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Microstructural and ageing response assessment of eutectic Al-Cu alloy due to isothermal heat treatment in semisolid state

Abhimanyu Chaudhari 1, Purnendu Nasker 1, Ankur Srivastava 2, Sudeep Paul 3 and Ajit Kumar Chakrabarti 4

1 Department of Mechanical Engineering, Indian Institute of Technology (BHU), Varanasi—221005, India
2 Department of Metallurgical Engineering, Indian Institute of Technology (BHU), Varanasi—221005, India
3 Dr. M N Dastur School of Materials Science and Engineering, Indian Institute of Engineering Science and Technology, Shibpur, Howrah—711103, India
4 Department of Metallurgical and Materials Engineering, National Institute of Technology, Durgapur—713209, India

E-mail: abhimanyu.iiest@gmail.com

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Abstract

An as cast Al–33%Cu eutectic alloy has been processed by semisolid heat treatment, with the ultimate objective of developing a ductile and strong eutectic composite material for probable application as bearing materials and other sliding wear components. In this phase of work only microstructural characterises has been attempted. The as cast sample of Al–Cu alloy is subjected to isothermal heat treatment at a temperature of 560 °C for varying periods of time and followed by water quench. The microstructures of the semisolid heat treated (SSH) samples are analysed using an optical microscope and scanning electron microscopy (SEM). The microstructures of the quenched Al–33%Cu alloy samples show lamellar to lamellar + dendritic transition after SSH treatment. The quenched microstructure after 20 min of holding time primarily consists of copper aluminide dendrites + supersaturated α–Al grains. A massive copper-aluminide (>80%Cu) intermediate phase is observed after 3 to 6 min SSH. The sample configuration did not change after semisolid heat treatment and water quenching. This suggest that complete remelting and overburning did not occur during the semisolid heat treatment. The SSH sample shows maximum hardness, after 10 min holding time compared to solution treated (at 560 °C) and aged (at 150 °C) sample of a standard Al–4.5%Cu cast alloy. The Transmission electron microscopy (TEM) micrograph of the as quenched 10 min. SSH sample shows rod shaped CuAl 2 (θ) precipitates, a dislocation network, cellular subgrains and an extremely fine lamellar eutectic. Solute cluster probably Guinier–Preston (GP) zones, precipitates and fine α –Al grains was observed in the peak aged sample. The x-ray diffraction (XRD) analysis of aged SSH treated sample shows several intermetallic copper-aluminide phases in each sample.

Introduction

In recent times, much focuses have been made on materials having light weight and high specific strength. Aluminium alloys have the potential to fulfil the increasing demand of light weight structural materials. Semisolid processing techniques is a well-established manufacturing process, which helps to produce superior quality product at faster rate and can also modify the property of the parent alloy. The project was undertaken to develop a ductile and strong eutectic composite alloy. In the first phase only, microstructural modification was attempted. The aforementioned manufacturing technique was originally developed by Flemings et al [1]. Since then several other route of semisolid processing of cast alloys like rheocasting and thixocasting were developed by various groups of investigators [2, 3]. Irrespective of the semisolid processing route, the common objective has been to develop spherical grains free form microsegregation [4]. However, still there are grey areas which demand further investigation. A technique of isothermal heat treatment in the semisolid state followed by water quenching has been successfully tried for modification of the microstructures of some Al–alloys and Cu-Sn.
bronze [5, 6]. However, a eutectic alloy like the Al-33%Cu alloy presents a challenge in the sense that prolonged isothermal heat treatment above the eutectic temperature may result in complete melting and distortion of the of the as cast configuration [7, 8]. Therefore, there is a need to optimize the isothermal heat treatment time and temperature in order to achieve the desired goal of micro structural modification without distortion of the cast form. An Al 33% Cu eutectic composite consist of modified α + θ (Cu Al2) phases is likely to be strong and ductile and may be serve as a suitable engineering material for bearing and other sliding wear application. A review article by Kurtz et al [9] is relevant in the present context. He had presented a model for eutectic to eutectic + dendritic growth under non equilibrium solidification situations. Later investigations indicated that the lamellar eutectic structure of the Al-Cu alloy may undergo transformations on rapid re-solidification after laser surface melting [10], or increasing growth velocities during solidification [11] or under high axial magnetic field. Kurtz et al has further investigated the effect of interface temperature and growth rate on dendritic growth in eutectic alloys [12]. Another investigation had examined the relation between columnar dendritic growth and constitutional under cooling [13]. In the light of the above observations it appears that the final micro structure of a eutectic Al-33%Cu alloy subjected to isothermal heat treatment in the semisolid state followed by water quenching will depend very much on the volume fraction of the liquid formed, the magnitude of the interface under cooling and rate of growth of the solid phase during re-solidification.

