Thesis

On

STUDY OF MECHANISMS TO PRODUCE ULTRA-FINE/ NANO GRAINED COPPER THROUGH THERMAL CYCLING PROCESS

Submitted in partial fulfillment of the requirements for the award of degree

of

Master of Engineering
IN
PRODUCTION AND INDUSTRIAL ENGINEERING

Submitted By

Mridul Rai
Regd. No. 800982013

Under the Guidance of

Dr. Tarun Nanda	**Dr. B. Ravi Kumar**	**Dr. O.P. Pandey**
Assistant Professor	Scientist E-II	Professor & Head
MED, TU, Patiala.	MST Division, NML, Jamshedpur.	SPMS, TU, Patiala.

DEPARTMENT OF MECHANICAL ENGINEERING

THAPAR UNIVERSITY

(Established under section 3 of UGC Act, 1956)

Patiala -147001, Punjab, India

July, 2011

DECLARATION

I, Mridul Rai hereby declare that the work being presented in the thesis entitled, **'Study of Mechanism to produce High-Strength, High-Conductivity Ultra-Fine Grained Copper through Thermal Cycling Process'** by me in partial fulfillment of the requirements for the award of degree of Master of Engineering in Production and Industrial Engineering, from MED, Thapar University, Patiala is an authentic record of my own work carried under the supervision of Dr. Tarun Nanda, Assistant Professor, MED, TU, Patiala; Dr. O.P. Pandey, Professor & Head, SPMS, TU, Patiala and Dr. B. Ravi Kumar, Scientist E-II, MST Division, National Metallurgical Laboratory (NML), Jamshedpur.

The matter presented in this report has not been submitted in any other University/Institute for the award of Master of Engineering or any other degree.

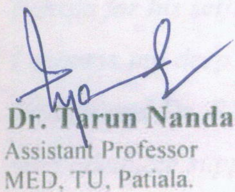
Mridul Rai

(Mridul Rai)

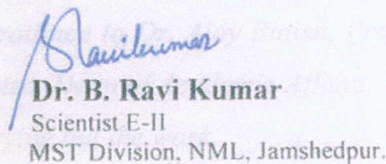
Date 14-07-11

CERTIFICATE

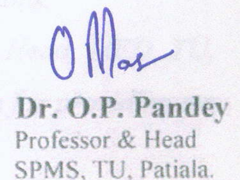
This is to certify that the thesis entitled, **'Study of Mechanism to produce High-Strength, High-Conductivity Ultra-Fine Grained Copper through Thermal Cycling Process'**, being submitted by Mridul Rai (Regd. No: 800982013), in partial fulfillment of the requirements for the award of degree of Master in Engineering in Production & Industrial Engineering of Mechanical Engineering Department, Thapar University, Patiala, is a record of candidate's own work carried out by him under our supervision. The matter embodied in this thesis is original and has not been submitted for the award of any other degree.



Dr. Tarun Nanda
Assistant Professor
MED, TU, Patiala.

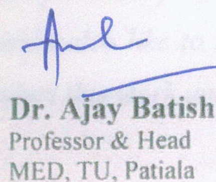


Dr. B. Ravi Kumar
Scientist E-II
MST Division, NML, Jamshedpur.



Dr. O.P. Pandey
Professor & Head
SPMS, TU, Patiala.

(Countersigned by)



Dr. Ajay Batish
Professor & Head
MED, TU, Patiala

Dr. S.K. Mohapatra
Dean of Academics Affairs
TU, Patiala

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Mridul Rai

ABSTRACT

Reducing the average grain size of polycrystalline metals and alloys is a traditional way of increasing their strength. While high strength and good ductility rarely exist simultaneously in any material, ultrafine grains exhibit the optimal combination between both. One of the principles to develop high conductivity and high strength is the thermal cycling process. Pure copper and copper alloys are widely used because of their high electrical conductivity, high heat transfer, corrosion resistance and excellent formability. One of the main challenges before the manufacturers is to produce high conductivity copper with the right combination of mechanical properties for specific applications. The strength of pure copper is low and any strength gained through cold working comes at the expense of decrease in electrical conductivity. The present work aims to propose a methodology for developing copper, which possesses good strength and also high electrical conductivity simultaneously. Most researches have concentrated on Cu–Al, Cu–Zn, Cu–Au, Cu–Ag, Cu–Cr alloys and so on, while the studies on pure copper have been very limited. In the present work, the influence of thermal cyclic treatment on the kinetics of recrystallization has been determined. Solution annealed copper has been subjected to heavy cold deformation followed by subsequent thermal cycling to produce ultra fine grained structure. The effect of this treatment on microstructural changes and property enhancement of pure Copper has been investigated. The work closely describes the recrystallization and grain growth kinetics under the cyclic process. The ultra fine grained copper with submicrometer grains can achieve superior mechanical properties and electrical conductivity.

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CHAPTER 1
INTRODUCTION

1.1 General

Copper and its alloys have continued to serve mankind from the dawn of civilisation in the form of castings both because of the ease with which these can be produced and because of the strength and toughness which they possess. Other advantages include high electrical and thermal conductivities, non-magnetic qualities and excellent resistance to both corrosion and wear. Copper shows excellent resistance to most chemicals other than the strong mineral acids and ammonia and this fact combined with its malleability and high thermal conductivity makes it a favourite material for chemical plants, especially where heat transfer is involved. Many plumbing installations including waste pipes and sanitary systems are now entirely of copper and its alloys. On account of its high resistance to corrosion by most soils, copper piping is very suitable for underground distribution of water and gas. A chemical engineer, as well as a builder and a plumber are particularly interested in the resistance of copper to corrosion by chemicals, water and atmosphere and in the ease with which it can be formed into intricate shapes and joined by welding or other means.

Due to the fast developments in electronics industry, there is a great demand of high-strength and high conductivity materials. Copper and many of its alloys are characterised by moderate strength combined with high ductility. These alloys can be easily produced at low temperatures into sheet, strip and wire from its wrought form. Copper is mostly used in electrical transmission and plumbing. Electrical and electronic applications already consume more than 50% of all copper and will probably place further demands in the future. Moreover, its other applications like cathedral roofs and kettles also exist. High purity copper exhibits better thermal and electrical conductivity than any known substance except silver. According to the International Annealed Copper Standard (IACS), the specific resistance of pure annealed copper at 20˚C is 1.7241 micro-ohm-cm and its conductivity is therefore 0.58001 $\mu\Omega^{-1}cm^{-1}$ (Yamane, 2001). Copper is a metallic element and has an atomic number of twenty-nine. Its atomic weight is 63.54 g/mole. Copper and copper alloys have a specific and predictable recrystallization grain growth response to annealing. After cold working to a specified reduction in thickness, copper and its alloys can be annealed to any of the several grain size ranges.

1.2 Need of Improvement in Mechanical Properties

Copper and its alloys are known to have problems of poor mechanical properties (low yield strength, poor fracture and fatigue strengths) because they contain a large variation of transformation temperature with composition and high elastic anisotropy. In order to solve these problems, it is required to enhance the mechanical properties of Cu and its alloys and to avert the boundary fracture. Several methods have been suggested to overcome this problem. These include cold working, adding alloying elements, stabilization with ageing, control of texture by preferred orientation and grain refinement method. It has extensively been reported that grain refinement method is more effective in the protection of boundary fracture (Wang *et al*., 2006).

1.3 Methods to Improve Properties

These are several techniques to improve the mechanical properties of copper and its alloys. The most effective methods are however based on the principle of refining grains to smaller (micro or nano) sizes. In the recent past, tremendous efforts have been given to produce a variety of nano structured and ultra fine grained materials for diverse applications. These materials are attractive for many applications ranging from biomedical to aerospace industries. While high strength and good ductility rarely exist simultaneously in any material, ultra fine grained (UFG) alloys exhibit the optimal combination between both.Some of the main techniques utilized to improve the properties of copper and its alloy are discussed as follows:

1.3.1 Cold Rolling

Cold rolling is a technique applied industrially to increase the strength. All cold working operations harden and strengthen the material with diminution of its ductility, making continued deformation progressively more difficult. For many purposes this additional strength and hardness is desirable, but softness can always be restored by annealing in order to permit further cold working operations, e.g. spinning, pressing, deep drawing, coining, bending or otherwise forming into finished articles. In certain cases, the strength and hardness of the product can be greatly increased by heat treatment of copper alloys. After heavy reduction by cold drawing, conductivity of Copper is drastically decreased due to more dislocation densities.

1.3.2 Solid Solution Strengthening

Another refining method includes addition of alloying elements which allow the increment of nucleation sites. They further provide the formation and solidification of fine compound phase in the matrix. However, in alloyed Copper, alloying elements act as impurities and thus electrical conductivity of these materials is inherently lower than the unalloyed counterpart.

The main alloying elements for Copper are Ag, Be, Cr, Sb, Sn, Zr, and Zn etc. The primary reason for strengthening through alloying is formation of one or more solid solutions in copper alloys.

1.3.3 Grain Refinement

The main limitation of using alloying as a technique to improve mechanical properties of Copper alloys is decrease in conductivity (Hosseini *et al*., 2009). To resolve this problem, ultra-fine grained (UFG) or nano structured (NG) commercial pure copper, with no alloy additions can be used. Ultra Fine Grained (UFG) materials may be defined as polycrystals having very small grains with average grain sizes less than ~1 µm. Thus, the grain sizes of UFG materials lie within the sub micrometer (100 – 1000 nm) and nanometre (less than 100 nm) ranges. While high strength and good ductility rarely exist simultaneously in any material, UFG alloys exhibit the optimal combination between both. The following are the main methods of grain refinement:

1.3.3.1 Severe Plastic Deformation

Severe Plastic Deformation (SPD) techniques are commonly used laboratory methods to produce bulk nano crystalline materials. SPD can be explained as deformation of a material to large strains below recrystallization temperature without intermediate thermal treatments. Several novel techniques have been developed to create the high strain in metals with minimal changes in the initial sample dimensions, such as Equal-Channel Angular Pressing (ECAP), High-Pressure Torsion (HPT), Multi Axial Forging (MAF), and Accumulative Roll-Bonding (ARB) (Valiev *et al*., 2000).

The mechanism of grain refinement based on plastic straining has been extensively investigated in numerous materials. For materials with medium or high Stacking Fault Energies (Fe, Cu and Al etc), coarse grains are refined upon continued straining by various dislocation activities. It involves the following processes:

- Manipulation of lattice dislocations.
- Formation of dislocation cells and/or dense dislocation walls that subdivide the original coarse grains into refined blocks.
- Transformation of the dense dislocation walls or cell walls into sub boundaries; and
- Evolution of sub-boundaries into conventional grain boundaries with large misorientation (or sharpening of grain boundaries).

Drawback of these methods, however, is that they involve multiple stages of deformation to generate large plastic strain and the ductility is quite low in relation to the conventional coarse-grained metals. Further these techniques suffer from limitations in terms of quality, grain size distribution, residual stresses or internal strains and sample size (Gupta, 1975).

1.3.3.2 Thermo-Mechanical Treatment

Thermo-Mechanical Treatment (TMT) is a large-scale industrial process and can be more readily optimised as compared to the SPD techniques. A recent novel route of forming UFG/NG structure in copper and its alloys involves annealing of heavily cold-worked specimens. In this process after heavy cold working, dislocation density increases which provides more nuclei sites during annealing leading to fine grains.

After SPD thermal stability of copper becomes very low. The strength of pure copper is low and the strength gained during cold working will decrease quickly after annealing. During heating, some of the stored energy is relieved as a result of the dislocation motion and there is a reduction in the number of dislocations. It is well known that some fraction (about 90%) of the strain energy expended on plastic deformation is stored in the metal. The changes in the material behaviour after being subjected to SPD suggest a change in the mechanisms of deformation.

1.3.3.3 Thermal Cycling Process

Thermal Cycling (TC) process is a temperature modulation process developed to improve the performance, strength and ductility of a variety of materials. This technique consists of repetitive cold rolling and annealing to reduce grain size. The basic mechanism of grain refinement by cyclic thermal process may be hypothesized as (Kumar *et al*., 2009):

- Nucleation prefentially occurs in high strain energy regions during the first few thermal cycles and sets in increased strain heterogeneity between recrystallized and residual deformed regions.

- On subsequent thermal cycles, nucleation takes place in the residual deformed regions, as these are the more potential sites owing to their high stored strain energy, in preference to the recrystallized regions.
- The driving force for the high energy grain boundary migration for grain growth of the recrystallized grains is small due to inherent sluggish diffusion rates and mobility of high angle grain boundaries. Also precipitation in copper alloys as the second phases increases which provide more nucleus sites and hence reduce the grain size.

1.4 Applications

The major applications and uses of copper are described as follows:

- ***Electrical Applications***

Approximately 65% of copper produced is used for electrical applications. Copper has the highest electrical conductivity of any metal, apart from silver, leading to applications in:

  - Power generation and transmission, generators, transformers, motors, bus bars and cables provide and deliver electricity safely and efficiently to homes and businesses.
  - Electrical equipment - providing circuitry, wiring and contacts for PCs, TVs and mobile phones.

Copper also has a key role to play in energy efficiency. The judicious use of 1 tonne of copper in the energy sector makes it possible to reduce CO_2 emissions by 200 tonne per year on average. Figure 1.1 shows the major application areas of copper (*Copper Development Association*).

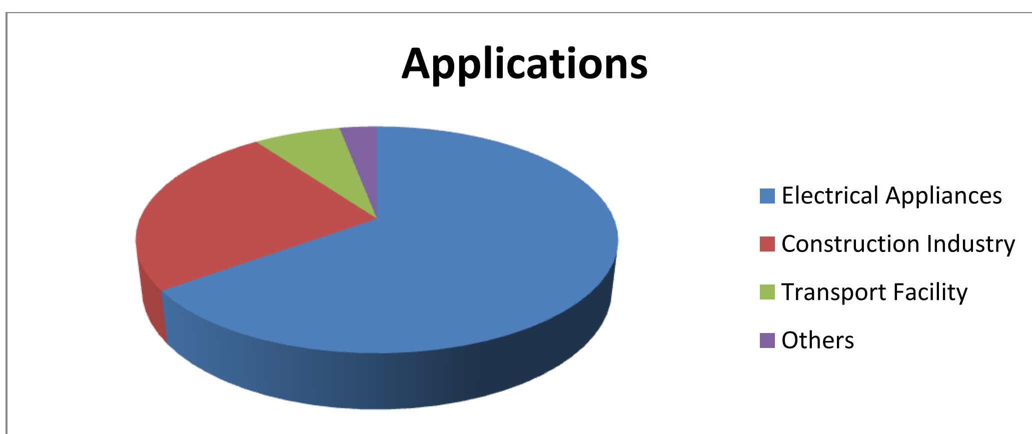


Figure 1.1 Major Application Areas of Copper

- ***Construction***

Around 25% of all the copper produced is used in buildings for plumbing, roofing and cladding. Copper provides light, durable maintenance-free structures that are naturally good looking, long lasting and fully recyclable. Copper's naturally antimicrobial properties can be exploited in hygienic surfaces for hospitals and healthcare facilities.

- ***Transport***

Trains, trams, cars and Lorries all need copper and transport accounts for 7% of copper usage. The high purity copper wire harness system carries the current from the battery throughout the vehicle to equipment such as lights, central locking, on-board computers and satellite navigation systems. Electric super trams in cities such as Manchester, Sheffield and Croydon, provide clean, efficient transport powered by electric motors. The overhead contact wires are either copper-silver or copper-cadmium alloys.

- ***Others***

Remaining 3% of copper is used for coins, sculptures, musical instruments and cookware.

1.5 Scope of Present Work

The studies on grain refinement processing are of specific practical importance in material science and engineering. Ultrafine grained (UFG) metallic materials lead to improved mechanical and physical properties and arouse a great interest among metallurgical researches. Severe Plastic Deformation (SPD) of metallic materials results in ultrafine grained microstructures with mean grain sizes smaller than 1 μm. The UFG materials show very high strength which is 3-4 times higher than what is offered by the same material with conventional grain sizes. Not only mechanical properties but electrical and thermal conductivities are also important for copper and its alloys. Extremely high density of lattice defects, especially grain boundaries are introduced in the SPD processed materials which affect ductility and electrical conductivity. Further, the SPD techniques have their own limitations for commercial applications, such as large load requirements, limitation on size of products, and high labour and fuel expenses. However, high strength and high conductivity are a contradiction for copper. To achieve this combination of diverse properties, and hence to overcome the limitations of the SPD techniques, the thermo-mechanical treatment has been evolved. Thermo-mechanical methods, unlike SPD techniques, depend upon conventional cold rolling and annealing for grain refinement, are also being investigated. In this process, copper is given heavy cold working followed by

an annealing treatment. Cold working creates high dislocation density, with finer grains. The subsequent annealing treatment creates a large number of nucleation sites which facilitate obtaining even a finer grain structure. However, the thermo-mechanical treatment decreases the thermal stability of copper owing to lowered recrystallization temperature. Most of the researchers have been worked on copper alloys and work is still lacking in case of pure copper. Highly alloyed copper is the most widely used where high strength required. Since in alloyed copper, alloying elements play role as impurities, electrical conductivity of these materials inherently lower than unalloyed counterpart. Also a limiting factor for the implementation of thermo-mechanical processes in pure copper is the absence of phase transformation.

