surface of the equation in the meta-stable region. The limits of the stability of the meta-stable states of the liquid and crystals on the phase diagram are obtained. The mechanism of the crystal decomposition of the stability limit is well examined. The stochastic properties of the particle system were investigated in the region of the spinodal alloy and the k-entropy and the dynamic memory time were calculated.

Singh et al. (2007) carried an investigation on the microstructure of the transfer and the underlying severely plastically deformed layers (SPDL). The layers were formed in the dry
sliding of spinodally hardened Cu-15Ni-8Sn wrought alloy against stainless steel as the counterface material. The scanning electron microscope and transmission electron microscope were used to evaluate the microstructure of the wrought spinodal alloys. It was observed that the SPDL consists of Cu-Ni-Sn solid solution with elongated nano-grain. This is because of extensive dislocation glide and twinning. The alloy consists of a transfer layer of 2-3µm thick of equi-axed nano composite. The nano composite consists of Cu-rich metallic phase with (Fe₃Cr)₂O₃ base oxide precipitate. De-alloying was undergone by the spinodal bronze in this process. The dispersion of the oxide in the layer reveals different type of mechanical mixing. The layer is formed to improve the wear resistance of the spinodal wrought alloy. The coefficient of friction showed a similar characteristics for all the test which had a transient period followed by a single state regime as shown in Figure 2.14

![Figure 2.14: Coefficient of friction curves for Cu-15Ni-8Sn spinodal alloy](image)

(Singh et al. 2007)

Sadi and Servant (2007) studied the tensile properties of Cu-9Ni-6Sn and Cu-9Ni-2Sn wrought spinodal alloy. The alloys were homogenised, cold rolled and solution treated at 825°C for 10 hours. Further, the alloys were aged at 400°C for 24 hours. The optical image of the as-cast alloys showing the dendritic structure is shown in Figure 2.15. It is reported from the investigation that the yield strength value of Cu-9Ni-6Sn and Cu-9Ni-2Sn wrought spinodal alloys increases and reaches 300 MPa and 600 MPa respectively as shown in Figure 2.16 and Figure 2.17. The alloys were examined for precipitation sequences while aging. It was observed that the spinodal alloys containing lower Sn content did not form any precipitate upon aging. The kinetics of precipitation dominated the ratio of Sn/Ni chemical content in the Cu-Ni-Sn wrought spinodal alloys.
Figure 2.15: Optical micrograph of as-cast alloy showing dendritic segregation
(Sadi and Servant 2007)

Figure 2.16: Effect of aging time on tensile strength, yield strength and tensile elongation after ageing at 400°C for Cu-9Ni-2Sn spinodal alloy.
(Sadi and Servant 2007)

Figure 2.17: Effect of aging time on tensile strength, yield strength and tensile elongation after ageing at 400°C for Cu-9Ni-6Sn spinodal alloy.
(Sadi and Servant 2007)
Zhang et al (2008) studied the wear characteristics of Cu-15Ni-8Sn cast spinodal alloy. Investment casting method was used to process the Cu-15Ni-8Sn alloy. The wear test was conducted under dry sliding lubrication condition. The parameters used for the test were load 1470 N, speed- 200 rpm, test duration- 60 minutes. The alloy was melted in an induction furnace and poured at 1300°C. The alloy was homogenised at 820°C for 10 hours and was cooled in the furnace itself. The alloy was solutionised to get a supersaturated solid solution. Aging was performed for the alloy at a temperature of 400°C for various periods of time. It was observed from the investigation that an equilibrium precipitate consisting of α and γ were observed along the grain boundaries as observed in the Figure 2.18 The equilibrium precipitate were observed at an aging temperature of 400°C for 1 hour. As the aging time is increased the precipitation grow more and fills the matrix grains as observed in Figure 2.18. It was also observed that the hardness values of the aged specimens were found to increase and then decrease with the aging time as shown in Figure 2.19. The maximum hardness was found to be at an aging time of 120 minutes. It is observed from the study that the alloy exhibit good wear resistance characteristics. It can be reported from the Figure 2.20 that the wear rate is found to decrease and then increase with the aging time. It was also reported from the Figure that the coefficient of friction was found to be a constant for different aging treatment.