In the present work Al-33%Cu eutectic alloy was subjected to isothermal heat treatment in the semisolid state, for varying periods of time followed by water quenching. The phase detection was done by using x-ray diffraction pattern (XRD). The surface morphology of the samples was studied by SEM. The detailed microstructure and elemental analysis were done using Transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS). Further, hardness of aged semi solid heat-treated Al-33%Cu alloy was compared with that of the standard solution heated and aged Al-4.5%Cu cast alloy.

**Materials and methods**

The Al-33%Cu alloy was melted in a graphite crucible in an induction furnace under a covering flux. The change consisted of electrolytic purity copper strips and aluminium wire. The alloy melt was cast in the form of 30 mm rods in metal moulds. For the purpose of comparison of the ageing behaviour of the experimental alloy, a standard Al-4.5%Cu alloy was similarly cast. The compositions of the alloys are given in table 1.
Approximately 10 mm thick metallographic samples were sectioned from the cast rods. These samples were isothermally heat treated in the semi solid state at 560 °C, the eutectic temperature being 548.2 °C. After heat treatment for 3 min, 6 min, 10 min and 20 min the respectively, samples were water quenched. Isothermal heat treatment beyond 20 min resulted in fusion and distortion of the samples, and therefore the maximum heat treatment time was restricted to 20 min. However, the sample quenched after 10 min of isothermal heat treatment, were directly aged at 150 °C up to 60 min. For comparison, the standard Al-4.5%Cu alloy samples were first solution treated at 515 °C for 120 min, water quenched and then similarly aged at 150 °C. The as cast and as quenched samples were polished using alumina and diamond paste. Further, the samples were etched in Keller’s reagent examined in a light microscope and SEM (Model Hitachi S-3400M). Energy dispersive x-ray spectroscopy (EDS) analysis was also carried out on the separate phases as observed in SEM. The Vickers’s hardness of the samples was measured under 500 gf load allowing a dwell time of 15 s for indention. (Diamond Indenter Model: U–PMTVC 4 F 6790, Olympus) Thin foils for TEM examination were prepared from the as quenched and peak aged Al-33% Cu alloy samples by twin jet electropolishing of 80-micron dishes. The electrolyte was perchloric acid (10%). The temperature of the electrolyte bath was maintained around 12–14 °C. The thin foils were examined in a transmission electron microscope (Philips CM 20) at 200kv operating voltage. To determine the various phases, XRD studies were carried out using Bruker D8 Advance Diffractometer with a scan speed of 0.02° sec⁻¹. The radiation used was Cu Kα (λ = 1.5604Å0) with operating voltage 35 KV and 25 mA current on both as-cast as well as SSH samples of Al-33%Cu. The XRD data was recorded in the range of 20° to 120°.
Results and discussions

Figure 1 represents the binary phase diagram of Al-Cu system. From the mentioned phase diagram, it can be observed the Al alloy with 33 wt% Cu will contain saturated $\alpha$ phase and CuAl$_2$ phase at room temperature. Further, the declined trend in solid solubility of Cu in Al along solvus line was observed with decreasing temperature. The aforementioned nature of the Al-Cu system can influence the age hardening behaviour of the alloy.