The present research work intends to investigate the important microstructural changes occurring in cold deformed grains during thermal cycling in the absence of phase transformations. Further, it attempts to predict the factors affecting kinetics of recrystallization during thermal cycling process. The proposed research work is an attempt to over these limitations of the SPD and thermo-mechanical processes. In the proposed work, these specific copper would be subjected to heavy cold deformation followed by subsequent thermal cycling. The effect of this treatment on microstructural changes and property enhancement of pure Copper would be investigated.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

This chapter provides literature based background information for the present investigation. The first section identifies the characteristics of plastic deformation in metals and alloys, their relevant mechanism, and presents the different aspects of grain refinement process. This section also discusses about the crystallographic features of copper as an engineering material. The next section presents a detailed review of literature and results of experimental work conducted in the subject area.

2.2 Nano Crystalline/ Ultrafine Grained Material

Nanoscale science and technology is experiencing a rapid development and nano-materials have made profound impact on every field of materials research. Scientists believe that nanoscale science and technology will bring revolutions in human history due to the unique properties of nano-materials. A summary of properties of ultrafine grained materials is shown in Figure 2.1.

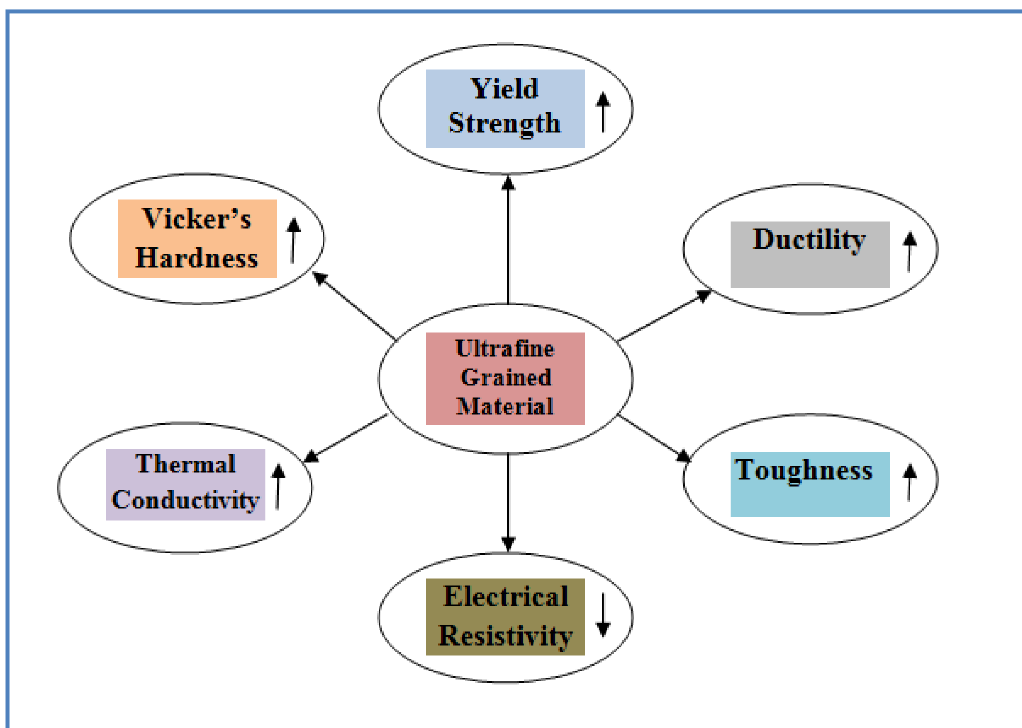


Figure 2.1 Properties of Ultrafine Grained Materials

Two basic and complementary approaches have been developed for the synthesis of nano-materials. These are known as ‘bottom up’ and ‘top down’ approaches. In the ‘bottom up’ approach, atoms, molecules and even nano-size particles themselves can be used as the building blocks for the creation of complex nanostructures. Whereas, in the ‘tops down’ approach coarse-grained materials are refined into ultrafine-grained/ nano-structured materials. Ultrafine grained (UFG) materials may be defined as polycrystalline materials having average grain size less than ~1µm. The grain sizes of UFG materials may ranges within the sub-micrometer (100-1000 nm) range (Kommel *et al.*, 2006).

One of the most notable properties of nanostructure/Ultrafine grained Materials is their extremely high hardness and strength, which makes them attractive for structural applications where strength and weight are critical. With the increasing number of applications of Ultrafine Grained Materials (UFG) in micro electro-mechanical systems (MEMS), micro/nano devices, precise cutting tools, surface coating and high performance structural application, it is important to understand the deformation and refinement mechanism in these materials.

2.3 Plastic Deformation of Metals

When a material is stressed below its elastic limit, the resulting deformation or strain is temporary. Removal of stress results in a gradual return of the material system to its original dimensions. When a material is stressed beyond its elastic limit, plastic or permanent deformation takes place, and the material does not return to its original shape on removal of load. The ability of metals to undergo plastic deformation is probably the most outstanding characteristic in comparison with other materials. The principal mechanism of plastic deformation in metals and alloys is intragranular shear displacement of some portions of a crystal relative to other portions, which can be brought about by various kinds of dislocation movements. The shear mechanisms for plastic deformation are quite diverse, but the principal ones are:

i Slip

ii Twining

iii Combination of slip and twinning

2.3.1 Deformation by Slip

If a single crystal of a metal is stressed in tension beyond its elastic limit, it elongates slightly and a step appears on the surface indicating displacement of one part of the crystal with respect to the rest, and the elongation stops. Increasing the load causes another step. It is as if neighbouring thin sections of the crystal had slipped past one another like a sliding card on a deck. Each successive elongation requires a higher stress and results in the appearance of another step, which is actually the intersection of a slip plane with the surface of the crystal. Progressive increase of load eventually causes the material to fracture.

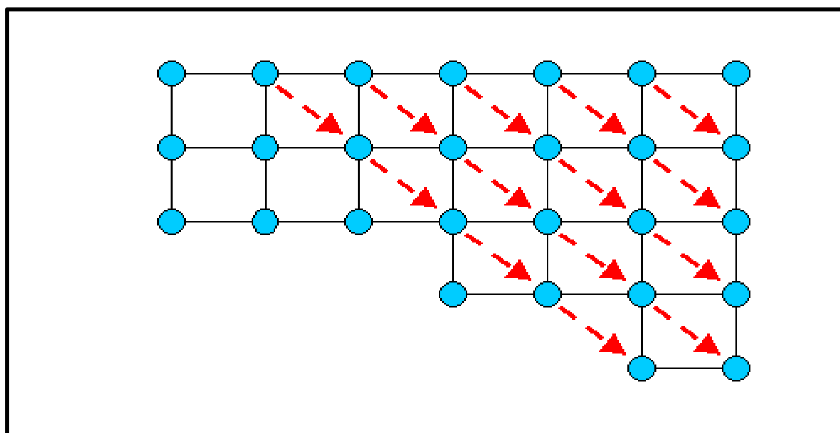


Figure 2.2 Effect of slip on Lattice Structure

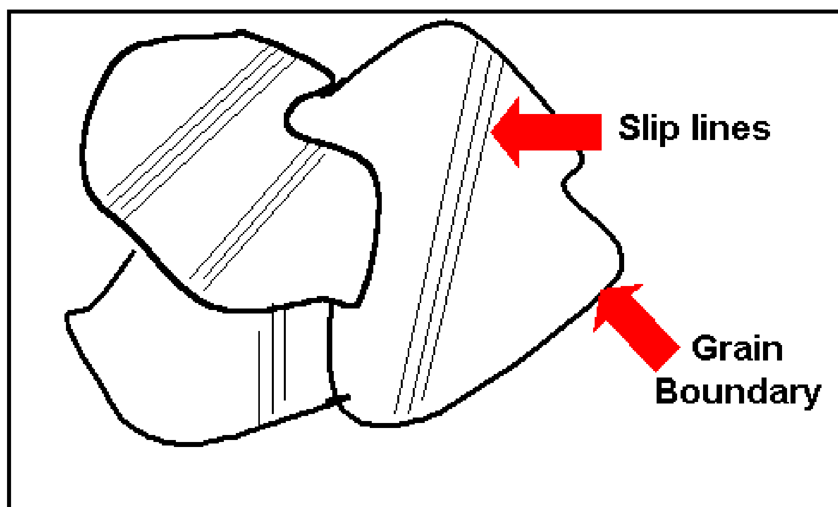


Figure 2.3 Appearance of Slip under Microscope

Slip occurs in directions in which the atoms are most closely packed, since this requires the least amount of energy. Figure 2.2 shows that when the plastic deformation is due to

slip, the atoms move a whole inter atomic space (moving from one corner to another corner of the unit cell). This means that overall lattice structure remains the same. Slip is observed as thin lines under the microscopes (Figure 2.3) and these lines can be removed by polishing. The appearance of slip lines in copper is shown in Figure2.4.

Figure 2.4 Slip Lines in Copper

2.3.2 Deformation by Twinning

When mechanical deformation is created by twinning, the lattice structure changes. The atoms move only a fraction of an interatomic space and this leads to rearrangement of the lattice structure as shown in Figure 2.5.

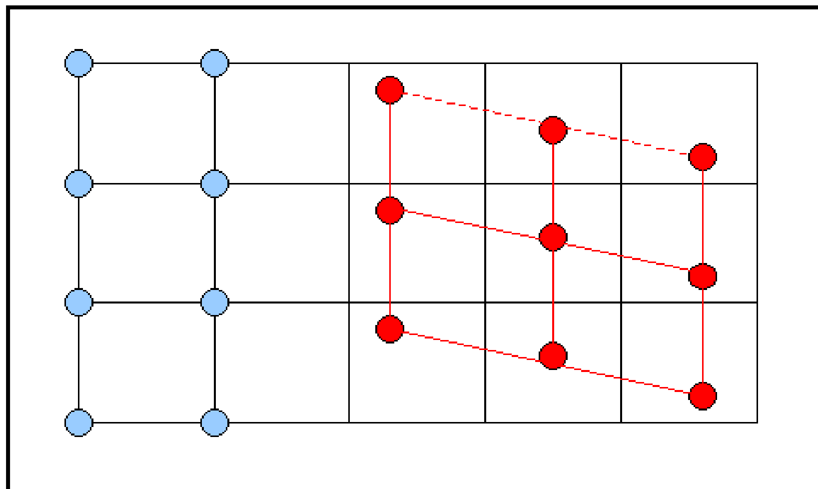


Figure 2.5 Effect of Twinning on Lattice Structure

Twinning generally occurs in the absence of sufficient number of independent slip systems. Deformation twinning can be characterized by high rates and the evolution of

energy in the form of sound occurs. Twinning is observed as wide bands under the microscope as depicted in Figure 2.6 and Figure 2.7. These wide bands cannot be removed by polishing. Two kinds of twins are of interest to the metallurgists which includes:

- *Deformation* (or Mechanical) *Twins* which are most prevalent in close packed hexagonal metals (magnesium, zinc etc.) and iron with large amount of ferrite.
- *Annealing Twins* which are most prevalent in face centered cubic metals (aluminium, copper etc) and iron with austenite. Annealing Twins are generally observed in metals which have been previously worked and heat treated. The twins are formed because of a change in normal growth mechanism.

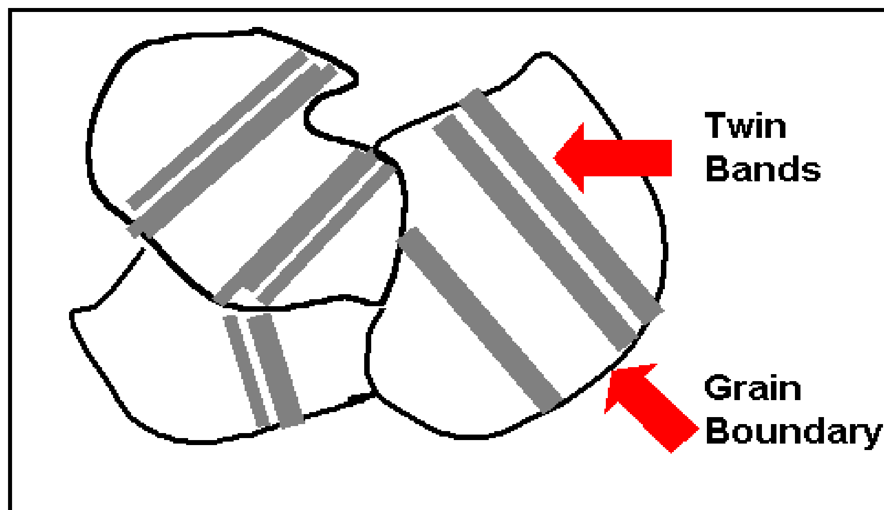


Figure 2.6 Twin bands

Figure 2.7 Twin Bands in Zinc

2.3.3 Stacking Fault

All crystals whose structures can be described by layers are prone to defect called Stacking Fault. Stacking fault is any defect that alters the periodic sequence of atomic layers. These defects affect the whole crystals or a finite region.

A stacking fault is a one or two layer interruption in the stacking sequence of the crystal structure. These interruptions carry certain stacking fault energy. The width of stacking fault is a consequence of the balance between the repulsive force between two partial dislocations on one hand and the attractive force due to surface tension of the stacking fault on the other hand. The equilibrium width is determined by the stacking fault energy (SFE). When the SFE is high, the dissociation of a perfect dislocation into two partial is unlikely and the material deforms only by dislocation glide. Lower SFE materials display wider stacking faults and have more difficulty for cross-slip and climb. The SFE modifies the ability of a dislocation in a crystal to glide onto an intersecting slip plane. When the SFE is low, the mobility of dislocations in a material decreases. Within FCC metals, close-packed atom layers are stacked in ordered ABC ABC ABC sequences. For HCP structure, the stacking sequence is given by AB AB AB. However errors or faults in the stacking sequence can be produced in most metals by plastic deformation. This is often produced by the dissociation of a unit dislocation of into two imperfect dislocations. This occurs to minimise the overall defect energy. The stacking-fault energy (SFE) is a material property on a very small scale. It is noted as γ_{SFE} in units of milli joules per square meter. Table 2.1 shows values of stacking fault energy of a few materials.

Table: 2.1 Stacking Fault Energy of Different Materials

Material	Stacking Fault Energy (SFE) , mJ/mm^2
Silver	25
Gold	50
Copper	80
Nickel	150
Aluminium	200
304 SS	18
316 SS	78

2.4 Strain Hardening

Strain hardening is the process of making a metal harder and stronger through plastic deformation. When a metal is plastically deformed, dislocations move and generation of additional dislocations or multiplication of dislocations takes place. Increase in density of dislocations within a material decreases the average distance between dislocations. It results in more interaction among them and they become pinned or tangled, blocking the motion of each one. Thus, of the dislocations decreases and an increasing stress is required to produce additional plastic deformation. Thus the metal apparently becomes stronger and more difficult to deform. This type of strengthening is commonly called cold-working. It is called cold-working because plastic deformation must occur at a temperature low enough that atoms cannot rearrange themselves. Strain hardening is coupled with other microstructural features such as development of preferred lattice orientation, formation of localized shear band, formation of sub grains and residual stress. The reorientation of grains during plastic straining can further increase the resistance to deformation.

2.5 Deformation Mechanism

Copper and its alloys being of FCC lattice structure are expected to deform by the movement of dislocations through slip. However, temperature, strain rate, and strain are important parameters which can affect the deformation mechanism from slip induced to twinning and hence the deformation microstructure of Copper and its alloys (Utyashev and Raab, 2007). Among the material properties, SFE is one of the most important factors for changes in the deformation microstructure in copper and its alloys (Sakai *et al*., 2007).

A specific feature of all these methods is the accumulation of large deformations in the material, which result in formation of fragments, whose sizes depend on the material nature and the deformation technique (Valiev and Aleksandrov *et al*., 2000).

2.5 1. Materials

The possibility of structure refinement in different metals, alloys, intermetallic compounds, and composite materials using Severe plastic Deformation (SPD) methods has been demonstrated in many studies. More complicated chemical and phase composition of the material higher the melting temperature of the material reduces the sizes of the fragments in it during deformation.

2.5.2. Temperature

To obtain extremely refined grains in metal, the deformation should be carried out at a temperature below the temperature of the onset of recrystallization. Therefore, the temperature conditions are chosen to be corresponding to cold deformation of metals; at the same time, the possibility of coarsening of the fragments formed due to deformation induced heating is noted.

2.5.3 Degree of Deformation

A number of studies have demonstrated the role of degree of deformation on grain refinement. It is observed that for a few initial passes (say 4 passes in ECAP pressing) with a true deformation degree ($\varepsilon > 1$), during each pass, sub micro-crystalline grains with size greater than 0.1μm get formed. With subsequent passes and thus accumulation of deformation, further grain refinement stops or decelerated. During deformation, energy is stored in the material mainly in the form of dislocations. This energy is released in three main processes, viz recovery, recrystallization, and grain coarsening.

- ***Recrystallization***

It is the formation of a new grain structure in a deformed material by the formation and migration of high angle grain boundaries driven by the stored energy of deformation. High angle grain boundaries are those which suffer greater than a 10–15° misorientation. The process of recrystallization of plastically deformed metals and alloys is of central importance in the processing of metallic alloys for two main reasons.

1. The first is to soften and restore the ductility of material hardened by low temperature deformation (that occurring below about 50% of the absolute melting temperature, $0.5T_m$).
2. The second is to control the grain structure of the final product.