Figure 2.18: Optical micrographs showing representative microstructures of Cu–15Ni–8Sn alloy for aging times of (a) 0 min, (b) 60 min, (c) 420 min and (d) 1680 min.

The aging temperature was 400°C.

(Zhang et al. 2008)
Figure 2.19: The Vickers hardness vs. aging time, aging treatment at 400°C.  
(Zhang et al. 2008)

Figure 2.20: Wear rate versus aging time of Cu-15Ni-8Sn alloy  
(Zhang et al. 2008)

Alili et al. (2008) have investigated the redistribution of solute and precipitation reaction of Cu-15Ni-8Sn wrought spinodal alloy. The alloy was obtained from Trefimetaux (France) in the form of rods. The alloy was re-melted in an induction furnace and were cast into rod forms. The rods were homogenized at 825°C for 10 hours and were water quenched. Slab shaped were cut from the rods for the testing of properties. Slabs were cold rolled in order to reduce the grain size. The specimen were cold rolled with different thickness reduction ranging from 50% to 95%. To remove the plastic deformation of the alloys, the alloys were annealed at 822°C. Aging treatment were performed at the temperature from 527°C to 677°C for various period of time. To evaluate the morphological changes in the alloy, optical and TEM analysis have been used. It was observed that the discontinuous precipitate reaction proceeds much faster in ternary Cu-Ni-Sn spinodal alloy with change in morphological factors like change of growth,
direction, appearance and disappearance of solute rich $\gamma$ lamellar. A single Ni and Sn rich phase within the solute depleted $\alpha$ lamellar was observed from the alloy. The partitioning of the alloying elements were analysed by using EDAX. It was reported from the EDAX that Ni and Sn elements were located in the $\gamma$ lamella. However, the formulae for the $\gamma$ lamellar was found to be close to $\text{Cu}_3\text{Sn}$ which infers that the copper atoms are replace by the nickel atoms.

Razmov (2008) investigated the formation of intermediate ordered states on spinodal decomposition of wrought spinodal alloys. The author suggested a model for the diffusion phase transformation in the spinodal alloys with a tendency towards ordering. It accounts the possible completed of the process, decomposition and the vacancy mechanism diffusion. It is inferred that the spinodal decomposition into the components A and B from a homogeneous initial state may pass through the stage of formation of isolation of the ordered phase with their formation of isolation of the order phase with their stability being qualitatively increased the region of low temperatures. The growth of colonies on the spinodal decomposition of a meta-stable ordered state has also been investigated in this study.

Zhang et al. (2010) studied the dry sliding wear behaviour of Cu-15Ni-8Sn spinodal alloy. Pure form of Cu, Ni and Sn were melted in an induction melting furnace. The melting was carried out under vacuum atmosphere. Investment casting was used as the casting method. Further, the alloys were homogenised and solutionised at a particular temperature. The cast spinodal alloy was then aged for 400°C at different aging time. The wear test for the spinodal alloy was conducted using the pin-on-disc wear testing apparatus. The microstructure images for Cu-15Ni-8Sn investment cast spinodal alloy aged at 400°C for different period of time are shown in Figure 2.21. It was reported from the investigation that the wear rate was inversely proportional to the hardness of the spinodal alloy. The minimum wear rate was reported when the alloy contained 10% volume of the cells that got precipitated along the grain boundaries. It is observed from Figure 2.22 that the wear rate was found to decrease initially and found to increase after 240 min. The friction coefficient was found to be constant for all treatment times. It was inferred from the SEM image of the wear debris and the pin that the removal process of the surface material included subsurface deformation, crack initiation, crack propagation and de-lamination of the material.
Figure 2.21: Microstructures of Cu-15Ni-8Sn alloy obtained after different ageing times of (a) 0 min, (b) 120 min, (c) 240 min and (d) 420 min. The aging temperature was 400°C. (Zhang et al. 2010)

Figure 2.22: Friction and wear properties of Cu–15Ni–8Sn alloy as a function of the aging time: (a) wear rate and (b) friction coefficient. (Zhang et al. 2010)
Caris et al. (2010) investigated the effect of changes in the microstructure and heat treatment on the mechanical behaviour of Cu-15Ni-8Sn spinodal alloy in uniaxial tension. The spinodal alloy was processed by powder metallurgy technique. Processes like cold working and heat treatment on the spinodal alloys reported a significant effect on the tension behaviour of the spinodal alloys. The result obtained are rationalised in the failure mechanism observed by SEM. The optical micrograph of the alloy are shown in Figure 2.23.