The microstructure represented in figure 2 confirms the presence of lamella eutectic mixture $\alpha + \theta$ (CuAl$_2$) phase in as cast Al-Cu system. It is a typical cellular structure where the lamellar symmetry is not fully maintained at the cell boundaries. However, the eutectic lamellae bend to some extent in an attempt to maintain...
the symmetry in orientation. The lamellae are considerably thickened and develop partially balled up tips at the eutectic colony boundary.

Semisolid heat treatment of the eutectic Al-Cu alloy samples was carried out at 560 °C. Further, samples were quenched successively after 3 min, 6 min, 10 min and 20 min isothermal treatment.

Figure 3, shows the optical image of the system after 3 min of isothermal treatment, which indicates the formation of different phases and apparently homogeneous distribution of the evolved phases.

The SEM micrograph in figure 4 confirms the different phase formation in Al-33 wt%Cu alloy after 3 min heat treatment. Moreover, the presence of a globular phase growing in close proximity of the lamellar eutectic was observed. Bandyopadhyay et al studied that the dendritic structure in a cast Cu-12.6 wt% Sn alloy can be transformed to a globular structure due to semi solid heat treatment at three different temperature [6].

Further, EDX analyses of different phases of 3 min heat treated Al-33 wt%Cu alloy was presented in figure 5. Which indicates, the dendritic α-phase (Spectrum1) is a copper aluminide intermetallic whereas the globular eutectic phase (Spectrum2) is a supersaturated solid solution of copper in aluminium.

However, figure 6 shows the independent dendritic growth of the initial lamellar copper aluminide phase is more clearly revealed after 6 min SSH.
A SEM micrograph and the corresponding EDS analysis of 6 min heat treated sample was represented in figure 7. It shows that lamellar eutectic (Spectrum 6) is present along with massive phases (Spectrum 5 and 7) of copper aluminide intermetallics. Aforementioned Al–Cu intermetallics phases contents 76.00% to 81.33% Copper. Further, dendritic growth of the copper aluminide lamellae may also be noted. The corresponding EDS analysis (Spectrum 6) suggest that the lamellar phase is also not an equilibrium phase.

The separation of the copper aluminide dendrites and the $\alpha$–Al solid solution is nearly complete after 10 min SSH (figure 8). The SEM micrograph shows that the fragmentation of lamellae had progressed considerably. The process however is still not complete. The massive copper rich intermetallic phase present in the 6 min heat treated sample (figure 7), completely disappear after 10 min of heat treatment as shown in figures 8(a) and (b). Instead, independent dendrites growth of copper aluminide phase is observed in figures 8(a) and (b). Quenching cracks in dendrites had developed probably due to a wide difference in the solidification contraction of the $\alpha$–Al and copper aluminide phases. The value of coefficient of negative thermal expansion (or coefficient of thermal contraction) for $\alpha$–phase and CuAl$_2$ are $23.1 \times 10^{-6} ^\circ$C & $17 \times 10^{-6} ^\circ$C respectively [16]. The $\alpha$–Al matrix is also a supersaturated solid solution of Cu in aluminium. The boundaries of the $\alpha$–Al grains are clearly observed in figure 8(b).

The separations of the two phases are more clearly illustrated in the SEM micrograph of the 20 min SSH sample in figure 9. The massive grain analysed 81.39% Al and 18.61% Cu suggesting that it is a solid solution of Cu in Al. The dendritic phase analysed 64.17% Cu and 35.45% Al, which means that this is basically a copper...
aluminide phase. Complete homogeneity is not achieved even after 20 min SSH. Hence the compositions of the phases were not uniform throughout. But the SEM micrographs and the corresponding EDS analyses clearly reveal the kind of transformations the lamellar eutectic undergoes during SSH at 560 °C.