- ***Recovery***

All annealing processes occurring in deformed materials that occur without the migration of a high angle grain boundary is called recovery. Typically, recovery processes involves the rearrangement of dislocations to lower their energy, for example by the formation of low-angle sub-grain boundaries.

- ***Grain Coarsening***

Grain coarsening can be defined as the process involving migration of grain boundaries when the driving force for migration is solely the reduction of the grain boundary area itself. Grain coarsening is the growth of the mean grain size driven by the reduction in grain boundary area. Coarsening can take place either by 'normal' grain growth, whose main mechanism is the disappearance of the smallest grains in the distribution, or 'abnormal' grain growth. The latter process involves growth of a few grains which become much larger than the average.

2.5.4. Strain Rate

An increase in strain rate activates dislocation slip and twinning. Therefore, an increase in this parameter can lead to the formation of smaller fragments due to the intensive formation of cells, blocks, and twins.

2.6 Crystallographic Features of Copper

Copper in its almost pure form is refined electrolytically to 99.9% purity. Copper melted under non-oxidizing conditions is called oxygen free copper. The most popular form of pure copper is the standard electrical wire grade of copper (C11000) which contains 99.95% Cu, 0.03% O_2, and less than 50 ppm of other metallic impurities. It has a high electrical conductivity, in excess of 100% IACS. In the as cast form, copper is called Electrolytic Tough Pitch (ETP) copper.

The structure of as-cast copper is dendritic in which cuprous oxide particles form a network, outlining the dendritic cells and pores, seen as dark spots in the microstructure. When the as-cast ETP copper is hot rolled, the structure is completely destroyed. The microstructure of hot rolled copper contains many small grains. Parallel straight lines extending across many of the grains are called annealing twins. They appear after the metal has been mechanically worked at high temperatures, called annealing, and deformed. The inter-dendritic network of cuprous oxide particles is destroyed by hot rolling.

Solid copper can be described as the arrangement of copper atoms in a Face-Centered-Cubic (FCC) configuration as shown in Figure 2.8. The atoms are held in place in the structure by the energy of the atomic attractions between them. It is this particular face-centered cubic arrangement of atoms which gives copper its high ductility and toughness.

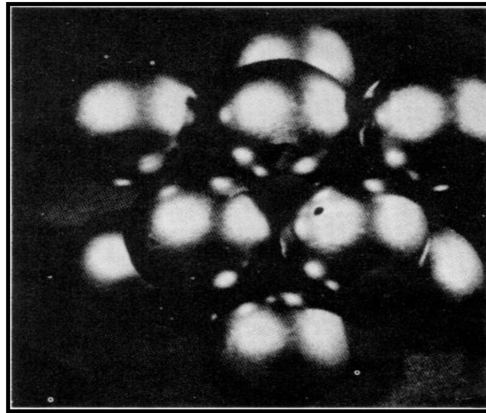


Fig. 2.8 Unit Cell of Copper

In the FCC structure of copper, the movement of atoms occurs preferentially in any or all of three directions along a specific geometric plane of atoms within the lattice. The copper cell has four such planes. If movement can occur in three directions on all four planes, there are twelve possibilities for the occurrence of slip. This is the maximum number of possibilities for slip found in any metal structure. Hence, copper has excellent ductility and toughness and is resistant to fatigue and creep. But the strength of copper is low. Nevertheless, there is a great interest in improving the mechanical properties of commercially available copper, so that materials could be better utilized in electrical conductors for railways and contactors of various microelectronic devices, mobile phones, etc.

The next section presents a detailed literature review with regards to work done by various researchers in improving the properties (combination of high strength and high electrical conductivity) of copper and its alloys.

2.7 Review of Literature

This section presents a detailed review of the existing academic writings for improving the strength and other properties of copper and its alloy by grain refining mechanisms:

Gupta S.P. (1975) studied the effect of thermal cycling on Cu-In alloys and reported that grain size was refined uniformly from 400 μm to 10 μm in one cycle. The technique has the potential to further reduce the grain size through repeated thermal cycling. A significant reduction in grain size was noticed after the fourth cycle. The refining of grain size during multi-cycle annealing has been attributed to the drag produced owing to clustering of solute atoms at dislocations.

Liu and Baker (1993) studied the dependence of recrystallization and stored energy on rolling strain in polycrystalline copper. Stored energy of cold work (E_{cw}), increased linearly with increasing strain until a saturation stored energy of cold work, (E_{sat}), was reached at a rolling reduction of about 96%. The increase in E_{cw} increasing strain produced a concomitant decrease in recrystallization temperature, T_R. However, once E_{sat} was attained increasing the rolling strain further did not lead to a further reduction in T_R.

Mandal and Baker (1995) observed values of the stored energy, microhardness and recrystallization temperature, as a function of depth for rolled polycrystalline copper. The study showed that stored energy decreases from the surface to the centre. The surface had greater stored energy per unit strain and thus a high rate of work hardening at low strain. The recrystallization temperature increased with increasing depth into specimen.

Ping *et al.* (1999) obtained a strip of microcrystalline Cu-Cr alloy by rapidly solidifying the material on a rotating cooled drum. After aging of the alloy at 500º C for 30 or 60 minutes, its strength and hardness increased but its electrical conductivity decreased. The deciding factor in the increase of strength and hardness after aging was the occurrence of coherent dispersion-hardening. Aging resulted in a 160 percent increase in micro-hardness. 27 percent of the increase was due to grain refinement and 73 percent was attributed to coherent dispersion-hardening.

Vinogradov *et al.* (2001) investigated the structure, thermal stability and properties of a Cu–Cr–Zr alloy with Ultra fine grains (of 160 nm) diameter produced by severe plastic deformation. It showed that post-ECAP aging makes the precipitation hardened ultra-fine grained structures remain stable under both thermal and mechanical influence under cyclic loading. Substantial improvement of fatigue life was evidenced in comparison with conventional coarse-grained materials. Strengthening mechanisms resulting from a combination of intensive cold work through ECAP and subsequent aging showed advantage to successfully produce materials with desired electro-mechanical properties (including sufficient ductility for forming and adequate resistance to fatigue loading).

Nokhrin *et al.* (2003) investigated the temperature at which recrystallization initiated in microcrystalline copper. Copper was obtained by equal channel angular pressing at room temperature with the use of 4 cycles, 8, 12 and 16 cycles respectively. After 12 cycles of pressing, the recrystallization temperature rose to 180º C from 110º C recorded with 4

cycles. However the recrystallization temperature turned out to be lower i.e. 150°C when the number of pressing cycles was increased to 16. The decrease in recrystallization temperature with a change in number of cycles from 12 to 16 was attributed to an increase in the density of defects introduced into the material and their effect on the activation energy for grain boundary diffusion.

Nestorovic *et al.* (2003) investigated the degree of deformation in rolling on anneal hardening effect of a cast copper alloy containing 8 percent aluminium. The alloys, and pure copper for the sake of comparison, were subjected to cold rolling with a final reduction of 30, 50 or 70%. The cold rolled copper and copper alloy samples were isochronally and isothermally annealed up to the recrystallization temperature. It was observed that, aluminium, as an alloying element has a pronounced effect on the increase in the recrystallization temperature of copper. Anneal hardening effect was observed in the alloy in the temperature range 180–300°C, followed by an increase in the electrical conductivity. The amount of strengthening increases with increasing degree of prior cold work.

Zhu *et al.* (2006) studied the effects of annealing process on electrical conductivity and mechanical properties of Cu-Te alloys. The results showed that recrystallization and precipitation occurred simultaneously during the annealing process. Tellurium precipitates in the form of Cu_2Te as a secondary phase. The grain size increased with the increasing of annealing temperature and time. Firstly, tellurium dissolved in copper and improved the recrystallization temperature of copper. Meanwhile, the solute atoms congregated near the dislocations, blocked the diffusion of vacancies and, thus the recrystallization grains of Cu-Te alloys appeared to be smaller than that of pure copper. With increase in the annealing temperature, recrystallization occurred, and then the density of dislocations decreased and the deformations recovered. At the same time, some added elements precipitated as the secondary phase. This blocked the rearrangement of dislocations and movement of sub-grain boundary, leading to formation of high density areas of dislocation near the precipitation. These actions favoured the recrystallization nucleation. On the condition that annealing temperature is higher and time is longer, the recrystallization and precipitation of Cu-Te alloys continued, recrystallization grains grew up. The reduction of dislocation density and bigger grains made the scatter to electrons decrease, thus the electrical conductivity increased. Also the precipitated second phase strengthened the Cu-

Te alloy during recrystallization process, and thus tensile strength of Cu-Te alloys was reported to be higher than that of pure copper.

Hui *et al*. (2006) investigated the effects of different extrusion ratios and different extrusion temperatures (100°C to 600°C) on microstructures and properties of submicron crystalline Cu-5%Cr alloy. Most part of the microstructure of as-extruded Cu-5%Cr was sub-crystalline produced by dynamic recovery, only a few recrystallized existed, and the average size of these grains was not larger than 400 nm. With extrusion temperature rising, the tensile strength and micro-hardness of Cu-5%Cr decreased, and elongation increased gradually. It was very difficult for Cr particles to produce large deformation during extrusion, and only very small deformation was produced in Cr phase. The possibility of recovery and recrystallization of Cr phase was very small because the extruding time was very short, not more than 10 s, and then cooled to room temperature rapidly. However, the recovery temperature and recrystallization temperature of Cu was very low, so the dynamic recovery and dynamic recrystallization of Cu-5%Cr produced during extrusion were mostly produced in Cu matrix.

Xiong *et al*. (2007) studied the microstructures and properties of sub-microcrystalline Cu-5%Cr alloy after cold drawing and subsequent annealing. The results showed that, the microstructure of submicron crystalline Cu-5%Cr alloy could be further refined by cold drawing. After cold drawing, the grains of this alloy reduced from a grain size of 400-500 nm to 100-200 nm. Dislocation glide was reported as still the main mechanism in plastic deformation of submicron crystalline Cu-5%Cr, but grain boundary slide and diffusion may play more and more important roles with drawing deformation increasing. When the cold drawn Cu-5%Cr wires were annealed at 550° C, fine recrystal grains with grain size of 200-300 nm were obtained. Furthermore, there were lots of fine Cr particles precipitated during annealing, by which the recrystallization softening temperatures of the cold drawn Cu-5%Cr wires could be increased to 480-560° C. Due to the fact that Cr particles have the effect of restricting Cu grain growth, a favourable structural thermal stability of the submicron crystalline Cu-5%Cr can be achieved, and the submicron grained microstructure can be retained at even high temperature annealing.

Kazeminezhad M. (2008) proposed a model modified by using Turnbull–Fisher nucleation rate model to simulate the ultra-fine microstructure evolution during annealing of pure copper processed by equal channel angular pressing (ECAP). The simulation was

utilized to predict the grain size of pure copper samples at different annealing temperatures and different pass numbers of ECAP. A good agreement was achieved between the simulation results and experimental data. The results of simulation showed that the grain size of samples processed by ECAP increased with increasing the annealing temperature. Also, at a constant annealing temperature and time, the grain size decreased with increasing the pass number of ECAP.

Hosseini *et al.* (2009) studied the microstructure, mechanical properties and electrical conductivity of commercial pure copper strips processed by accumulative roll-bonding. The strips produced by eight cycles of accumulative roll-bonding process showed ultra-fine grains (180 nm in size) with high angle grain boundaries. Also tensile strength and micro-hardness of the accumulative roll-bonding processed samples increased with increasing the number of accumulative roll-bonding cycles. However, the elongation dropped abruptly at the first cycle, above which it increased slightly. The electrical conductivity decreased with increasing accumulative roll-bonding cycles up to six cycles and then increased up to eight cycles of accumulative roll-bonding process. For the specimen after six cycles, dislocation density increased, while, density in cells decreased and the cell size became finer. The fraction of the ultra-fine grained regions increased with increasing the number of ARB cycles, i.e. strain. The specimen, after eight cycles, was filled with the ultra-fine grains with average grain size of 180 nm, homogenously distributed. On the other hand, as the number of ARB passes increased, temperature increase was observed in the work piece in the 7th and 8th passes. The strength of ARB-processed copper increased with increasing the accumulative strain.

Sakai *et al.* (2009) studied the evolution mechanisms of new high-angle boundaries as well as ultrafine grains at large strains in FCC metals during severe plastic deformation. Investigations were carried out by means of Multidirectional Forging (MDF) on pure copper at low temperature. The structural changes were characterized by evolution of deformation bands such as micro shear bands at moderate strains. Dynamic recovery operated as the main restoration process. The misorientations between (sub) grains increased gradually with increasing cumulative strain, finally leading to the development of a new fine-grained structure. In other words, the temperature effect on the development of high-angle boundaries was negligibly small at an early deformation. This is purely strain-induced and athermal phenomenon that is associated with a grain fragmentation by

cold working. On the other hand, the average misorientations that developed at strains above 2.0 were remarkably affected by processing temperature. Increasing temperature accelerated full release of internal stresses evolved by prior plastic working and promoted dislocation rearrangement in the interiors of microshear band intersections. This resulted in the formation of perfect grain boundaries. The strain-induced grain formation during SPD resulted from not only the dynamic formation of high-angle boundaries at lower strains (i.e. which was an athermal process), but also the frequent operation of dynamic recovery in the regions of new grains at large strains (i.e. which is a thermal process).

Takata *et al.* (2009) studied the microstructure of ARB processed Cu alloys. The structure of alloys were quantitatively characterized by electron back scattering diffraction (EBSD) technique for clarifying the formation process of UFG microstructures during the ARB. Extremely high densities of lattice defects, especially grain boundaries, were introduced into the SPD processed materials. The mechanical properties and electrical conductivity of the ARB processed Cu alloys were also investigated. A large driving force for recrystallization corresponding to high density of lattice defects (mainly dislocations) accumulated due to the SPD. The strength increased significant during the initial (up to 5 cycles) ARB process and then nearly saturated after higher ARB cycles. Especially, the strength of DLP alloy reached 472 MPa after 8 ARB cycles, which was nearly three times higher than that of the starting materials with conventional grain size. The electrical conductivity slightly decreased with increasing the number of ARB cycles, but the decrease in electric conductivity was very small (decrease was limited to a max of 4% of IACS). The electric conductivity decreased and strength increased with decreasing of grain size. The electric conductivity of pure Cu nearly kept a constant value over 95 IACS% till the grain size decreased down to 200 nm. When the grain size became smaller than 100 nm, the electron conductivity significantly decreased. In contrast, the yield strength continuously increased with decreasing the grain size down to 30 nm but resulted in poor uniform elongation. Thus UFG Cu alloys with sub-micrometer grain sizes can achieve both superior mechanical properties and high electrical conductivity.

Nestrovic and Markovic (2010) studied the influence of thermal cycling treatment on the anneal hardening effect in Cu-10 Zn alloys. Zinc as an alloying element has a pronounced effect on the increase in recrystallization temperature of Cu-10 Zn alloy, in comparison to pure copper. The solution treated plates were subjected to a final reduction

of 20, 40, & 60 percent by cold rolling, the final thickness of all samples being same. This was followed by annealing with and without thermo cycling treatment below the recrystallization temperature. Samples were subjected to thermal cycling in the temperature range between 150-500º C. The heating and cooling rates were 10°C/s. Specimens were subjected to three cycles during the process. Anneal hardening effect was observed in samples and was followed by an increase in the hardness and electrical conductivity. It was found that amount of strengthening increases with increasing the degree of prior cold working. The electrical conductivity of TC and simple annealed samples remained unchanged up to 200°C and then started to increase due to anneal-hardening effect. Thermal cycling treatment had more pronounced influence on anneal hardening than only the annealing treatment.

Nestorovic and Markovic (2010) investigated the influence of thermomechanical treatment on the hardening mechanisms and structural changes of cast Cu alloy for the hardness and electrical conductivity measurements. The hardness of all samples increased with an increase in the percent of reduction and it was attributed to the deformation hardening. The increase in hardness was attributed to increases in both the dislocation density and the grain boundary density caused by the cold work. The electrical conductivity of pure copper was higher than that for a Cu–6.6Ag alloy, and the conductivity of both samples decreased similarly with the increased deformation degree due to the increase of electronic scattering from lattice distortion or internal fault structure. After annealing above 450°C, the hardness considerably decreased but the electrical conductivity increased due to recovery and recrystallization. Thus the study showed that anneal hardening effect appeared on the cast Cu–6.6 Ag alloy in the temperature range of (160–400°C) and was followed by an increase in the hardness and electrical conductivity. The analysis of obtained results confirms the higher hardness for the Cu–6.6Ag alloy than for pure copper.

Mousavi and Bahadori (2011) studied the effects of post annealing on the mechanical properties, the microstructure and the texture evolutions in 99.96% copper under SPD processing by twist extrusion process (TE). SEM micrographs illustrated that annealed material contained new formed grains that could not grow due to lack of sufficient time.

