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Ageing Behaviour of Minor Sc and Zr Doped Cast Cu-10Al Alloys

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Abstract*—The age hardening effect in minor scandium and zirconium added cast Cu-10Al alloys have been studied through isochronal and isothermal ageing at various temperatures for different times. It is observed that significant hardening takes place in the aged alloys due to the precipitation of copper aluminides. Formation of* Al_3Sc *and* Al_3Zr *precipitated through Sc and Zr addition improve the thermal stability of the alloys and Sc addition accelerates the ageing due to precipitates of* Al_3Sc*. It is also observed that thermal conductivity decreases with the increase the ageing temperature due to formation of fine precipitates. The effects of minor Sc and Zr addition on microstructure and recrystallization properties of alloys are also studied by optical microscopy. The results show that Sc and Zr addition can refine grains of the as-cast alloys by precipitation of primary* Al_3Sc *and* Al_3Zr *particles formed during solidification as heterogeneous nuclei. Secondary* Al_3Sc *and* Al_3Zr *precipitates formed during ageing treatment strongly pin the movement of dislocation and subgrain boundaries, which can effectively inhibit the alloys recrystallization.*

Keywords—Cu-Al alloys; Age hardening; Precipitates; Grain-refinement; Thermal conductivity; Absorbance

1. INTRODUCTION

The performance of copper can be expanded by alloying two or more different metals to face a lot of industrial applications [1]. The fundamental properties of copper alloys are highly influenced by copper itself. Copper alloys are grouped into families, based on their composition. There are more than 400 copper alloys, each with a unique combination of properties, to suit many applications. Aluminum bronzes are significant copper based aluminium alloys. These bronzes have different percentage of Aluminum that is incorporated as a major alloying element usually in the range 5% to 14% by weight but other alloying elements such as Iron, Nickel, Manganese, Silicon, Zinc and Tin with varying proportions, subjected to applications of Aluminum bronze [2, 3]. The consumption of aluminium bronzes have increased sharply due to their property of being non-rusting in marine environment as well as also their resistance to corrosion in highly aggressive environments. Besides their strength, toughness, corrosion resistance in a wide range of aggressive media, wear resistance, low magnetic permeability, non-sparking characteristics, aluminium-bronzes can be readily cast, fabricated and machined. They can also be readily welded in either cast or wrought form.

Grain refinement of copper and its alloys can improve their mechanical properties, casting properties, deformation treatment properties, and surface quality [4, 5]. Therefore, grain refinement is an important research topic in the modern copper processing industry. Literature suggests that Sc and Zr evidently act as a potent grain refiner in aluminium alloys [6, 7]. Further, it has a pronounced effect on the microstructure and properties of Al alloys through the formation of the coherent Al3Sc and Al3Zr compound. However, such effect of Sc and Zr is not well reported for Cu alloys [8]. It is also known that grain size affects the spectral characteristics of particulate materials. Particle size also plays an important role in determining the strength of absorption features and this has significant implications for the interpretation and understanding of remotely acquired spectral data [9, 10].

The aim of this work is to investigate the effect of Sc and Zr additions on the mechanical properties and its influence on grain refinement of cast Cu-10Al alloys.