![Optical micrograph of the alloy](image)

Figure 2.23: Optical images of polished and etched longitudinal cross-sections of the alloy in the (a) as-received condition and heat treated at 370 °C for (b) 3 h, (c) 5 h, and (d) 24 h (Caris et al. 2010)

Dersaime et al. (2010) investigated the phase transformation of Cu-9Ni-6Sn wrought spinodal alloy at high temperature. The highly rich Cu content Cu-Ni-Sn alloy system are frequently studied for the high UTS and better electrical properties. In the present investigation the phase transformation of the alloys at high temperature is focussed. The presence of an unexpected peak at 985°C on the differential thermal analysis is observed.

Hui et al. (2010) studied the precipitation sequence and property evaluation of Cu-15Ni-8Sn alloy coating produced by laser cladding using direct aging treatment. It was reported that the segregation of Sn in the Cu-15Ni-8Sn alloy solidification is effectively relieved. Before aging the spinodal alloy, only two phase exist (i) α-Cu solid solution dendrites with a solubility of Sn of 7wt-% and (ii) Sn enriched in small fraction as inter-dendrites. A precipitation sequence is experienced for the dendritic α-Cu solid solution in the order of spinodal decomposition, DO22 structure and discontinuous γ-DO3 precipitates. The alloy was subjected for an aging of 370°C after the coating was conducted without the tradition solution pre-treatment. The hardness was
found to increase and then decrease with the aging time as observed in the Figure 2.24. The micro-hardness of the alloy was found to be 390HV$_{0.5}$ due to the solidification of the fine grain and the hardening effect of spinodal decomposition. It was also reported that the Sn-enriched δ-phase at the inter-dendrites decomposes into the laminar discontinuous precipitates γ DO$_3$ phase after aging. A noticeable change was observed in the change in property of the alloy.

![Micro-hardness of the coatings with different aging time](Hui et al. 2010)

**Donald R. Askeland et al. (2011)** in their research summarised the property variation of some copper alloys obtained by various strengthening mechanisms.

**Ilangovan and Sellamuthu (2012)** investigated the effect of Ni content on sand cast Cu-Ni-Sn spinodal alloys. The sand cast alloys were homogenised, solutionised and aged to induce spinodal or ordering reaction. Further, the heat treated specimens were used for hardness measurement and wear testing. The wear testing was conducted as per ASTM standard using pin-on-disc wear testing apparatus. It was observed from the investigation that the Ni content increases the hardness and decreases the aging time which implies the Ni contribute significantly to spinodal decomposition process. The wear rate was found to decrease with increase in peak hardness.
Ilangovan and Sellamuthu (2013) studied the effect of tin addition on hardness, wear rate and COF of sand cast spinodal Cu-Ni-Sn alloys. Alloys of varying wt-% Sn were melted in a crucible furnace under inert argon atmosphere. Sand cast specimens were solution treated at 825°C for 10 hr and aged for different period of time. It was observed that the hardness value increases reaches a peak value and then decreases with an increase in aging time as observed in Figure 2.25. COF was found to be independent of hardness and remained a constant as shown in Figure 2.26. The wear rate was found to decrease with increase in hardness.