2.8 Gaps in Literature

From the literature review, it is well understood that grain size has an important influence on the mechanical properties of polycrystalline materials. Most metals are polycrystalline, meaning they are made up of many small crystalline grains, each with the same structure but oriented in random directions. Researchers have long known they could make polycrystalline materials stronger by reducing the size of the grains to a few hundred nanometres. But similar to the effects of worked metals, smaller grains reduce the metal's ductility. After studying the literature, it can be concluded that the last few years have seen a major effort devoted to the investigation of copper based alloys in search for improvements in properties such as high strength in combination with good ductility, high conductivity and thermal stability at high temperatures. The work carried out by different researchers in the said area can be categorised into the following broad classes:

- Some investigators have studied the role of severe plastic deformation in producing ultra fine grained microstructure in copper and its alloys which leads to desired properties (high strength and high hardness). Most of the work in this category has focussed on explaining the mechanisms involved during plastic working and microstructures obtained during various deformation techniques.
- Few researchers have reported about the temperature ranges at which dynamic recovery and recrystallization initiates in microcrystalline copper. The effect of these process on microstructure and properties of copper alloys have been discussed. Some studies researchers have investigated the effect of strain path on structure and mechanical behaviour of ultra fine grained copper alloys.
- Many investigators have studied the effect of thermo-mechanical processing on copper alloys and have reported that these processes have specific practical importance. A few studies some have simulated the ultrafine grained microstructure evolution during annealing of metal processed by severe plastic deformation and have compared the results with experimental findings.
- Very limited literature is available on the annealing hardening process as a means of achieving grain refinement in copper alloys. Very few studies have reported the kinetics of recrystallization in the presence of secondary phases and its influence on electrical (mainly electrical conductivity) and mechanical properties of copper alloys.
- Most of the researchers have concentrated on Cu-Al, Cu-Ag, Cu-Au, Cu-Cr alloys and Cu-Sn alloys but very less literature is available on pure copper.

Despite considerable research in the area, there is a lack of literature available on processing of thermal cycling in pure copper. No literature has been reported which investigate the electrical conductivity of thermal cycling processed ultrafine grained copper.

Based on the literature survey and subsequent analysis of gap, the present work aims to investigate the effect of thermal cycling on various properties of copper. The present study focuses on the mechanical properties and electrical conductivity of thermal cycling processed pure copper. The correlation between microstructural parameters and mechanical and electrical properties of thermal cycling processed pure copper is discussed. The aim of the study is to assess the influence of thermal cycling treatment on recrystallization kinetics. Also the prediction of recrystallization behaviour when only the deformation strain and the recrystallization temperature are known. The boundary mobility and the driving force, as well as the nucleation density, are related to the true plastic strain of deformation through the microstructure also discuss in the present work.

CHAPTER 3
DESIGN OF THE STUDY

3.1 Introduction

This chapter presents overall design of the study which includes methodology adopted for carrying out the research work, the detail of work to be done in each phase and the tool and techniques to be used for analysis. The chapter also discusses objective of the study and experimental procedure to be followed to meet the objective function.

3.2 Methodology

The methodology involves identification of controllable and uncontrollable parameters and establishment of a series of experiments to find out the optimum combination of parameters which have greatest influence on the objective function and least variation from the designed target. The study involves selection of input parameters in the process of forming ultrafine/nano grains and determining the contribution of each parameter. The work has been carried out in three main phases.

Phase-I Preliminary phase aimed at study of recrystallization and grain growth phenomenon and the effect of various controlling factors on the process. All the analytical calculation such as dislocation density, recrystallization fraction calculations have been done in this phase. The result of preliminary study has been used to identify the appropriate range of working temperature and holding time during the process.

Phase-II Detailed study of the controlling parameters of the process. This includes experimental details, set up information, operating range of process parameters, description of kinetics involved and results drawn from experiments. For selecting various process parameters, a detailed study of each parameter from the previous researchers has been done.

Phase-III Analysis of all theoretical calculated values with experimental data and validation of result. Finally, the main conclusions to be drawn from the present research work are discussed.

3.3 Establishment of Objective Function

The objective of the present research is to study and understand the effect of cold deformation and repetitive thermal cycling on the microstructure and properties (strength and electrical conductivity) of commercial pure copper. This also enables to examine the deformation related issues in the plastic deformation regime. Further, the work tends to explore the effect of stresses on the kinetics of recrystallization. Since no work has been reported in the existing literature on the anisothermal recrystallization and coursing behavior of pure copper, the objective of the present study is to clarify the kinetics of recrystallization and grain growth in copper. The work proposes a new approach for microstructure refinement through rapid heating and cooling of pre-deformed copper.

The various key issues to be taken up during the research work as follows:

- Effect of cold rolling and annealing on the grain size of the copper.
- Effect of cold rolling and annealing on the electrical conductivity of the nano structured copper.
- To study the stress-induced recrystallization mechanism for grain refinement.
- Effect of cold rolling and annealing on the mechanical property of the copper.
- Kinetics of recrystallization in the absence of secondary phases.

The overall objective of the study is to report the effect of thermal cycling process on heavily cold rolled copper. First, dislocation density has been calculated for a selected percent of thickness reduction samples and after that recrystallization fraction has been determined for different annealing processes. After finalizing the temperature and time values for thermal cycling process, the effect on grain refinement was analysed. The primary aim of the present work is the formation of ultrafine/ nano grains in pure copper by using thermal cycling process.

3.4 Material Selection

As received hot rolled commercially pure copper was selected for the present study. The copper plates were solution treated at 600º C for 1 hour with subsequent quenching in water to achieve chemical homogeneity.

3.5 Experimental Setup

The experimental set-up involves the use of various machines and equipment for cutting, cold rolling, annealing and cleaning of samples. The testing equipment were used to

measure the properties of material like hardness, tensile strength and electrical resistivity. This also includes different material characterization techniques used for grain size measurement, phase identification and microstructural evaluation.

3.5.1 Machine and Testing Equipments

The machine and testing equipments were used to perform experiments and measurement of results which are described as follows:

3.5.1.1 Cold Rolling Mill

Multi pass unidirectional cold rolling with same thickness reduction per pass has been performed in a two-high rolling mill under oil lubrication. Cold reduction was carried out with inter-pass cooling. Inter-pass cooling was performed by quenching the specimen in cold water kept at room temperature after each pass. The setup of two-high rolling mill for thickness reduction is shown in Figure 3.1.

Figure 3.1 Two-Hi Rolling Mill

3.5.1.2 Precision Cutter

A precision cutter (Make: Metkon Microcut 125 Low speed) is a compact, multipurpose, precision saw designed to cut a wide variety of materials with minimal subsurface damage as shown in Figure 3.2. The sample is mounted to a sample holder and attached to the arm. An appropriate load is applied by adjusting the counterbalancing weight and the automatic stop switch is set. The sample is positioned in any starting position relative to the diamond wheel and then a micrometer is used for precise sample positioning. With the diamond wheel rotating slowly and coolant in the reservoir, the arm is gently lowered until the sample touches the diamond wheel. Cutting continues until the automatic cutoff switch is triggered.

Figure 3.2 Low Speed Precision Cutter

3.5.1.3 Muffle Furnace

The muffle furnace is usually a front-loading box-type oven or kiln used for high-temperature applications. The outer body is made of mild steel sheet. The inner chamber is made of stainless steel and heaters are clamped to its outside and operated at low heat. Glass wool insulation is used between the two walls. Temperature control is provided by a capillary thermostat which possesses excellent durability and accuracy. Heaters are made of 80/20 nichrome wire, uniformly wound on the muffle.

Figure 3.3 Muffule Furnace

A safety thermal fuse is provided to fuse, when the temperature exceeds the set temperature. A control box is fitted on the right side of the furnace and consists of indicating lamps, On/Off switch, contactor and digital temperature controller along with Cr/Al thermocouple sensor. The furnace is electrically operated at 230 Volts (AC), Single Phase, 50 Hz supply. The muffle furnace used in the present study is shown in Figure 3.3.

3.5.1.4 Ultrasonic Cleaner

Ultrasonic cleaning uses high frequency sound waves (usually from 20–400 KHz) to agitate an appropriate cleaning solvent (sometimes ordinary tap water). Cavitations bubbles induced by the agitation act on contaminants adhering to metal surface. This action also penetrates into blind holes, cracks, and recesses.

Figure 3.4 Ultrasonic Cleaner

The intention is to thoroughly remove all traces of contamination tightly adhering or embedded onto solid surfaces. Water or other solvents can be used, depending on the type of contamination and the work piece. Contaminants can include dust, dirt, oil, pigments, grease, polishing compounds, flux agents, fingerprints, soot wax etc. In an ultrasonic cleaner, the object to be cleaned is placed in a chamber containing a suitable solution as shown in Figure 3.4.

3.5.1.5 Vickers Micro Hardness Testing Machine

Micro-hardness is primarily determined with Vickers indenters under test loads in the range of 1 to 1000 gram-force and is used to measure the hardness of specific phases, small particles and brittle materials. Vickers Hardness Number is obtained by dividing the applied load in kilogram-force by the surface area of indentation. The area of indentation produced from the Vickers square-based pyramidal diamond is determined by the mean distance between the two diagonals of the indentation. Figure 3.5 shows the Vickers Micro-hardness testing machine (Make: Leica VMHT Auto) which is used to take micro-hardness with a low load of 25 gram-force. The dwell time and indenter speed are to be taken as 15 second and 30 μm/sec respectively.

Figure 3.5 Vickers Micro-hardness Tester

3.5.1.6 Tensile Testing Machine

The primary use of tensile testing machine is to create the stress-strain diagram. After the diagram is generated, a pencil and straight edge or computer algorithm can be used to calculate yield strength, young’s modulus, tensile strength or total elongation. For most materials, the initial resistance to force, or modulus, and the point of permanent deformation, is obtained from plots of force against elongation. The setup of tensile testing machine is shown in Figure 3.6.

Figure 3.6 Tensile Testing Machine

3.5.1.7 Electrical Resistivity Measuring Machine

Thermo Electrical Resistivity Machine (Model No: TER- 2000 RH ULVAC-RIKO) was used to measure the electrical resistivity of copper sample. The sample was cut to very thin section of required length for measurement. The average of 10 readings were taken in order to ensure reproducibility of results. The setup for electrical resistivity measuring machine is shown in Figure 3.7.

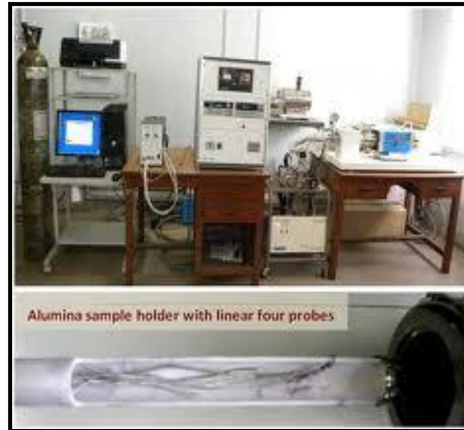


Figure 3.7 Thermo-Electrical Resistivity Measuring Machine

3.6 Experimental Procedure

The experimental procedure involves main steps as follows:

3.6.1 Cutting and Sizing

First of all, samples were cut as per size required for rolling. Initially, the thickness of copper plate was taken as 6mm which was further reduced up to 90% thickness reduction. A suitable length of copper strips was taken because the length of strips increases during rolling or thickness reduction. Manually operated hacksaw was used for cutting of samples.

3.6.2 Cold Rolling

The samples were brought to the rolling mill after sizing according to dimensions. A two-hi rolling mill was used for required thickness reduction of samples. Multi pass unidirectional cold rolling was done with same thickness reduction in each pass. The intermediate cooling cycle was used to bring the temperature lower after each pass. This process was done by simple quenching of samples in water. The samples were cold rolled from 30% to 90% thickness reduction in steps of 10 %.

3.6.3 Thermal Cycling

The thermal cycling process was given to sample having 90 percent thickness reduction because of high dislocation density and strain energy stored in it. Thermal cycling process was subjected to anisothermal annealing with short holding time. A holding time which is slightly larger than the estimated time was selected for the cycle annealing. This was to ensure that the equilibrium temperature reaches throughout the specimen thickness.

During the heating cycle, the specimen has been charged into the furnace after the desired temperature was achieved. The cooling cycle was consisting of water quenching after the isothermal holding time. Thus the thermal cycle was comprised of the heating cycle, isothermal annealing and finally quenching in water.

3.6.4 Sample Preparation for Metallography

After thermal cycling process, samples were cut and prepared for metallographic study. To prepare a sample for material characterization, the basic steps to be followed include: sectioning and cutting, mounting, planar grinding, rough polishing, final polishing, etching, and microscopic analysis. These steps are described as follows:

3.6.4.1 Sectioning and Cutting

All metallographic samples need to be sectioned to the area of interest and for easier handling. Depending upon the material, the sectioning operation can be obtained by abrasive cutting (metals and metal matrix composites), diamond wafer cutting (ceramics, electronics, biomaterials, minerals), or thin sectioning with a microtome (plastics).

Figure 3.8 Cutting Machine

Proper sectioning is required to minimize damage, which may alter the microstructure and produce false metallographic characterization. Proper cutting requires the correct selection of abrasive type, bonding, and size; as well as proper cutting speed, load and coolant. The machine used for sectioning and cutting is shown in Figure 3.8.

3.6.4.2 Mounting

Mounting of specimens is usually necessary to allow them to be handled easily. It also minimizes the amount of damage likely to be caused to the specimen itself. The mounting material used should not influence the specimen as a result of chemical reaction or

mechanical stresses. It should adhere well to the specimen, and if the specimen is to be electropolished later in the preparation then the mounting material should also be electrically conducting. Specimens can be hot mounted (about 150°C) using a mounting press either in a thermosetting plastic, e.g. phenolic resin, or a thermo-softening plastic e.g. acrylic resin. If hot mounting can alter the structure of the specimen a cold-setting resin can be used, e.g. epoxy, acrylic or polyester resin. A mounted specimen usually has a thickness of about half its diameter, to prevent rocking during grinding and polishing. The edges of the mounted specimen should also be rounded to minimize the damage to grinding and polishing discs. The mounting press and the mounted sample are presented in Figure 3.9 and 3.10 respectively.

Figure 3.9 Mounting Press

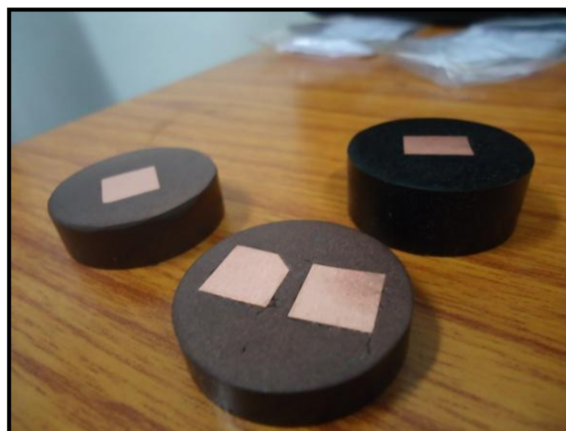


Figure 3.10 Mounted Samples

3.6.4.3 Grinding

Grinding is required to planarize the specimen and to reduce the damage created by sectioning. The planar grinding step is accomplished by decreasing the abrasive grit/ particle size sequentially to obtain surface finishes that are ready for polishing. The coarseness of the paper is indicated by a number: the number of grains of silicon carbide per square inch, e.g. 180 grit paper is coarser than 1200 grit. The grinding procedure involves several stages, using a finer paper (higher number) each time. Each grinding stage removes the scratches from the previous coarser paper. This can be easily achieved by orienting the specimen perpendicular to the previous scratches. Between each grade the specimen is washed thoroughly with soapy water to prevent contamination from coarser grit present on the specimen surface. Typically, the finest grade of paper used is the 2000 grit. The rotary grinding machine is used in the present experimental work is shown in Figure 3.11.

Figure 3.11 Rotary Grinding Machine

3.6.4.4 Polishing

Polishing discs are covered with soft cloth impregnated with abrasive diamond particles and an oily lubricant or water lubricant. Particles of two different grades are used: a coarser polish - typically with diamond particles of 6 microns diameter for removing the scratches produced from the finest grinding stage, and a finer polish – typically with diamond particles of 1 micron in diameter, to produce a smooth surface. Before using a finer polishing wheel, the specimen should be washed thoroughly with warm soapy water followed by alcohol to prevent contamination of the disc. The drying can be made quicker using a hot air drier. Mechanical polishing will always leave a layer of disturbed material on the surface of the specimen. Electro-polishing or chemical polishing can be used to

remove this, leaving an undisturbed surface. Figure 3.12 shows the polishing machine used in the present work.

Figure 3.12 Polishing Machine

3.6.4.5 Etching

Etching is used to reveal the microstructure of the metal/alloy system through selective chemical attack. In alloys with more than one phase, etching creates contrast between different regions through differences in topography or the reflectivity of different phases. The rate of etching is affected by crystallographic orientation, so contrast is formed between grains, for example in pure metals. The reagent also preferentially etches high energy sites such as grain boundaries. This results in a surface relief that enables different crystal orientations, grain boundaries, phases and precipitates to be easily distinguished.

The specimen is etched using a reagent. For example, for etching stainless steel or copper and its alloys, a saturated aqueous solution of ferric chloride, containing a few drops of hydrochloric acid is used. This is applied using a cotton bud wiped over the surface a few of times (Care should be taken not to over-etch; however, this is a difficult point to determine). The specimen is immediately be washed in alcohol and dried. Following the etching process there may be numerous small pits present on the surface. These are etching pits caused by localized chemical attack, and in most cases they do not represent features of the microstructure. They may occur preferentially in regions of high local disorder, for example where there is a high concentration of dislocations. If the specimen is over etched, i.e., etched for too long, these pits tend to grow, and obscure the main features to be observed.