2. EXPERIMENTAL

Cu-10Al alloys with 0.2% Sc and 0.2% Zr wear used in the current study. In the development of the alloys, the commercially pure copper (99.99% purity), aluminium (99.7% purity), aluminium scandium master alloy (2% Sc) and aluminium zirconium master alloy (10% Zr) were taken. Melting was carried out in a clay-graphite crucible in a natural gas fired pit furnace under suitable flux cover. The final temperature of the melts was always maintained at 1300±15°C. A preheated steel mould (200°C) size of 20×100×150 in millimeter was prepared which was coated inside with a film of water-clay. The melts were then allowed to be homogenized under stirring at 1200ºC and poured in that preheated mould. All the alloys were analyzed by spectrochemical method and the chemical compositions of the alloys are given in Table 1. The cast samples were first machined to skin out the oxide layer from the surface and $3\times20\times20$ mm^3 size obtained from the samples for microhardness and electrical conductivity measurement. The alloy samples were isochronally aged at different temperatures for one hour and isothermally aged at various temperatures for different periods of time. The samples were sanded mechanically with emery papers of rough one and the one of 1500 grits. Microhardness of the aged samples was measured with a Micro Vickers Hardness Tester. The knoop indenter was applied with 1Kg load for 10 seconds. At least seven indentations from different locations from each sample were taken. Electrical conductivity of the alloy in different heat treatment condition was carried out with an Electric Conductivity Meter Type 979. Thermal conductivity was calculated from those electrical conductivity data through the Wiedemann–Franz law [11]. Besides these, powder of the experimental alloys was prepared for measuring the absorbance by using UV Visible Spectrophotometer device. The optical metallography of the samples was carried out in the usual way. In case of using metallographic copper etchant a conventionally recommended one of Ammonium Hydroxide+ Hydrogen peroxide (3%) was used where the compounds were taken in 1:1 ratio. The washed and dried samples were observed carefully in optical microscope at different magnifications and some selected photomicrographs were taken.

Table 1: Chemical composition of the experimental alloys (wt %)

	Al	**Sc**	**Zr**	**Zn**	**Pb**	**Fe**	**Si**	**Sb**	**Cu**
Alloy 1	9.601	0.000	0.000	0.023	0.013	0.078	0.004	0.079	Bal
Alloy 2	9.451	0.198	0.000	0.034	0.020	0.156	0.002	0.078	Bal
Alloy 3	9.470	0.000	0.189	0.006	0.011	0.064	0.005	0.081	Bal

Remarks:

Alloy 1	Cu-10 wt% Al
Alloy 2	Cu-10 wt% Al- 0.2 wt% Sc
Alloy 3	Cu-10 wt% Al- 0.2wt% Zr

3. RESULTS AND DISCUSSION

3.1 Age-hardening behaviour of the cast alloys

3.1.1. Isochronal Ageing

The results of isochronal ageing of cast Cu-10Al Alloy 1, minor Sc added Alloy 2 and minor Zr added Alloy 3 at different temperatures for 60 minutes are shown in Fig. 1. It is seen that all the alloys have been shown ageing response. The results of the present experiments clearly indicate that the age hardening effect shown by the alloy is due to addition of Al. During solidification and ageing, various intermetallic phases are formed by reaction of Al and Cu, such as: $CuAl_2$, AlCu, Cu_4Al_3, Cu_3Al_2, Al_4Cu_9 [12]. The main intermetallic phases which affect the hardness of the alloy are Al_4Cu_9 and Cu_3Al_2. At the intermediate stage of aging a decrease in hardness for all the alloys are observed. Dissolution of some phases present into the alloys should be responsible for this [13].

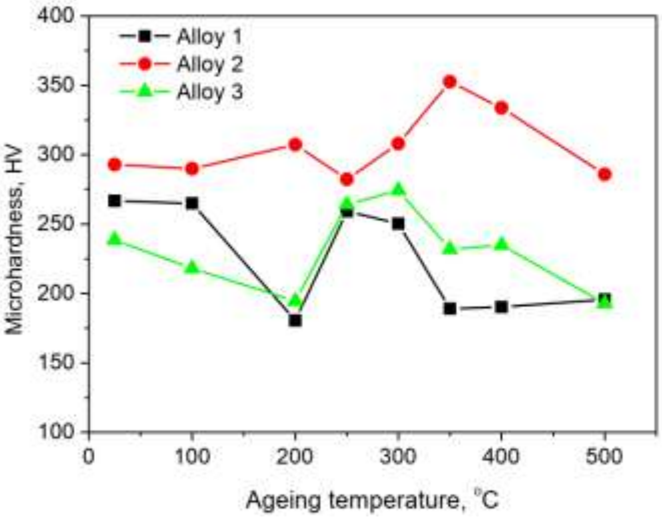

Figure 1: Isochronal ageing curve of the cast alloy, aged for 1 hour.