The ageing curve of the SSH eutectic alloy and the standard Al-4.5% Cu alloy are compared in figure 10. It was observed the time required for achieving the peak hardness was about 30 min for the Al-4.5% Cu alloy [17]. The hardness of the eutectic Al-33% Cu continuously goes on increasing with ageing time. Even after isothermal heat treatment of Al-33% Cu alloy in the semisolid region, the Cu content in the α-solid solution (tables of figures 5, 7 and 9) continued to be higher than the equilibrium value predicted by the Al-Cu phase diagram in figure 1. The amount of precipitation of copper aluminide in Al-Cu alloy matrix increased and its resultant hardening effect continued during the period of heat treatment in the present investigation. TEM examination of both the as quenched and quenched and aged samples after 10 min SSH treatment present several unique features.

The TEM micrographs in figure 11(a) show remnants of lamellar eutectic structure and figures 11(b) and (c) show numerous rod and globular shaped precipitates had also formed within the darkish lamellar region. The rod-shaped precipitates are probably those of copper aluminide. However, within the lamellar phase, spacing is very small, around 0.25 μm, as against the interlamellar spacing of 0.5 μm measured on the TEM micrograph in figure 11(a). It therefore appears that part of the molten pool still solidified as lamellar eutectic during quenching after SSH for 10 min and it was resolved only on TEM examination.

Figure 10. The ageing curves of a standard Al-4.5%Cu alloy and the experimental eutectic Al 33%Cu alloy, SSH for 10 min at 560 °C and then water quenched.

Figure 11. TEM micrograph of Al-33% Cu alloy after 10 min SSH and then quenched. (a) Remnants of lamellar eutectic structure. (b) and (c) Numerous precipitates in the matrix.
Dark clusters formed inside $\alpha$-Al lamellae after ageing at 150 °C shown in figure 12. These are likely to be GP zones. The ageing response of the eutectic alloy was higher. Independent selected area diffraction patterns could not be taken in this experiment. Hence the precipitates and GP zones identified only provisionally by analogy with those reported in the published literature [18, 19].

Figure 13 shows the XRD pattern of Al-33%Cu alloy of the as-cast, SSH 10 min and aged samples. The intermetallic phase consists of Cu$_9$Al$_4$ and some non-equilibrium phases like Cu$_9$Al and Cu$_5$Al$_6$, which form after semisolid heat treatment thereby confirming the EDX analysis as mentioned earlier.
Conclusions

On isothermal semi solid heat treatment (SSH) for short periods at 560 °C followed by water quenching, the lamellar microstructure of the Al-33%Cu eutectic alloy undergoes significant transformations.

(i) The following sequential transformations have been identified in the microstructure:

Stage I: Lamellar partial independent growth of copper aluminate lamellae + aluminium rich Al-Cu solid solutions super saturated with respect to Cu + few massive precipitates of copper rich (75%–80% Cu) Cu-Al solid solution + remnants of lamellar eutectic.

Stage II: Separate growth of copper aluminate dendrites + aluminium rich Al-Cu solid solution super saturated with respect to copper. The massive copper rich phase is not visible at this stage.

(ii) Age hardening response of the SSH (at 560 °C) + quenched and aged sample (at 150 °C) is higher that of a standard cast Al-4.5%Cu alloy solution treated (at 560 °C) and aged at 150 °C.

(iii) The existence of fine lamellar eutectic is isolated spots of the 10 min SSH + quenched sample could be detected on TEM examination only. Rod shaped precipitates, probably CuAl2 precipitates, were also observed in the quenched sample.

(iv) On ageing at 150 °C, numerous dark clusters, presumably those of GP zones, formed inside the α–phase of the lamellar eutectic.

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ORCID iDs

Abhimanyu Chaudhari  ♦  https://orcid.org/0000-0002-7737-9544

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