3.6.4.6 Leveling

Ideally the surface to be examined optically should be perfectly flat and level. If not, then as the viewing area is moved across the surface it will pass in and out of focus. In addition,

it will make it difficult to have the whole of the field of view in focus - while the centre is focused, the sides will be out of focus. By using a specimen levelling press (shown in Figure 3.13) this problem can be avoided, as it presses the mounted specimen into plasticene on a microscope slide, making it leveled. A small piece of paper or cloth covers the surface of the specimen to avoid scratching.

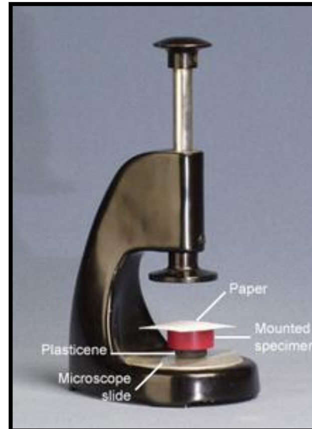


Figure 3.13 Levelling Machine

3.6.5 Microstructural Evaluation

The next step to be followed after metallographic sample preparation was to evaluate the microstructure with different material characterization techniques. Knowledge of the details of formation of microstructures is essential in order to understand the relationships between processing parameters and behaviour of materials in practical application. Since the most important technological properties are strongly influenced by microstructure and this understanding is important for the development of metallic materials. The various material characterization techniques which used in this study were described as follows:

3.6.5.1 Optical Microscopy

Metallic materials are usually opaque and therefore investigations of plane cross-sections by incident light prevail in metallography. However, the transparency of some metals and silicon to infrared light in thin sections has been effectively exploited. Optically, the individual components of a metallic alloy differ in their amplitude and phase characteristics. While amplitude objects become visible owing to differences in light absorption and thus appear in different grey shades or even colours, phase objects only differ in the refractive indices which cannot be recognized without additional provision. The preparation of cross-sections, the enhancement of contrast by etching and other

methods, as well as the microscopic set-up must be carefully optimized for the material under investigation and adjusted to the purpose of the investigation in order to get maximum information from a microscopic study. The optical microscope used in the study is shown in Figure 3.14.

Figure 3.14 Optical Microscope

3.6.5.2 X-ray Diffraction Technique

Considering that grain size is the most important microstructural parameter to describe nanocrystalline materials, various techniques have been proposed to experimentally measure the grain size, which include transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction. Among these XRD has unique advantages which includes, sample preparation and information from (XRD) a large area and has been widely used to determine an average grain size. For nanocrystalline materials, the microstructure has been shown to be inhomogeneous with a wide distribution in grain sizes.

Figure 3.15 XRD Machine

The single parameter of the average grain sizes appears to be insufficient to describe the microstructure features of nanocrystalline materials. The distribution range of grain size is important when considering the mechanical properties of nanocrystalline materials. In addition to grain size measurement, XRD technique has been recently developed to measure the dislocation density and type of crystal defects in nanocrystalline metals and thereby can provide valuable information on the deformation mechanism of nanocrystalline materials.

3.6.5.3 Electron Beam Scattered Diffraction

Electron beam scatter diffraction (EBSD) is a microstructural-crystallographic technique used to examine the crystallographic orientation of many materials, which can be used to elucidate texture or preferred orientation of any crystalline or polycrystalline material. EBSD can be used to index and identify the seven crystal systems, and as such it is applied to crystal orientation mapping, defect studies, phase identification, grain boundary and morphology studies, regional heterogeneity investigations, material discrimination and micro-strain mapping etc.

EBSD is conducted using a Scanning Electron Microscope (SEM) equipped with an EBSD detector containing at least a phosphor screen, compact lens and low light CCD camera. For an EBSD measurement, a flat/polished crystalline specimen is placed into the normal position in the SEM chamber, but is highly tilted (~70° from horizontal) towards the diffraction camera (to increase the contrast in the resultant electron backscatter diffraction pattern). The phosphor screen is located within the specimen chamber of the SEM at an angle of approximately 90° to the pole piece and is coupled to a compact lens which focuses the image from the phosphor screen onto the CCD camera.

3.6.6 Grain Size Measurement

The microstructures obtained through, transmission electron microscopy or optical microscopy was used to determine the average grain size. Microstructures were analyzed for recrystallization fraction and grain size determination by the *point count method* and *linear intercept method*, respectively.

3.6.7 Micro-Hardness Measurement

The micro-hardness measurements were taken of cold rolled sample and thermally cycled samples on the Vickers Hardness (HV) scale. The observed changes in hardness value were plotted on the graph. The different values of hardness were recorded by changing the

processing parameters. The average of minimum 10 readings was taken for micro-hardness to minimise the chance of error.

3.6.8 Tensile Property Evaluation

Flat tensile dogbone-shaped specimens of 25 mm gauge length as per the ASTM standard E-8M were machined from the as-received plate and from the thermally cycled specimens. Tensile tests were conducted at room temperature under displacement control at a strain rate of 1.3 x 10-4 sec-1 using Instron 8862 system of 100 kN capacity. Elongation was measured by an extensometer of 25 mm gauge length.

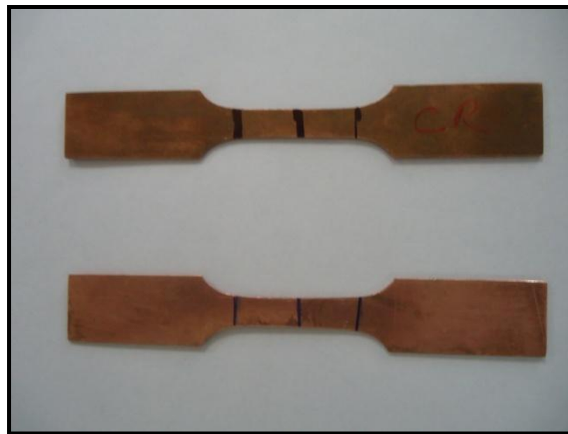


Figure 3.16 Tensile Testing Specimen

3.6.9 Electrical Resistivity Measurement

Copper is known for its good electrical conductivity. In the present work, resistivity measurement has been done in order to analyse the effect of thermal cycling process on electrical properties of copper. Thermo-Electrical Resistivity measuring machine has been used to measure resistivity parameter of copper sample.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Introduction

This chapter deals with the overall theoretical calculations done by using some empirical formulae and presents the results of various experiments performed on the basis of calculated values. Analytical investigation has been done in order to validate the result from experimental data. In this study, an attempt has been made to understand the thermal cycling process for heavily cold rolled copper and recrystallization behavior during the process. The study also explains the various factors influencing the grain refinement process.

4.2. Theoretical Calculations for Dislocation Density

Dislocation density increases with increasing the extent of cold deformation. New dislocations are created by cold deformation which interacts with those already existing in the material. Cold working induces dislocations in the strain free grains. The dislocation density is directly related with the stored strain energy in the material. The density of dislocations can be correlated with the amount of cold deformation and is represented by an empirical equation as below (Chia *et al.*, 2005)

$$\sigma = \sigma_o + \alpha G b \rho^{-1/2} \qquad \text{Equation 4.1}$$

where,

α = Constant value of order of 0.5

σ = Flow stress after cold deformation

σ_o = Initial flow stress

G = Shear modulus

b = Burger vector

ρ = Dislocation density

The dislocation density *(ρ)* generally increases with increase in true strain *(ε)*, and with decrease in grain size (d).

Further, flow stress (σ) is related to strain (t) as described by the relationship between flow stress and strain for many materials as given by *Ludwik relation* (Samuel and Rodriguez, 2005).

$$\sigma = K \, \varepsilon^{n}$$ Equation 4.2

However several researchers have observed deviations of the flow relation from the *Ludwik relation* for copper. Orwan, (1943) observed that yield stress would vary as the material deforms due to work hardening strain rate and temperature changes. Further, Freshwater (1995) Swift's stress strain law. This stress strain law for the yield function was adequate to demonstrate the versatility of newly formulated classical rolling solution for hot and cold rolling. Thus a wider range of function may be used to represent the yield stress characteristics as represented in Equation 4.3.

$$\sigma = \sigma_o \, (1 + B \, \varepsilon)^{n}$$ Equation 4.3

For the given values of σ_o, B and n for pure copper as determined by Freshwater (1995), the variation in true stress (σ) as a function of true strain (ε) were determined in the present work. The result is plotted in Figure 4.1. The graph does not show a linear relationship. The nonlinearity may be attributed to the work hardening of copper.

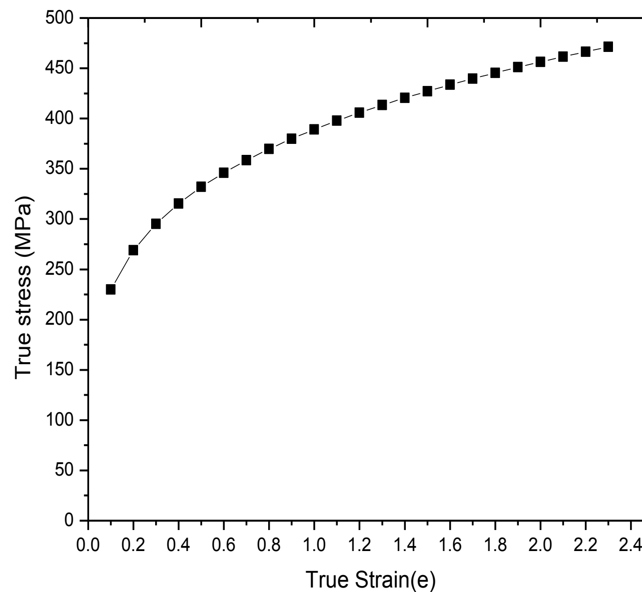


Figure 4.1 Stress- Strain Relationships

Figure 4.1 can be used to calculate the dislocation density from Equation 4.1 for a given stress level. The values of other parameters are taken as $\sigma_o = 70$ MPa, $\alpha = 0.5$, G = 40 GPa, b = 2.55Å (Raghavan, 2004).

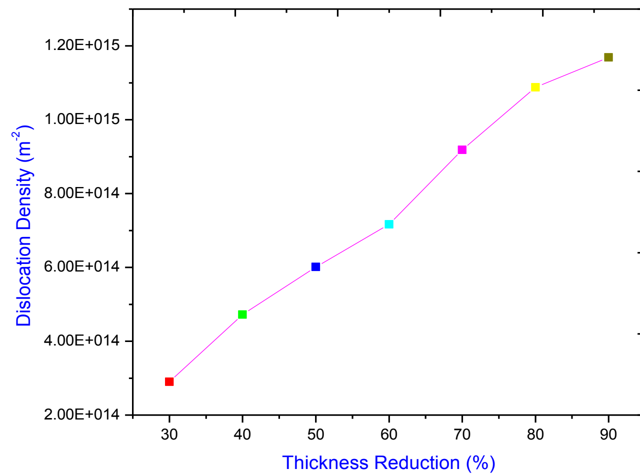


Figure 4.2 Variation of Dislocation Density

Figure 4.2 shows the variation of dislocation density with percent of cold reduction. There is an increase in dislocation density with increase in the extent of cold deformation.

4.3 Experimental Validation of Dislocation Density

Copper plates were cold rolled to different thickness reductions starting from 30 percent to 90 percent. Multi pass unidirectional cold rolling with same thickness reduction per pass was performed in a two-high rolling mill under oil lubrication. The macro hardness was measured on vickers scale. (Make: Reicherter Stiefel Mayer, VH-3) using a load of 5kgf for dwell time of 10s.

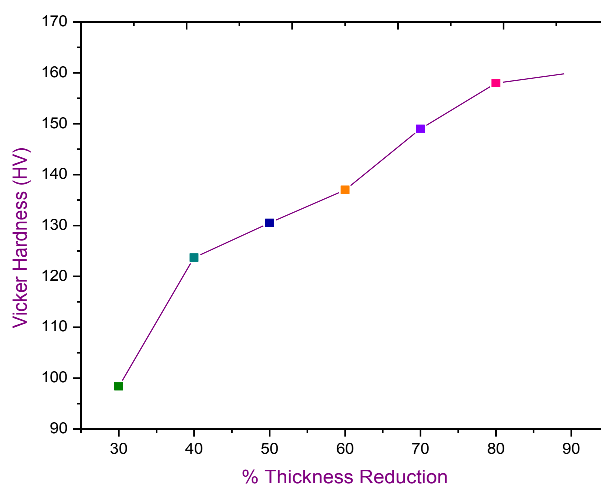


Figure 4.3 Variation of Hardness Value with Cold reduction

The average values of hardness (10 measurement for each specific condition were taken) were plotted against percentage of cold reduction as shown in Figure 4.3. It was well understood that when a material is cold worked, hardness of the material increases. A similar trend has been observed in the present work. As shown in Figure 4.3, the hardness value stabilizes at 90 percent reduction. This percentage of cold deformation has been selected as a suitable percentage for the present study.

The data pertaining to Figure 4.3 has been used to calculate dislocation density with percent of thickness reduction. The dislocation density is correlated with hardenss values by the Linear Bailey-Hirsch relationship (Narutani and Takamura, 1991) as presented in Equation 4.4.

$$HV\ [GPa] = 0.7 + 3 \times 10^{-8} \rho^{1/2} \qquad \text{Equation 4.4}$$

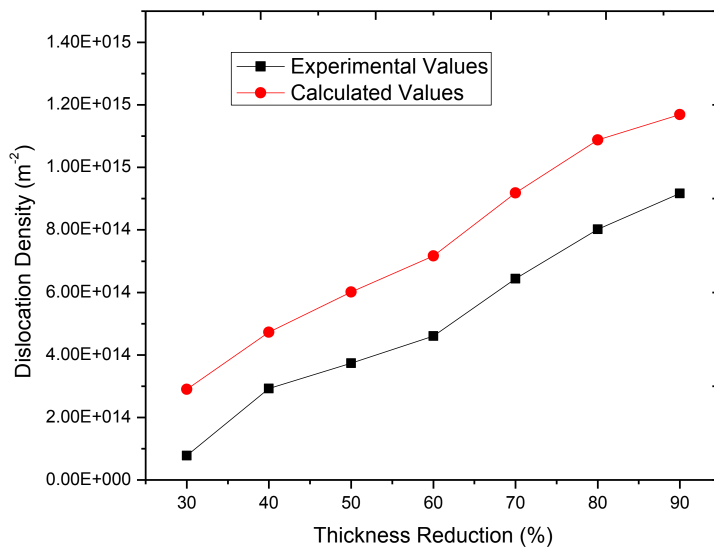


Figure 4.4 Relation of Dislocation Density with Thickness Reduction

Figure 4.4 shows the variation in dislocation density (ρ) with change in thickness reduction. The magnitudes of dislocation density (ρ) obtained from hardness plot (experimental data values) and calculated from Swift's stress strain relationship (calculated values) show a reasonable agreement.

4.4 Recrystallization and Grain Growth Kinetics

During recrystallization of deformed metals, some new dislocation free nuclei develop and grow by boundary migration until the entire deformed matrix is replaced by recrystallized grains. Many parameters affect the recrystallization process, the kinetics as well as the

recrystallized microstructure. The well studied parameters are the nucleation and grain growth phenomenon. These are discussed as follows:

4.4.1 Nucleation Density

Nuclei are assumed to be present at pre-existing high angle grain boundaries after deformation, and only the kinetics of grain boundary nucleated recrystallization is considered in the present work. Other potential nucleation sites, such as deformation bands and shear bands increase in significance when the deformation true strain becomes greater than 1.3. The probability of finding a critical sized subgrain on the grain boundary depends on the average sub grain size (r) and the unit volume grain boundary area (S_v). The nucleation site density, (N_v) in the grain boundary can be estimated using the expression given by Chen *et al*. (2002) as shown in Equation 4.5

$$N_v = C_d\, S_v/r^2 \qquad \text{Equation 4.5}$$

where, C_d is a calibration constant that determines the potency of the grain boundary as a nucleation site and is taken as 2.5x 10^{-4} (Chen *et al*., 2002).

Deformation can increase the nucleation site density for recrystallization through an increase in grain boundary area per unit volume (S_v) of the deformed structure. The value of S_v is dependent on the rolling strain and the initial grain size which varies with rolling strain in a manner described by the relation given by Chen *et al*. (2002) as in Equation 4.6.

$$S_V = \frac{1}{2d}[a+3a\sqrt{(1+2/a^2)} + 3\sqrt{(1+2/a^2)} + \sqrt{(2+2/a^2)}] \qquad \text{Equation 4.6}$$

and, $$a = e^{\varepsilon} \qquad \text{Equation 4.6 (a)}$$

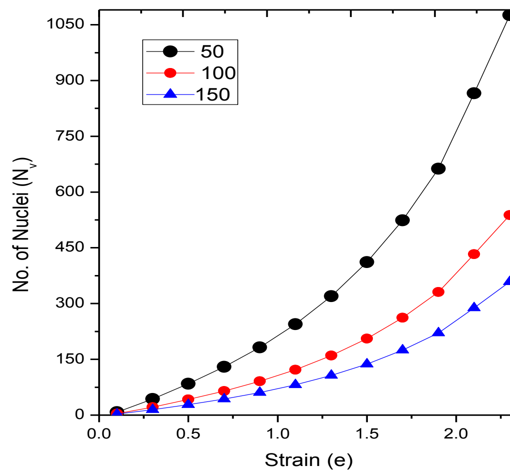


Figure 4.5 No. of Nuclei with Strain

Deformation strain in low stacking fault material is given by (Vatne *et al*., 1996) as shown in Equation 4.7.

$$r = 0.35 + 0.17/\varepsilon \qquad \text{Equation 4.7}$$

where,

ε = True strain for the rolling deformation.