When the alloys are aged at higher temperature a sharp decrease in hardness is observed for all the alloys. The softening of the alloys at higher temperatures may be due to the particle coarsening as well as recrystallization effects. Cu-10Al Alloy 1 shows this nature of softening at relatively lower temperature and Sc and Zr added alloys remain its hardness at wide range of temperature. Dispersoid particles of Al_3Sc and Al_3Zr, are formed during ageing of Alloy 2 and Alloy 3 respectively. These particles inhibit recrystallization and grain growth by pinning grain boundaries during subsequent heat treatments. Sc addition not only acts as potent grain refiner but also increasing the hardness of the Alloy 2 by producing finer Al_3Sc precipitates [14, 15].

Initial increase of thermal conductivity is due to stress relieving in the alloys during isochronal ageing (Fig. 2). The subsequent drop in conductivity is due to formation of fine precipitates [16]. Sc and Zr added alloys form Al_3Sc and Al_3Zr particles which provide strong obstacles for the dislocation movement. Which delayed the process, as a result rate of decreasing of thermal conductivity is low [17].

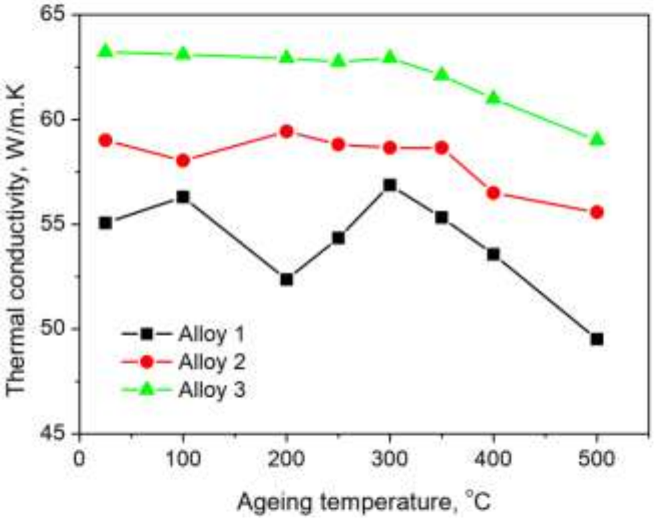

Figure 2: Variation of thermal conductivity of the cast alloys isochronally aged for 1 hour

3.1.2. Isothermal Ageing

Figs. 3-5 show the variations of hardness of the experimental alloys isothermally aged at 250, 300 and 350°C for different times respectively. It can be seen from the Fig. 3 at 250°C low ageing temperature that the aging peaks are present for all of the alloys, and higher hardness was attained. The age-hardening peaks are attained due to formation of various intermetallic phases like Cu_3Al_2, Al_4Cu_9 as discussed earlier. At the primary stage of ageing a little decrease in the hardness of all the alloys are shown, which is caused by dissolution of some metastable phase [18]. Isothermal ageing at 300 °C shows reduction in the time to reach peak hardness values (Fig. 4). At the higher temperatures of isothermal aging at 350°C, the hardness decreases of the Cu-10Al Alloy 1 due to over-aging as well as precipitation coarsening (Fig. 4). From the isothermal age-hardening curves, it is also shown that the Sc added Alloy 2 attained the maximum hardness at high aging temperatures and less time. Both the minor Sc and Zr added Alloy 2 and Alloy 3 are most effective in suppressing the softening effect during prolonged aging treatment. Sc form Al_3Sc second-phase particle generated in the solidification process, which can improve the performance of the alloy by refining grains, precipitation strengthening and inhibiting recrystallization. The addition of minor Zr into the alloy can form an Al_3Zr phase, which can refine the grain, have a strong nailing effect, Hinder the slip and climbing of the dislocation, inhibit grain-boundary movement, increase the recrystallization temperature and increased thermal stability of the alloy [19].