![Graph of Variation of Hardness with Aging Time](image1)

Figure 2.25: Variation of Hardness with Aging Time.
(Ilangovan and Sellamuthu 2013)

![Graph of Variation of COF with Hardness](image2)

Figure 2.26: Variation of COF with Hardness.
(Ilangovan and Sellamuthu 2013)
2.3 Previous studies on other spinodal alloys

The previous investigations conducted on other spinodal alloys are as follows:

**John W. Cahn (1966)** studied the particle coarsening and spinodal decomposition at the later stages of some typical spinodal alloys. The spinodal decomposition leads to two phases that depends on a number of features in the later stages and the particle coarsening can be obtained by considering terms in the diffusion equation. This would give rise to harmonic distortion of typical composition waves of spinodal decomposition. The composition depends on the thermodynamic factor in the diffusion. Two classes of distortion are identified which are related to the free energy curve. Even harmonics are found to be consistent with the lever rule. It is considered to be the minor phase from the average composition and a major matrix phase. The particle coarsening in the initial stages are described and two effects are distinguished.

**Butler and Thomas (1970)** studied the microstructure and properties of spinodally decomposed 51.5Cu-33.5 Ni-15 Fe alloy. The investigation was conducted to study the spinodal decomposition on these alloys and the associated change in the properties of the spinodal alloy after solution treatment and rapid quenching. The characterisation of the alloy was carried out by using TEM, magnetic analysis and diffraction. It is observed that during aging a two-phase microstructure get coarsen and the corresponding wavelength is determined by a (time) $^{1/3}$ law. The coherency is lost eventually when $\lambda \approx 1000 \, \text{Å}$ and an interfacial dislocation is created with $b = a/2 \, (110)$ are introduced and accelerated the coarsening rate. A change in the loss of coherency to the tetragonal symmetry is observed in this investigation. A change in the composition which is observed during the spinodal decomposition occurred very rapidly which is observed by the magnetic measurements. The mechanical testing results, Curie temperature and the wavelength measurements indicated the age-hardening response that is controlled principally by the difference in the lattice parameters of the two phases which is in agreement with the internal stress theory of Mott and Nabarro.

**Findik and Flower (1992)** investigated the spinodal decomposition in Cu-30Ni-2.5Cr and Cu-45Ni-10Cr alloys. The compositions were selected such that it lies in the Cu-rich end that is at the centre of the miscibility gap. The alloys were quenched at 950°C for the low Cr content alloy and at 1050°C for the higher Cr content alloy. Further, the alloys were subjected for aging
at a temperature range of 300-800°C. The process of spinodal decomposition was followed by the measurement of the hardness and the characterisation of the alloy by using SEM, TEM and X-ray diffraction. The modulated wavelength for the alloys were measured form XRD and micrographs. The hardness values were plotted for different periods of aging time at various aging temperature as shown in Figure 2.27

![Figure 2.27](image.png)

**Figure 2.27:** Hardness (HV10) as function of aging time (min) for (a) Cu–45Ni–10Cr and (b) Cu–30Ni–2.5Cr alloy

*(Findik and Flower 1992)*

**Findik and Flower (1993)** investigated the strength of Cu-Ni-Cr alloys. The results obtained were compared with the binary Cu-Ni alloys which is dependent upon heat treatment. The specimens were solution treated at a particular temperature and aged at lower temperature to induce spinodal hardening. It was reported from the investigation that the decomposition into two phases may occur due to nucleation or growth or by a spinodal reaction. The above process depends upon the alloy composition and the heat treatment temperature. The spinodal decomposition of Cu-30Ni-5Cr and Cu-45Ni-15 Cr (wt-%) have been investigated within the spinodal range. Further, these alloys were rapidly quenched in water at a temperature of 1050°C and were then aged at a temperature of 300- 800°C. Hardness measurement XRD, TEM and SEM were used for characterising the alloys after the spinodal decomposition. The morphological changes have been reported for the spinodal alloys. It was observed that during the early stages of aging, the modulation wavelength was found to be a constant while the hardness values increased continuously and remained a constant at its peak value. The modulated wavelength was found to increase continuously. Figure 2.28 shows the wavelength versus aging time for the spinodal alloys.
Ji-Cheng Zhao and Michael R. Notis (1999) studied the ordering transformation and the spinodal decomposition in Au-Ni alloys. Characterising the spinodal alloy (Au-40% Ni and Au-50% Ni) by using TEM revealed the microstructure as spinodal modulated structure. The objective of the investigation is to test for the existence of long range order phenomenon within the miscibility gap. The L\textsubscript{10} long range-order phase in Au-50% Ni was observed from the investigation. The phase was observed for the spinodal alloy when the alloy was re-annealed at 490°C. The literature revealed the existence of the transient long range order which exist in the Au-Ni system. A single phase homogenous solid solution, L\textsubscript{10} and L\textsubscript{12} long range order phases were formed during the spinodal decomposition process except in very thin films, the time-temperature-transformation diagrams for the two Au-Ni alloys were constructed. The spinodal decomposition process and the discontinuous precipitates structures were observed only in the anneal bulk alloys.