Figure 4.5 shows the variation in nucleation density with changes in true strain for three different grain sizes. As the stain (ε) increases, the nucleation site density (N_v) increases significantly as a result of both an increase in S_v and a consequent decrease in r.

4.4.2 Growth Rate

The migration of low and high angle boundaries is the most important atomic scale mechanism that occurs during recovery and recrystallization of the deformed materials. The relation among rate of migration of the interface (V), driving pressure for boundaries with a specific energy (P) and mobility (M) moving into a uniformly deformed matrix is provided in Equation 4.8 as given by Chen *et al*. (2002)

$$V = M.P \qquad \text{Equation 4.8}$$

where, P is the driving pressure that is assumed to arise from the stored energy of the dislocations in the sub grain boundaries and in the sub grain interior. The mobility (M) of grain boundaries is temperature dependent and is usually found to obey an Arrhenius type relationship of the form Chen *et al*. (2002)

$$M = M_0 \exp (Q/ RT) \qquad \text{Equation 4.9}$$

The slope of the plot of ln (M) or ln (V) and critical again (1/T), for a constant (P) value yields the value of apparent activation energy (Q).

4.4.3 Recrystallized and Critical Grain Size

To determine the recrystallized grain size the relation as given by Di Schino *et al*., (2003) has been used as shown in Equation 4.10.

$$F_v = \frac{4}{3}\pi N \left(\frac{\varepsilon}{2\rho b}\right)^3 \qquad \text{Equation 4.10}$$

By assuming recrystallization fraction, F_v as 0.5, nucleation density (N) was calculated equal to 1.88 x 10^{16} for a dislocation density of 1.2 x 10^{15} m^{-2} and a burger vector equal to 2.55 Å. For this calculated nucleation density, the recrystallized grain size (d_{rex}) was calculated as per the relation given by Sellars and Zhu (2000) shown in Equation 4.11.

$$d_{rex} = A\, N_v^{-1/3} \qquad \text{Equation 4.11}$$

where, A is a geometric parameter to relate the surface linear intercept size and spatial diameter of grains and is equal to 2.347 (Sellars and Zhu, 2000). Recrystallized grain size was calculated as 0.1 μm.

As per Estrin *et al*. (1999), as long as the recrystallized grain size (d_{rex}), is smaller than the critical size (d_c), vacancy generation increases and thus reduces the overall driving force for grain growth. This result in a dramatic slows down in growth kinetics. The critical grain size has been calculated using Equation 4.12 (Krill *et al*., 2001).

$$d_c = 48N\,k\,T\,Z[(\delta V/A]^2 M/D \qquad \text{Equation 4.12}$$

where,

d_{rex} = Initial grain size

T = Annealing temperature

K = Boltzmann constant

γ = Grain boundary energy

D = Bulk diffusion coefficient

N = Number of atoms per unit volume

Z = Atomic coordination number

Using Equation 4.12, the critical grain size for pure copper was to be calculated 1μm. Hence, it was concluded that critical grain size for grain growth is bigger than ($d_{rex} < d_c$) that of calculated initial recrystallized grain size. This could result in retardation of grain growth kinetics after each thermal cycle.

4.4.4 Determination of Recrystallization Fraction by JMAK Relation

The recrystallization kinetics can be described by Johnson-Mehl-Avrami-Kolmogorov (JMAK) relation (Krishnan *et al*., 2006) which is based on the assumption that recrystallized nuclei form randomly in the already existing microstructure and that the growth rate of these nuclei is constant and isotropic. Krishnan *et al.* (2006) reported that accelerated recrystallization follows the JMAK type relation as given by Equation 4.13.

$$X = 1 - \exp[-(k\,t)^n] \qquad \text{Equation 4.13}$$

Where, X is the fraction recrystallized after time t, and the exponent n depends on the mechanism of recrystallization. In general, n takes a value of in the range $1 \leq n \leq 2$ for one-dimensional growth; $2 \leq n \leq 3$ for two-dimensional growth; and $3 \leq n \leq 4$ for three-

dimensional growth. For no change in mechanism, *n* is insensitive to temperature, whereas *k* is the temperature-dependent constant given by Equation 4.14.

$$k = k_0 \exp(-Q/RT) \qquad \text{Equation 4.14}$$

where k_0 is a constant, Q the activation energy, R the gas constant (R = 8.314472 J mol^{-1} K^{-1}) and T is the absolute annealing temperature. For pure copper, the activation energy was taken to be 55 KJ/mol as given by Benchabane *et al.* (2008). The value pre-exponential constant (k) and exponent (n) was calculated using the plot as shown in Figure 4.6.

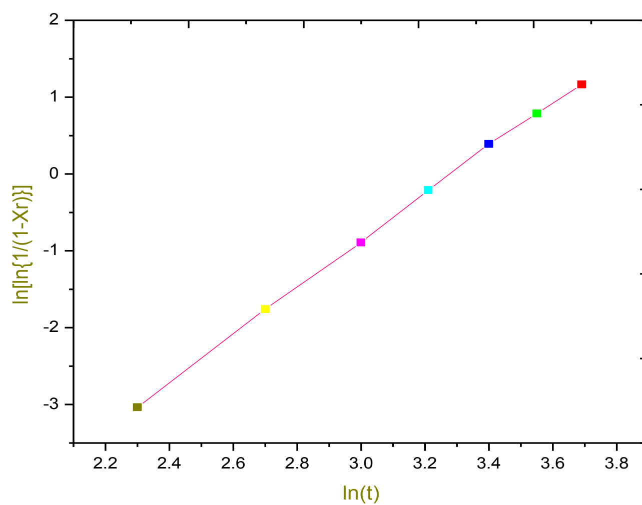


Figure 4.6 Pre-exponential Factor and Exponent of JMAK Equation

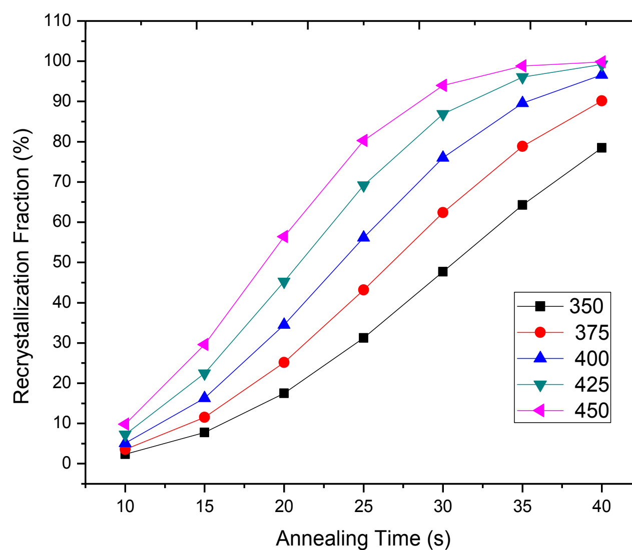


Figure 4.7 Recrystallization Fraction with Annealing Time

By putting the value of k in Equation 4.13, recrystallization fraction for different annealing time periods. (60, 50, 40, 30, 20, and 10 s) corresponding to different annealing temperature was determined. The variation of recrystallization fraction with change in annealing periods is depicted in Figure 4.7.

Figure 4.7 showed that recrystallization fraction increases with increase in annealing time. A higher temperature requires less time for complete recrystallization as compared to a lower temperature.

4.4.5 Determination of Recrystallization Fraction by Hardness Measurement

Recrystallization fraction of the cold worked copper was also determined by hardness measurements. The relation as given by Kumar *et al*, (2009) was used to determine the recrystallization fraction (F_v) for any given annealing time (t). The relationship is shown in Equation 4.15.

$$Fv = \frac{\delta(c)-\delta(t)}{\delta(c)-\delta(R)} \qquad \text{Equation 4.15}$$

where, $\delta(R)$ and $\delta(c)$ are the hardness of fully recrystallized and cold worked microstructure respectively. $\delta(t)$ is the hardness of the specimen after annealing for any given time (t). The boundary conditions δ (F_v =0) = $\delta(c)$ and δ (F_v =1) = $\delta(R)$ were used to determine the relation between recrystallization fraction and hardness.

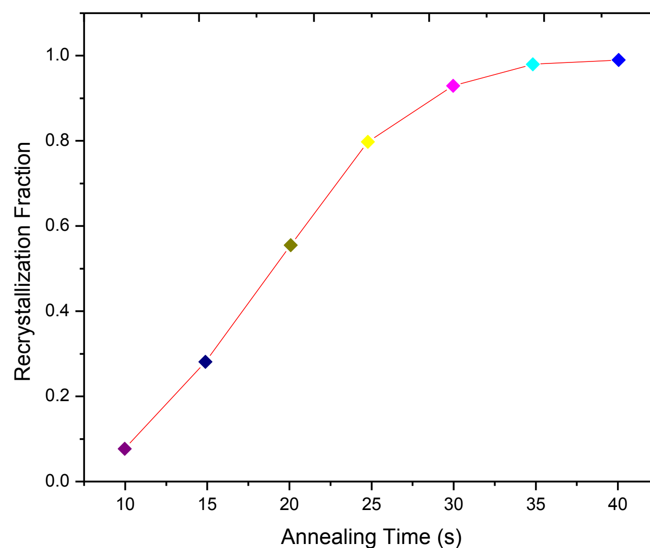


Figure 4.8 Recrystallization Fraction vs Annealing Time

The values of recrystallization fraction were plotted against the annealing periods at 450°C, as shown in Figure 4.8. The recrystallization fraction value showed by Figure 4.8 was similar to the calculated values for any annealing period as shown in Figure 4.7.

4.5 Driving Force for Recrystallization and Grain Growth

It is well known that the driving force for primary recrystallization in a metal is mainly related to the reduction of deformation energy introduced by cold working. The driving pressure (P_d) for recrystallization is provided by the dislocation density (ρ), which results in the stored energy (E_D) given by Equation 4.16. The resultant driving force for recrystallization is then given approximately as:

$$P_d \sim E_D = \alpha \rho G b^2 \qquad \text{Equation. 4.16}$$

Where, α is a constant of the order of 0.5, dislocation density (for 90 percent reduction) was calculated as 1.2×10^{15} /m^{-2}, shear modulus of rigidity of 40 GPa, and burger vector equal to 2.55 Å.

Substituting all the values in Equation 4.16, the driving force for the primary recrystallization was found to be 1.56 MPa.

On the other hand, the driving pressure for grain growth was calculated by grain boundary energy. When a spherical new grain of radius (R) is growing into the deformed structure, there is an opposing force (driving force) which comes from the curvature of a high angle grain boundary of specific energy γ. The grain boundary area gets reduced and the energy lowered if the grain were to shrink, and there is thus a retarding pressure on the boundary given by the Gibbs-Thomson relationship (Humphereys and Hathely, 2004). The relation is given as equation 4.17.

$$P_C = \frac{2\gamma}{R} \qquad \text{Equation 4.17}$$

For a grain boundary energy of 0.5 J/m^2, the driving force P_C is equal to P_d when the radius R is ~1 μm. For pure copper, the grain boundary energy is given as 0.5 J/m^2 and radius of a new grain is assumed to be 1 μm. Thus, the driving force for grain growth is found to be 1 MPa (Humphereys and Hathely, 2004). Therefore, it was concluded that the driving force for recrystallization is greater than the driving force for grain growth in the present work.

4.6 Microstructural Evaluation

The results of metallographic investigations for the commercially-pure copper after cold rolling and cyclic thermal annealing are discussed as follows.

4.6.1. The Effects of Cold Rolling on Microstructure

The microstructures of commercially-pure copper plate before and after cold rolling are shown in Figure 4.9 and Figure 4.10 respectively. The microstructure of as-received material shows equi-axed grains of copper. This microstructural feature helps in interpreting that the as-received material had been recrystallized after cold rolling.

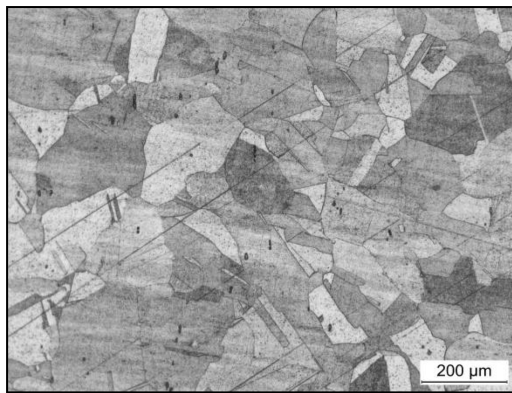
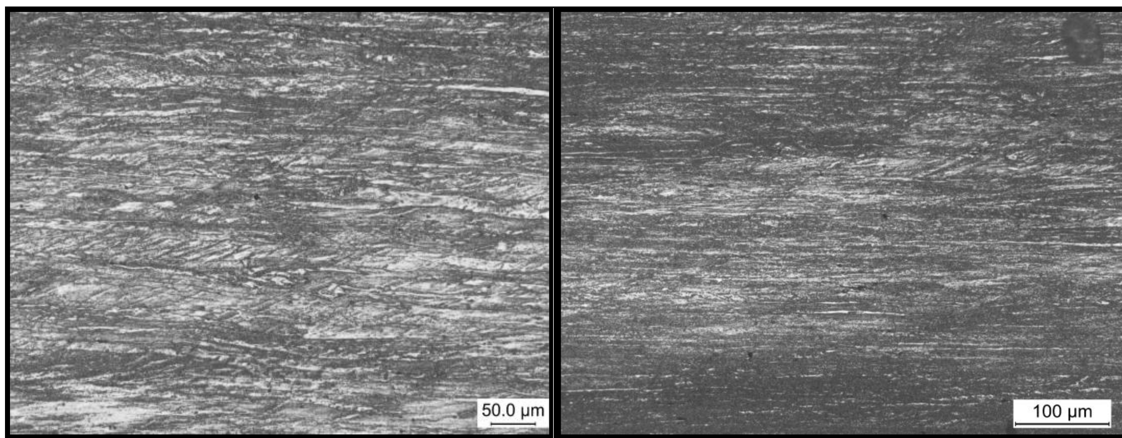


Figure 4.9: Microstructure of Full Annealed Copper



(a) 80 Percent Thickness Reduction **(b) 90 Percent Thickness Reduction**

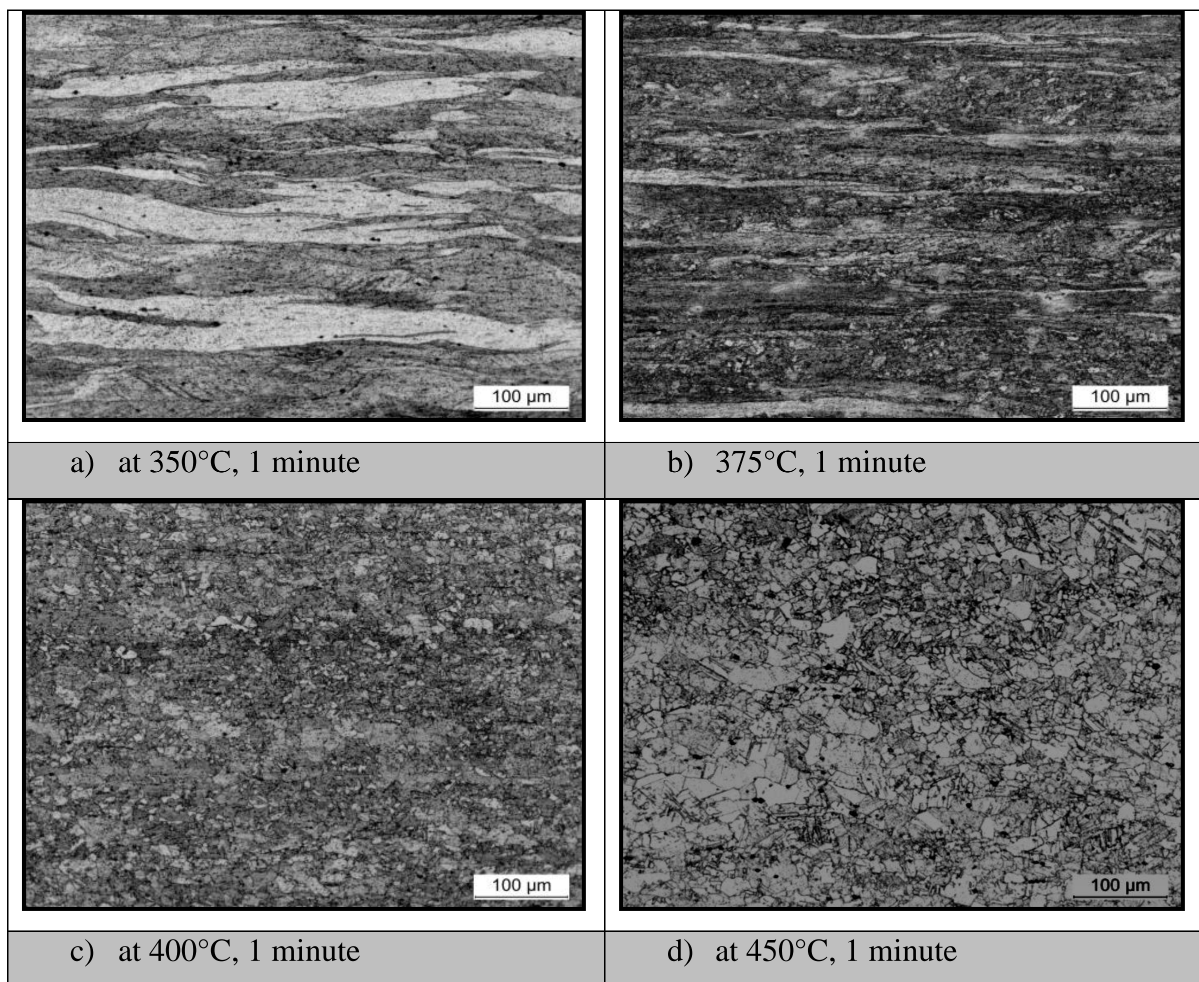
Figure 4.10 Cold Rolled Copper

Figures 4.9 and 4.10 indicate that with increase in percentage deformation, the grains became more elongated in the rolling direction. With increase in the amount cold working (CW), the grain structure can be clearly seen to be denser and more elongated in the

direction of rolling. The dislocation density increases with increasing cold deformation; new dislocations are created by cold deformations which interact with those already existing in the material. A considerable redistribution of impurities takes place during rolling; this material behavior results in reduction of segregation effect which was present in the original (as-received) material. At the same time, residual coring is eliminated and a more homogeneous product results due to the mechanical mixing action of rolling.