When the alloys are isothermally aged at 300°C, thermal conductivity of the Cu-10Al alloy increases due to the stress relieving, coarsening of the precipitates and recrystallization (Fig. 4). The thermal conductivity of the minor Sc and Zr added alloys remain fairly unaltered over the entire period of aging. The minor Sc and Zr added alloys delayed this process due to the formation of Al_3Sc and Al_3Zr trialuminide particles. Those are resistant to precipitates coarsening and recrystallization by giving rise to some good thermal stability of the microstructure. Small variation of conductivity is observed due to stress relieving in the minor added alloys during ageing.

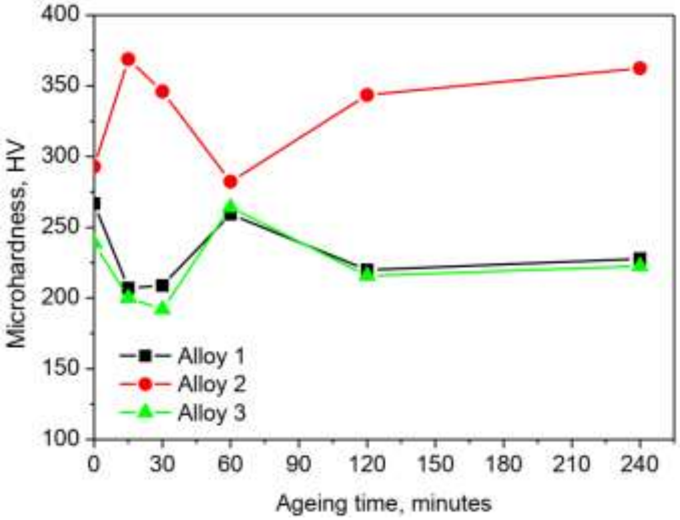

Figure 3: Isothermal ageing curve of the cast alloys aged at 250°C.

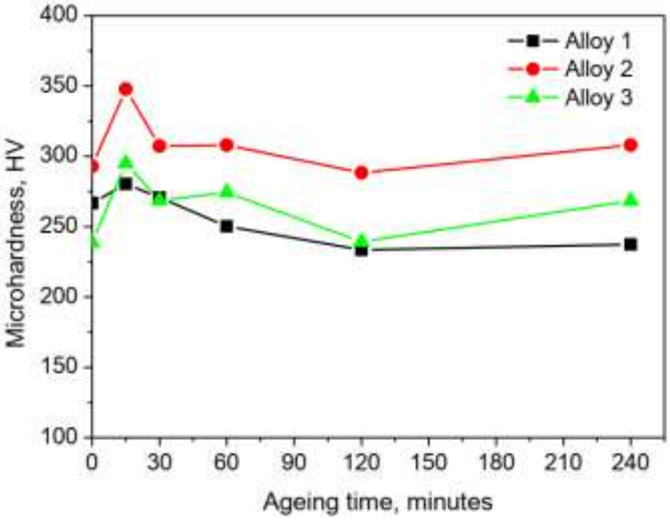

Figure 4: Isothermal ageing curve of the cast alloys aged at 300°C.