Vyazovikina (2000) investigated the effect of high chromium content on the microstructure, electrochemical, mechanical and corrosion properties of Fe-Cr alloys. The hardness and the wear resistance for the Fe-Cr spinodal alloy were found to increase with increase in Cr addition due to spinodal decomposition process. The presence of α′ phase in the high chromium content and α phase in the lower chromium content hinders the anodic passivation of the Fe-Cr alloys under potentiostatic dynamic polarisation condition.
Zhao et al. (2003) investigated the age-hardening behaviour of Cu-3.2 Ni-0.75 Si at 450°C. It was observed from the investigation that the YS and UTS increases continuously as the aging time increases reaches a peak value and then decreases. The % EL was found to decrease with increase in aging time. It is reported that an incubation period was found to be absent during the increase in YS. The TEM and X-ray were used for characterizing the spinodal alloys. Spinodal decomposition was found to take place followed by the nucleation of the (CuNi)\textsubscript{3} Si particle. Further, annealing of the alloy results in the formation of $\delta$-Ni\textsubscript{2}Si phase that nucleates within the (CuNi)\textsubscript{3} Si particle.

Findik (2002) investigated the spinodal decomposition in Cu-32Ni-3Cr and Cu-46Ni-17Cr alloys. The alloys were quenched from 950°C and 1050°C in water and aging treatment was carried at 300-600°C and 300-800°C respectively. The authors also studied the wavelength fluctuation in the composition of alloys which respond to spinodal decomposition. The nucleation process is characterised by the large composition variation. It was reported from the study that the spinodal alloys may possess same crystal structure. The micrographs reveals the presence of uniform dispersion of small, coherent interconnected particles. It has been reported from the experiment that the spinodal decomposition occurs in the metallic, ceramic and glass systems. TEM and XRD were used to observe the spinodal (modulated structure) in Cu-32Ni-3Cr and Cu-46Ni-17Cr (at-%) alloys. It was observed that 3 Cr and 17 Cr undergoes spinodal decomposition.

Findik (2012) studied the improvement of spinodal alloys from past to present. The author has reported the theory of spinodal reaction. A review on the spinodal hardening mechanism has also been discussed. Further, the spinodal decomposition in copper, iron and titanium based alloys have been in the article. The author has given a detailed account on the theory of spinodal decomposition in his research work.
2.4 Conclusion

In summary, Cu-Ni-Sn alloys can be used in most of the applications like wear plates, bushings and bearings. Since the wear behaviour and the mechanical properties play a vital role, it is important to determine the mechanical properties and the wear behaviour with respect to aging temperature, alloy composition and aging time. In summary all the previous investigations were conducted to find the hardness, wear behaviour and the YS of a few compositions mostly in Cu-Ni-Sn wrought spinodal alloys. No studies have been reported on the variation of %El, UTS, optimum aging temperature and optimum aging time with variation in nickel or tin content cast in metal mould (permanent mould casting / gravity die casting). It is necessary to conduct an investigation on the cast spinodal bronze alloys as spinodal bronze utilisation in cast condition requires a set of base data’s for evaluating the mechanical properties such as hardness, wear behaviour, UTS, YS and %El. Since most of the spinodal bronze alloys are used in cast condition in many industries, casting finds an economical process in the field of manufacturing processes and selection of the specific casting method is also highly warranted which will lead to the application of the alloy in the industry level.