4.6.2 Effect of Isothermal Annealing on Microstructure

Isothermal annealing is the process of annealing at constant temperature for a suitable period of holding time. An appropriate holding time for isothermal annealing was chosen and the effect of any change in temperature on microstructure was observed. The samples were heated and held in the range 350°C to 450°C in the interval of 25°C for 1 minute each.



a) at 350°C, 1 minute
b) 375°C, 1 minute
c) at 400°C, 1 minute
d) at 450°C, 1 minute

Figure 4.11 Micrographs after Isothermal Annealing at different Temperatures

The microstructure shows highly dislocated region (or deformed structure) in the temperature range of 350°C - 375°C and a partial recrystallized region starts to grow by further increases in temperature. At 400°C, almost complete recrystallization takes place in the material and further increase in temperature results in increase in grain size. Figure 4.11 shows a clear difference in microstructure of un-recrystallized, partial recrystallized and fully recrystallized region.

As the microstructures reveal, different amount of recrystallization takes place during isothermal annealing at different temperatures. From the micrograph study, it was observed that recrystallization was started at 375° C and only a small portion recrystallized. The microstructure shows dislocations tangled, highly deformed region and nearly 35 percent recrystallized region.

In the present study, a thermal cycling process was used to obtained ultrafine microstructure in commercially pure copper. A repetitive isothermal annealing process was carried out by imposing a cooling cycle after a short holding time. It was required that complete recrystallization takes place in a selected number of thermal cycles; a small portion being recrystallized in each cycle. Hence, an appropriate temperature of 375°C was selected as a suitable temperature for the present study.

4.6.3 Effect of Cyclic Thermal Annealing on Microstructure

Thermal cycling process results in accelerated kinetics with significant impact on productivity and energy consumption (Krishnan *et al.*, 2006). The accelerated recrystallization behavior observed in the present study under this process was attributed to non isothermal part of the cyclic thermal processing, during heating and cooling segment. Basically, thermal cycling process is a temperature modulation process in which a higher annealing temperature and lesser holding time are required for high nucleation rate and for avoiding grain growth respectively.

At a constant temperature of 375°C, four thermal cycles were given for different annealing periods of 20, 25, 30, 35 and 40 s respectively. The minimum holding time was selected to be more than 15 s to ensure uniform heating throughout the sample. The recrystallization fraction in the present study was very small after the first thermal cycle as earlier stated by Gupta (1975) also. On subsequent thermal cycles, this fraction increased quite rapidly. After each thermal cycle, the strain heterogeneity further increase and some volume of sub grains became over critical nucleus. This was in accordance with the earlier work reported by Kumar *et al.* (2009). At the same time, some residual deformed region

was retained in the microstructure. Thus, a non homogenous distribution of stored energy resulted in varying recrystallization kinetics spatially. The spatial strain heterogeneity may be the driving force for accelerating recrystallization kinetics according to the predictions made by Luo *et al.* (2004). The microstructure for different annealing time periods at constant temperature (375° C) for four thermal cycles has been shown in Figure 4.12.

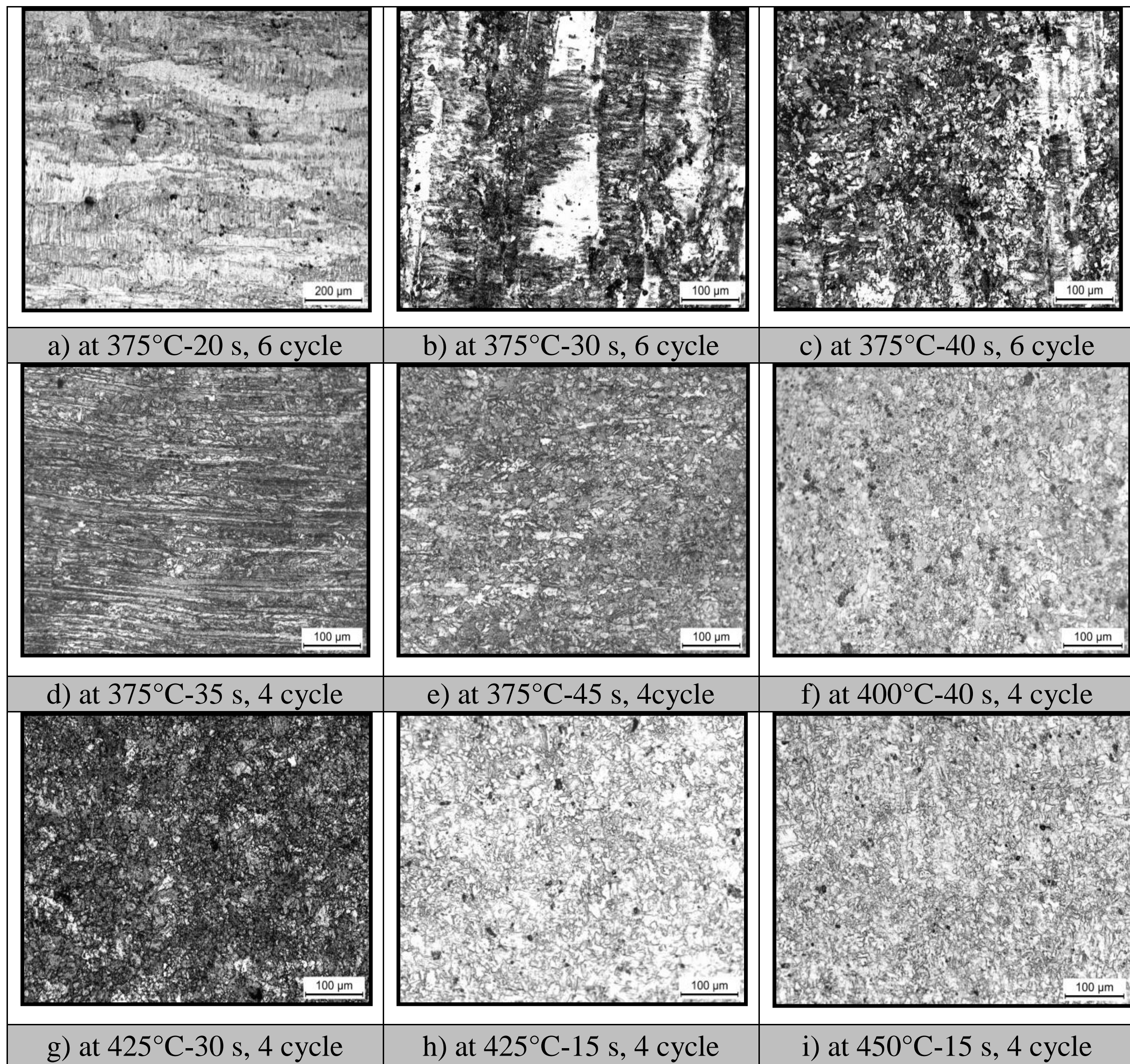


Figure 4.12 Micrograph of Thermally Cycled Copper

The number of thermal cycles required for complete reversion was larger at lower temperature compared to that at high temperature as reported by Kumar *et al.* (2009). The optical microscopic examination of thermally processed specimens revealed a microstructure consisting of ultrafine-grained and some residual cold-deformed regions

depending on processing parameters. After the first few cycles, the onset of ultrafine grain formation within the highly deformed regions could be noted in Figure 4.12. This also suggested that deformation bands and highly dislocated regions were the preferential nucleation sites for the formation of ultrafine grains. A review of various microstructures (shown in Figure 4.12) revealed that an ultrafine grained structure was observed at annealing temperature of 375°C with 35 s as holding time and four thermal cycles. However, in this specific microstructure (T= 375°C, t= 35, n=4), a small portion was as deformed region.

In order to remove the deformed region, the numbers of thermal cycles given to the sample were extended six thermal cycles as reported by Gupta (1975). However, when thermal cycling was continued at 375°C for 5th and 6th cycle, it was found that grain growth has been occurred in some portion as shown in Figure 4.12. So, a two step thermal cycling process was given to the material under this situation. In this process, a few thermal cycles (n = 4) were processed at a particular constant temperature (375°C) followed by another remaining thermal cycles (5th and 6th) at a lower temperature (350°C) with less holding time (25 s).

The resulting microstructure (with ultrafine grains and deformed region removed) is as shown in Figure 4.13. It may be noted here that nearly a full recrystallized microstructure was obtained only after the second stage of thermal cycling. This two-step cyclic thermal process, first step at high temperature and the next at low temperature, produced very closely distributed ultrafine grains.

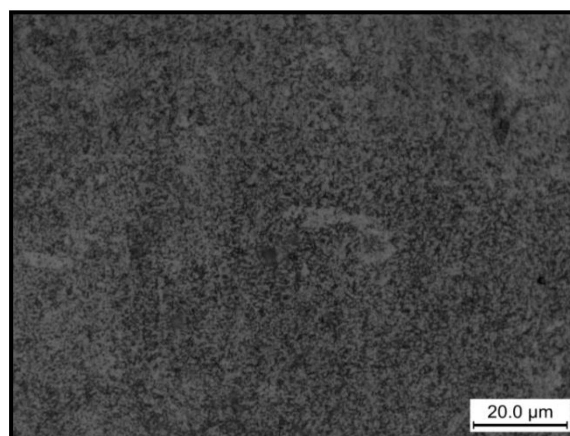


Figure 4.13 Ultrafine Grained Copper

Cyclically annealed material contained new formed grains that could not grow due to lack of sufficient time. Also the grain growth rate very small with increasing temperature in the

range of 350-400°C. Hence, it can be concluded that at even low cyclic annealing temperature, high amount of stored energy because of prior cold work is efficient in the formation of fine grained microstructure.

4.7 Grain Size Measurement

The grain size has been estimated both for solution annealed samples and samples obtained after cyclic thermal annealing. The measurement has been made by linear intercept method using optical micrograph.

4.7.1 Determination of the Initial and Final Grain Size

Figure 4.14 shows microstructure of solution annealed pure copper obtained by heating up to 600°C for 1 hour followed by water quenching. Generally, solution annealing treatment was given to as received hot rolled material in order to achieve chemical homogeneity. The solution treated copper specimens were characterized by polygonal grains along with annealing twins. Cold rolling of solution treated specimen resulted in general elongation of the grains in the rolling direction. The estimated average grain size of solution treated sample was found to be in the range of 90-100μm.

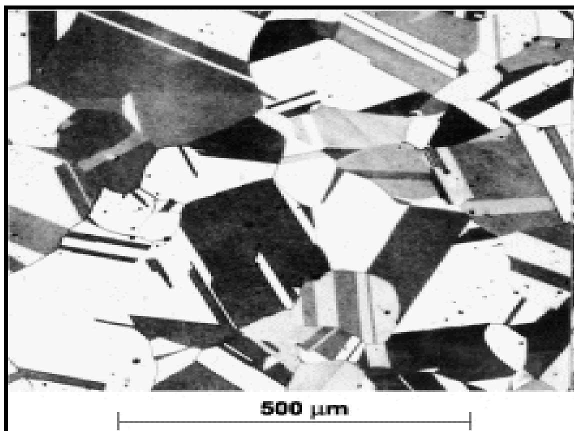


Figure 4.14 Solution Annealed Copper

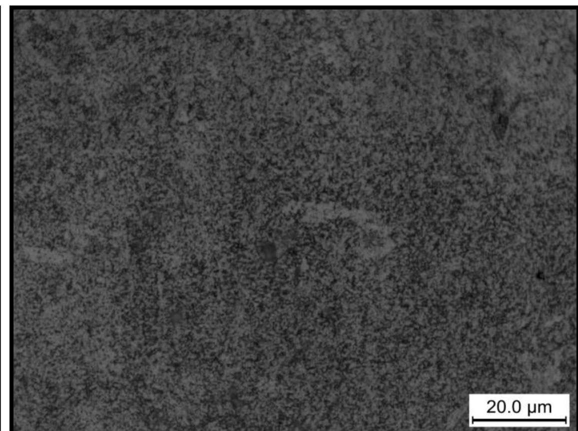


Figure 4.15 Ultrafine Grained Copper

Figure 4.15 shows the final microstructure of material after the two step thermal cycling process. From the above study it was found that a combination of suitable annealing temperature and time for six cycles (First step: T=375°C, t= 35 s, n=4; Second step: T= 350°C, t= 25 s, n=2) gives appropriate result in terms of grain size reduction. The microstructure showed a uniform distribution of ultrafine grains (< 1μm).

4.8 Evaluation of Mechanical and Electrical Properties

After the thermal cycling process, the results showed an increase in mechanical properties in terms of hardness and tensile strength. Also the electrical resistivity of thermally cycled copper was observed to be less than what is in the cold rolled state. Thus electrical conductivity of copper after the two step thermal cycling process was more than that in the deformed state.

4.8.1 Effect on Tensile Strength

The engineering stress strain curve of solution treated and 90% cold rolled specimens are shown in the Figure 4.16.

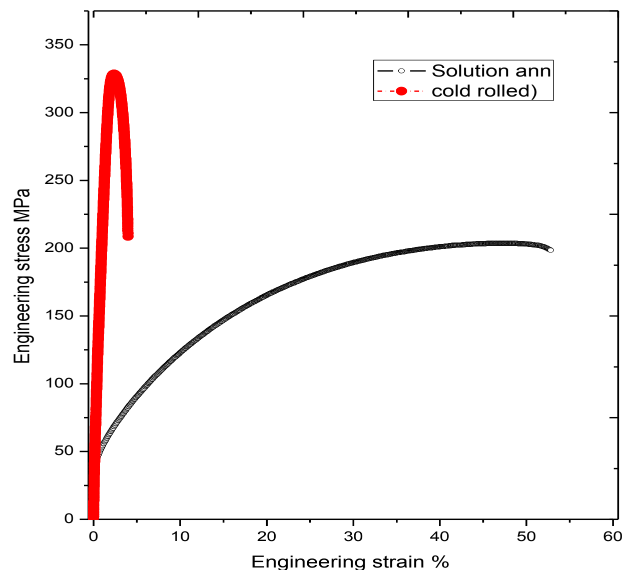


Figure 4.16 Stress Strain Curve of Solution Annealed and Cold Rolled Specimens

As expected, the solution annealed specimen showed high ductility percentage elongation of 50% with very low yield strength (60 MPa). Similarly cold deformation led to reduction in ductility with very high increase in the yield strength (325 MPa). This was due to the strain hardening of material due to cold rolling.

The mechanical properties of the cold rolled and thermally cycled copper exhibited a very high (7-8 times) offset yield strength, as compared to solution treated copper, and a very poor total tensile elongation.

The cyclic thermal process resulted in the formation of various microstructures. This had strongly influenced the tensile properties of the material. Figure 4.17 exhibits a typical

engineering stress strain curve of NG/UFG copper corresponding to the microstructures presented in Figure 4.15. The yield strength was observed to be 7-8 times of solution annealed specimen. The ultrafine grained microstructure exhibited very good combination of strength and ductility.

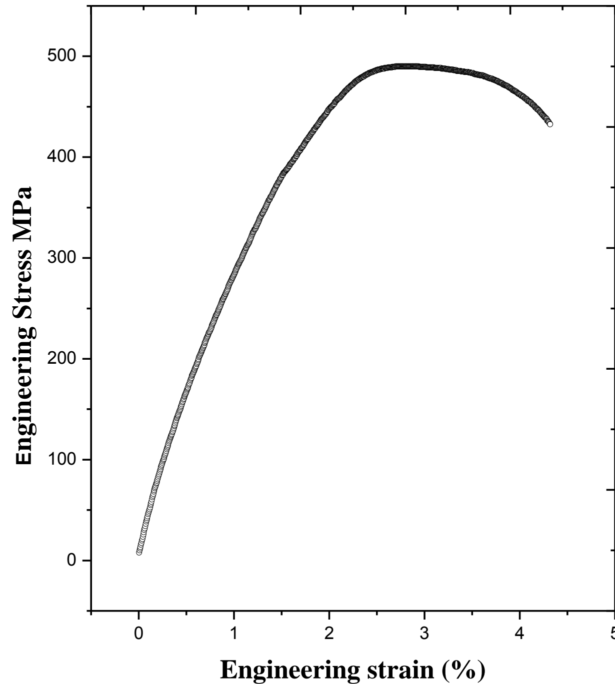


Figure 4.17 Thermal Cycled Specimen

Figure 4.17 demonstrated a tensile curve with almost negligible strain hardenability in the plastic regime. The corresponding microstructure revealed grain size of the order of < 1µm. These fine grains were noted to consist of large number of dislocations within it. The observed poor strain hardenability of this specimen could be due to the presence of dislocations in the fine grain, though not fully saturated. Probably, synergistic effects of fine grain size with large number of dislocations were responsible for poor dislocation storing capacity leading to poor strain hardenability.