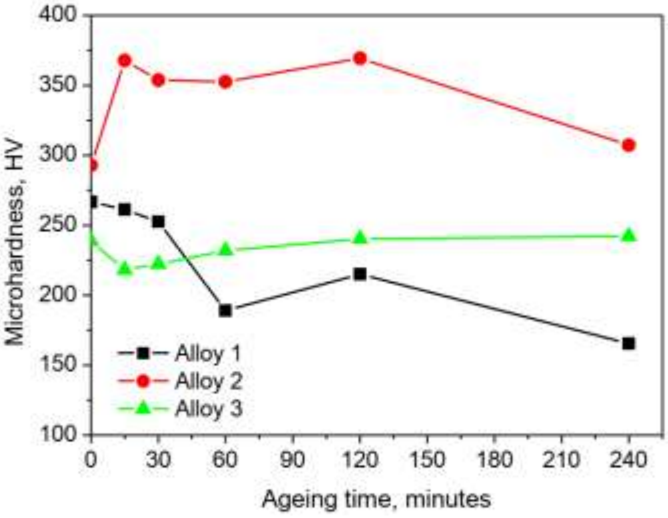

Figure 5: Isothermal ageing curve of the cast alloys aged at 350°C.

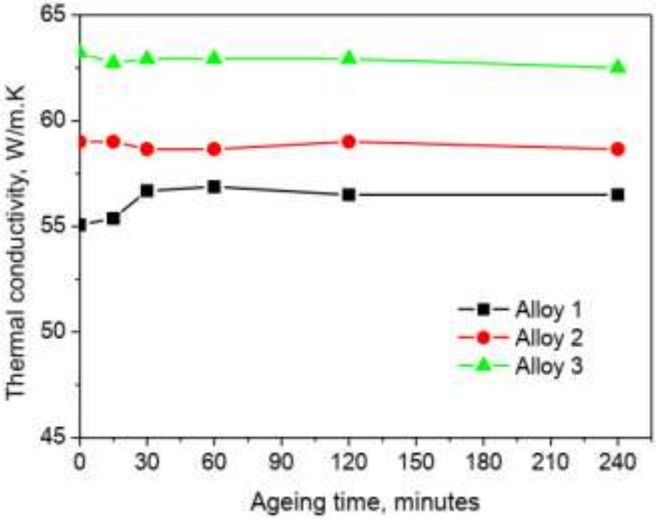

Figure 6: Variation of thermal conductivity of the cast alloys isothermally aged at 300°C

3.2 Absorption behavior

The curves of absorbance versus wavelength for undoped Cu-10Al alloy, Sc doped and Zr doped Cu-10Al alloys are given in Figure 7. The absorption entire the wavelength is lowest for Zr added alloy and followed by Sc added alloy. Cu-10Al alloy shows the maximum absorbance because different materials are capable to absorb different wavelengths, the dominance of transmittance varies with the wavelength even for the same concentration of Cu. This variation is obvious, because the absorption is the opposite phenomena of transmittance [20]. The decreasing of grain size in weak absorbers which stems from the increasing contribution of first surface scattering relative to volume scattering in very fine grained materials. It is well established that Sc and Zr act as potent grain refiner when added to aluminium and copper alloys.

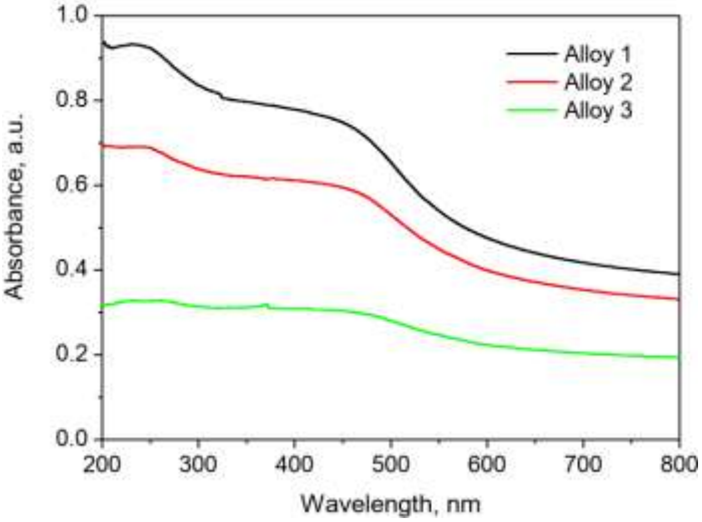

Figure 7: The absorbance as function of wavelength for Cu-10Al Alloy 1, minor Sc added Alloy 2 and minor Zr added Alloy 3.

3.3 Optical Microscopy

The optical microstructure of Cu-10Al Alloy 1, minor Sc added Alloy 2 and minor Zr added Alloy 3 as cast state is shown in Fig. 8. The microstructure of Cu-10Al alloy as shown in Fig. 8a is found to consist of three phases namely α-phase, retained β' phase and numerous K-phases [21]. K-phases are divided into four main types: κI, κII, κIII and κIV. K-phases, which chemical composition consists of Cu, Al, Fe, and Ni can occur in several forms in the alloy microstructure. It is become visible that dendrite arm spacing is decreased in the minor Sc added Alloy 2 and Zr added Alloy 3 with the consequent refinement of dendrites (Fig. 8b and 8c). Sc and Zr helps in nucleation of favourably oriented habit planes which reduces the shape strain in alloys [22, 23].This is ascribed to the modification of solidification speed by Sc and Zr during the growth of the dendrite structure.

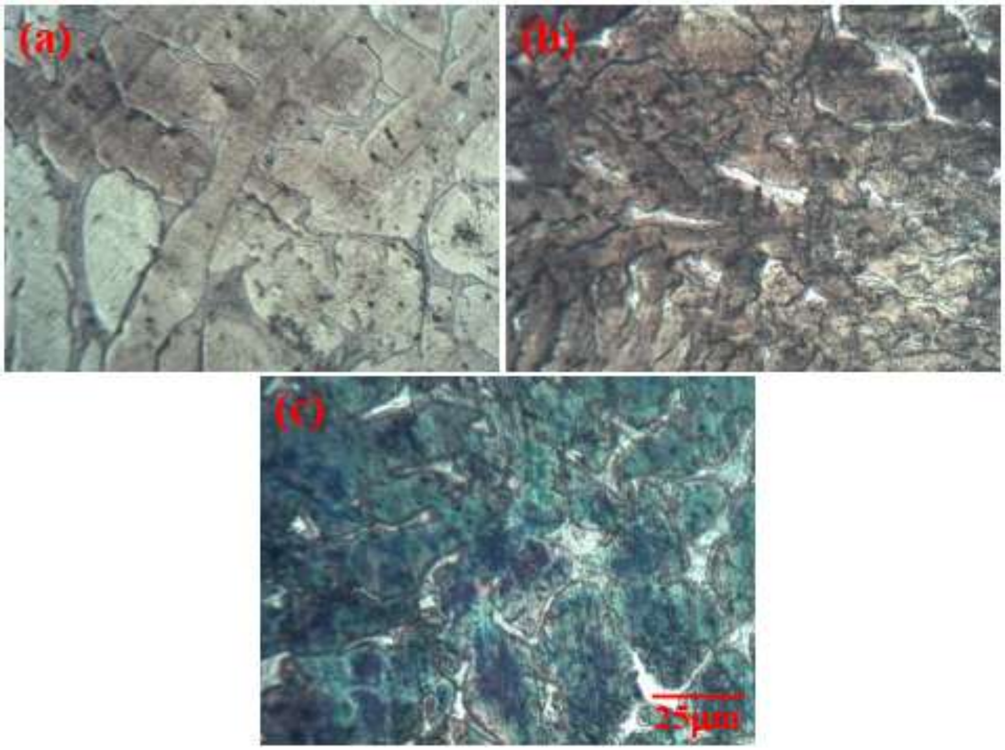

Figure 8: Optical micrograph of cast alloys a) Cu-10Al Alloy 1, b) minor Sc added Alloy 2 and c) minor Zr added Alloy 3.