4.8.2 Effect on Hardness Value

The analysis of data in Figure 4.18 indicates increase in hardness after cold rolling. This trend in hardness variation is due to strain hardening, which is in agreement with the literature. On application of stress greater than the yield strength (during cold rolling), the number of dislocations increase tremendously. Before deformation, the dislocation density

is about 10^8 m^{-2} of metal. After deformation or strain hardening, the dislocation density increased to about 10^{15} m^{-2} as also reported earlier by Hertzberg, (1996).

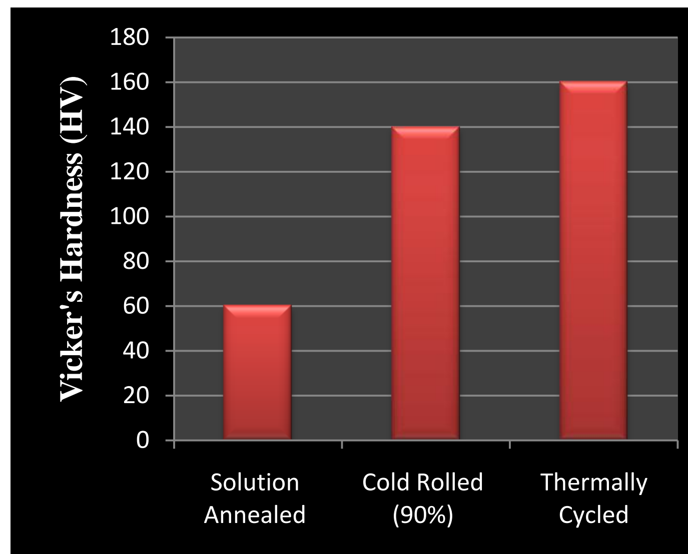


Figure 4.18 Variation of Hardness

4.8.3 Effect of Cold Reduction on Electrical Resistivity

As depicted in Figure 4.19 the resistivity of samples increased with increase in the percentage thickness reduction.

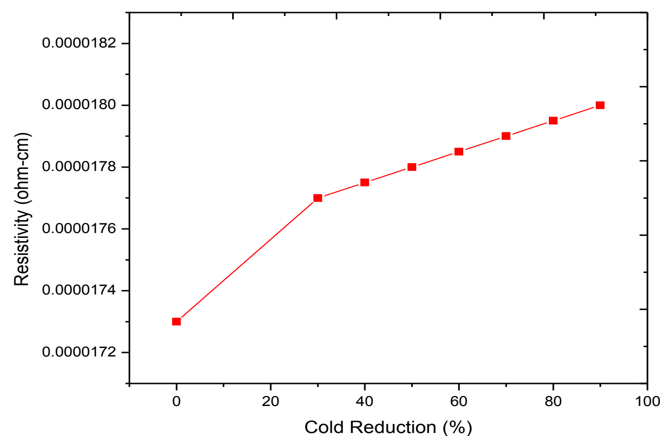


Figure 4.19 Resistivity Measurement

The increase in resistivity was attributed to the increase both in the dislocation density and grain boundary density caused by cold working. Also resistivity increased with the deformation degree due to the increase of electronic scattering from lattice distortion or internal fault structure.

4.8.4 Effect of Thermal Cycling Process on Electrical Resistivity

When thermal cycling process was given to pure copper, resistivity declined and thus conductivity increased. This rise in electrical conductivity is due to the elimination of point defects, and annihilation of dislocations because of more recrystallization which occurred with increase in number thermal cycles. After each cycle most of the stored energy consumed in recrystallization and hence the dislocations vanish.

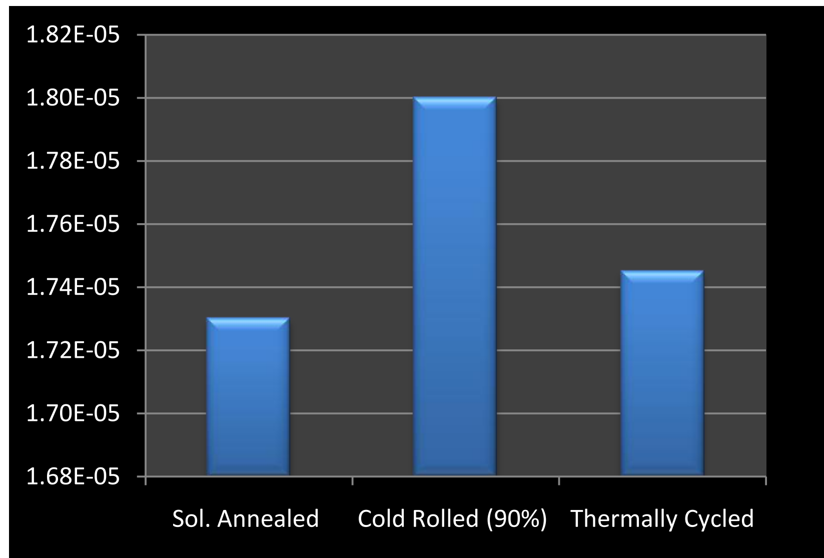


Figure 4.20 Resistivity Measurement

Figure 4.20 shows that resistivity increased after cold reduction but reduced during the thermal cycling process.

4.9 Discussion

The present work aimed at investigating the effect of cyclic annealing on the microstructure, mechanical properties, and the electrical conductivity of cold rolled samples. Recently, thermal cycling processing has received considerable attention for the synthesis of ultrafine grained materials or nanocrystalline materials. The major endeavor of material scientists has been directed in the development of ultrafine grained materials due to their higher strength to weight ratio and improved physical properties. The top down approach of material synthesis has given way to thermal cycling in the development of ultrafine grained materials. In the present study, thermal cycling process has been employed to process commercial high purity copper. Thermal cycling process with upto six cycles has been used followed by microstructural analysis and mechanical property evaluation.

The results show that a proper cycling annealing temperature with relatively short holding time enhances strength properties**.** The results presented in this chapter clearly show that UFG copper with sufficient strength could be readily obtained by thermal cycling process. If this process is applied to practical use, considerable increase in strength in pure copper can be achieved. Thus, pure materials, without any alloying element addition can be processed by this route to achieve better performance. This process can also address the recent social demands of recycling of materials.

Copper, as a medium stacking fault energy material, generates a large number of dislocations during deformation (10^{15} per m^2) which rearrange into a lower energy configuration, such as cellular structure or even subgrains, upon annealing (Hertzberg, 1996; Humphereys and Hathely, 2004). With increase in the percentage of deformation, grains become more elongated in the rolling direction. With increase in percentage cold working (CW) to 90% reduction, the grained structure clearly shows to be denser and more elongated in the direction of rolling. Some subgrains contain fewer dislocations in their interior than other subgrains, and thereby creating strain energy difference. Further, after the cold rolling, the trend observed in hardness variation is due to strain hardening as earlier observed by Cigdem and Bennett (1991).

On application of stress greater than the yield strength (during cold rolling), the number of dislocations increased tremendously. Before deformation, the dislocation density was about 10^9 $m^{-2,}$ and after deformation (or strain hardening), the dislocation density increased to about 10^{15} m^{-2}. Cold rolling also increases resistivity. It attributed to increase in both the dislocation density and the grain boundary density caused by cold working. Also resistivity increased with the deformation degree due to the increase of electronic scattering from lattice distortion or internal fault structure.

In general, during annealing, recovery proceeds with a sequence of structural changes, which include annealing out- of- point defects and their clusters, the annihilation and rearrangement of dislocations, the formation of subgrains (polygonization) and their subsequent growth. It has been suggested that this process can lead to the formation of recrystallization nuclei. Nucleation is a thermally activated process that requires recovery by climb in medium stacking fault energy materials like copper. Recovery consumes only about 10% of the stored strain energy. Thus, during recovery there is no significant change in the microstructure, and the subtle changes cannot be accurately detected by the conventional OM measurement. On the other hand, recrystallization is driven by the unreleased portion (~90%) of the stored energy, although there may be competition

between recovery and recrystallization for this energy, especially at the early stages of recrystallization. Recrystallization can take place by the nucleation and growth of new grains at the expense of the recovered matrix. These nuclei of newly formed grains are relatively strain-free, and on reaching the critical size, are surrounded or partially surrounded by high angle grain boundaries (HAGBs) with high mobility.

Recrystallization results in a drastic drop of microhardness due to the fact that a large volume of dislocations are swept by the migration of HAGBs which have a much higher mobility than LAGBs. As recrystallization proceeds to completion, impingements among these new grains occur with increasing frequency. Finally, the entire specimen is replaced by an aggregate of recrystallized grains. After annealing the specimen at suitable temperature, most of the elongated grains disappear and almost equi-axed grains appear. When primary recrystallization is complete, the structure is not yet stable, and further growth of the recrystallized grains may occur by the migration of grain boundaries with the grain-boundary free energy as the driving force. The grain boundary interfacial free energy is much lower than the stored strain energy. This results in a lower reaction order than during recrystallization. For a medium stacking energy material like copper, the drop in the growth rate could be more due to the impingement of the grain boundaries by the neighboring grains than due to the concurrent recovery in unrecrystallized matrix. This suggests that during grain growth, grain boundary self-diffusion is the rate-controlling mechanism. . When a spherical new grain of radius R, grows into the deformed structure, there is an opposing force (driving force) which acts as retarding pressure on the boundary given by Equation 4.1. For pure copper, the grain boundary energy is given as 0.5 J/m^2 and radius of a new grain is assumed to be 1 μm. Thus, the driving force for grain growth is found to be 1 MPa. Therefore, it is concluded that the driving force for recrystallization is greater than the driving force for grain growth in the present work, which results in a finer grained structure.

Interestingly, the cyclic thermal process resulted into different recrystallization and grain growth behaviour compared to isothermal annealing. On the other hand, it was mainly the heterogeneity in nucleation and growth behaviour due to spatial stored energy. Under the temperature 375°C, grain growth in the copper was very slow. This behaviour can be attributed to several causes that are interconnected like sluggish diffusion, low mobility of high angle grain boundary and low driving force for grain growth. Also in a pure material grain refining can be induced by high vacancy concentration (Estrin *et al.*, 2000). Vacancy concentration can be created by quenching from a high temperature and plastic strain.

Also the critical grain size (R_c) can be regarded as a limiting stable grain size above which grain growth inhibited at given temperature and time in cyclic thermal process. Hence the results indicated possibility of grain refinement by cyclic thermal process for pure copper which does not undergo any phase transformation. As a result of these phenomena, the ultimate strength and hardness values enhanced without impairing its conductivity.

CHAPTER 5
CONCLUSIONS

5.1 General

The present work on thermal cycling of high purity copper has showed some interesting results in terms of microsctructural characteristics, mechanical properties, and electrical conductivity. Materials with ultra fine grains lead to improved mechanical and physical properties. The substantial interest being shown in these materials stems from the fact that their structural and functional properties are significantly different from those of analogous coarse-grained materials. The development of high strength copper and its alloys which are characterized by high strength, high ductility and good electrical properties is a subject of significant interest worldwide. The demand of high strength copper with characteristic properties of high electrical and thermal conductivity and non-magnetic properties is increasing. Copper shows excellent resistance to most chemicals other than ammonia acid, also resistance to corrosion. Last few years have seen a major effort devoted to the investigations of copper in search for improvement in properties such as high strength, high thermal stability and high ductility with high conductivity at high temperatures. A route for improving the strength of copper alloys without degrading ductility is to anneal them subsequent to heavy cold working. This treatment produces nano/sub microns grain structures. This mechanism has gained wide acceptance. Many investigators have studied the effect of thermo mechanical processing on copper alloys and have reported that such processes have specific practical importance. Another process which has an influence on the increase of mechanical and electrical characteristics is the thermal cycling treatment. It consists of alternate heating and cooling of the material upto the recrystallization temperature. Thermal cycling is a temperature modulation process developed to improve the performance and strength of variety of materials. Materials processed by large strain (> 1.3) deformation are characterized by high internal stresses, which are associated with both high dislocation densities and non-equilibrium grain boundaries. The grains containing dislocation may be considered as potential nuclei for recrystallized grains. Highly deformed materials depend strongly on heating temperature for grain refinement. In the present experimental work on pure copper, after annealing at initial selected temperature of 350°C, the microstructure comprised of partially recrystallized and remaining highly deformed region. As a result, a still higher temperature

of 375°C was selected. With four cycles at this temperature and the remaining at a lower temperature of 350°C provided an ultrafine grain structure.

5.2 Results and Conclusions

The main results of the present work and the conclusions to be drawn are as follows:

- Commercially pure Copper contains thermodynamically stable phase at room temperature, and there was no phase transformation after the application of solution heat treatment.
- Commercial pure copper plates were solution treated at 600° C to achieve chemical homogeneity. The microstructure of the fully annealed material showed equi-axed grains of copper with grain size in the range of 90-100 micro meter.
- The stored energy is directly proportional to the dislocation density and varies with increasing percent thickness reduction. Initially the dislocation density increases nonlinearly with increasing strain and finally attains a saturation value.
- The dislocation density was calculated to be as 1.2×10^{15} which was comparable to the actual value as 0.9×10^{15} after 90 percent deformation for copper. The discrepancy could be due to statistical model used for calculation.
- The total number of nuclei increased with cold work, resulting in denser and more elongated grains in the direction of rolling.
- There was increase in the Vickers Hardness values from 50 - 150 HV with cold deformation from 20 to 90 percent thickness reduction.
- Resistivity measurement showed that value increased linearly with increasing percent of cold reduction from 0.173 to 0.182 μ-Ω-cm. This was in good agreement with the hardness measurement.
- Cold rolled specimens were subjected to annealing at various temperatures between 350°C to 450°C to obtain the recrystallization kinetics and obtain value of n and K for JMAK equation. The values of n and k were found as 4 and 5.29×10^{-5}.
- Two temperature regions separated at around 400° C were distinguished by their effect on microstructural changes during isochronal annealing for 1 minute. The microstructure was relatively stable against coarsening at temperatures below 400° C, while heating to higher temperature resulted in a rapid grain growth.
- The recrystallization fraction corresponding to different annealing time period (15 to 45 s) at constant annealing temperature (375-450°C) was found increase

nonlinearly. This variation was in accordance to the relation based on hardness measurement.

- The correlation between the hardness and microstructural changes of copper after cold rolling and thermal cyclic process was found. It was observed that for microstructure with highly deformed region, hardness was high and for fully recrystallized regions hardness was low.
- The tensile testing of the cold deformed copper showed increase in yield strength upto 325 MPa in comparison to 60 MPa of the coarse grained solution annealed copper with an appreciable reduction in ductility. The thermal cycled specimen showed yield strength of 480 MPa with good ductility combination.
- Driving force for grain growth and recrystallization were found to be 1 MPa and 1.56 MPa respectively. Since the driving force for recrystallization was greater, the given thermal cycling conditions accelerate the recrystallization and retard the grain growth.
- Resistivity of copper after the thermal cycling process decreased considerably due to recrystallization.
- The grain size was refined from 100 μm to less than 1 μm after processing through two step thermal cycling process with different process parameters (First step: T=375°C, t= 35 s, n=4; Second step: T= 350°C, t= 25 s, n=2).

5.3 Major Conclusions and Recommendations

- Mechanical properties, grain growth and relaxation processes can be stabilized by appropriate heat treatment. The results of this study confirm that low temperature thermal cycling of cold rolled copper leads to increase in mechanical properties through decrease in grain size.
- Reduction in dislocation density and grain size, as a result of thermal cycle make the electrons scatter less, thus the electrical conductivity of thermal cycled copper is more than cold rolled copper.
- Thermal cycling retards the grain growth kinetics and increases the recrystallization kinetics by imposing strain heterogeneity between the recrystallized and deformed region.
- Attempts to find ultrafine grains in the thermal cycle processed microstructure of pure copper are successful. Optical microscopy revealed various microstructures with deformation band, and polygonal grains.

- Fine grained material exhibits a high nucleation density, lower recrystallization temperature at low stored energies than its coarse grained counterpart. The opposite is true for higher stored energies, due to larger strains required to reach the stored energy level by a coarse grained material.
- The poor strain hardenability of nanostructure or ultrafine grained polycrystalline materials is attributed to the poor dislocation storing capacity of such grains.

5.4 Scope of Future Work

In spite of the fact that most of the objectives of this study have been achieved for grain refinement in pure copper, still there is a scope for further improvement in the microstructure to enhance the properties. The present work can be extended for to analysis of texture evolution during thermal cycling process and to study the effect of surface texture on properties of material. Moreover, apart from the studies of grain boundary mobility, the work can also be extended to explore the measurement of grain boundary diffusion in ultrafine grained materials. Further, studies can be conducted to examine the combined effect of boundary curvature and strain energy release during thermal cycling process.

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