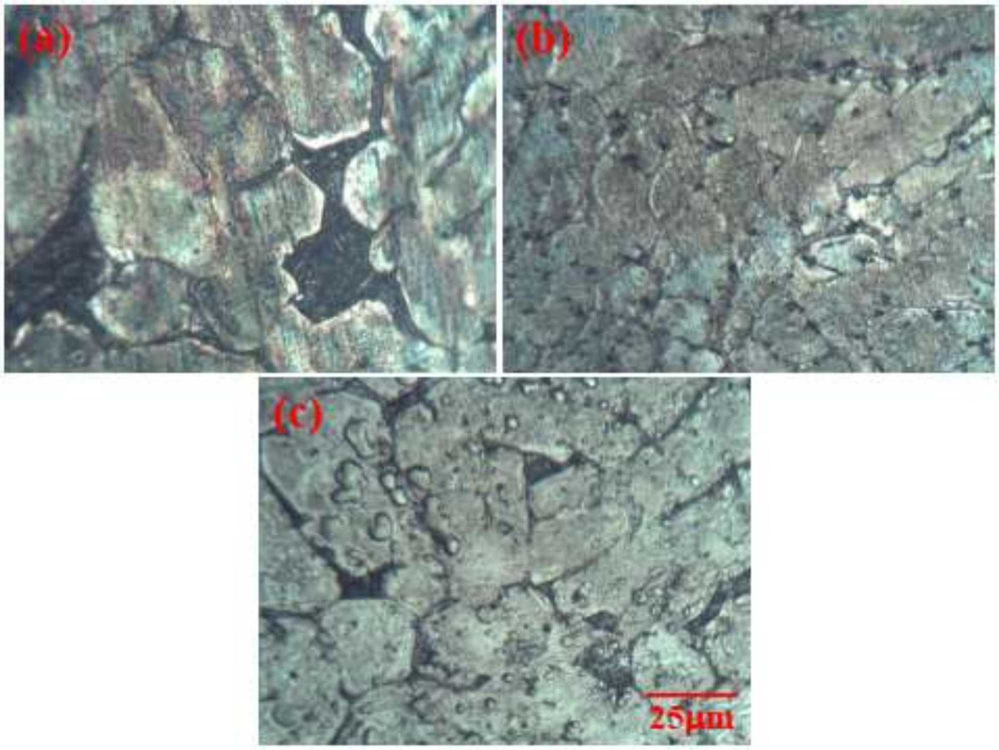

Figure 9: Optical micrograph of cast alloys aged at 400°C for 1 hour, a) Cu-10Al Alloy 1, b) minor Sc added Alloy 2 and c) minor Zr added Alloy 3.

Figure 9 show the optical micrographs of the experimental alloys after ageing at 400°C for one hour. After ageing treatment it is seen the Cu-10Al alloy to be recrystallised partially (Fig. 9a). The Sc and Zr added alloys, on the other hand do not recrystallise even when annealed at 400°C (Fig. 9b and 9c). When Sc is added to Cu-10Al alloy, Al_3Sc second-phase particle can be generated in the solidification process, which refines grains and inhibiting recrystallization. The addition of Zr into the alloy refines the grain through formation of Al_3Zr precipitates, which hinder the dislocation and inhibit grain-boundary movement. As a result increases the recrystallization temperature [7, 24].

4. CONCLUSION

The present study aims to understand the effect of minor Sc and Zr in Cu-10Al alloy subjected to isochronal and isothermal ageing. The ageing response of the alloys was analysed using microhardness and microstructural characterization and the following conclusions are drawn;

The peak hardness of the Cu-10Al alloy is attributed to the formation of main intermetallic Al_4Cu_9 and Cu_3Al_2 whereas Al_3Sc precipitates speed up the hardness of Sc added Cu-10Al alloy. The addition of Sc and Zr into the Cu-10Al alloy refines the grain by heterogeneous nucleation. They also form Al_3Sc and Al_3Zr precipitates respectively which also hinder the dislocation and inhibit grain-boundary movement consequence, inhibit recrystallization.

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