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Thermal Stability of Nanocrystalline AlCuZr Alloy Prepared by Mechanical Alloying

Vishwanath Lande[a], Dasharath S. M.*
a School of Mechanical Engineering, REVA University, Bangalore-560064, Karnataka, India

***Abstract*:**
In present study, grain growth kinetics and thermal stability of nanocrystalline Al based alloys was studied and processed through a powder metallurgy technique called mechanical alloying. The elemental (Al, Cu and Zr) powder was mixed and blended using high energy ball milling for 8h and followed by conventional sintering at a temperature of (550°C) for 1h. The produced Al alloy was analysed by means of analytical techniques XRD (X-ray diffraction), TEM(Transmission Electron Microscopy), DSC (Differential Scanning Calorimetry), SEM (Scanning Electron Microscopy) and energy dispersive spectrometry.

Key words: *Al-based alloys, thermal stability, grain growth, Mechanical alloying.*

1. Introduction

In the recent decades, Al alloys have been found as a promising materials because of their low density or weight and high specific strength and stiffness [1, 2]. Because of low density, Al alloys are widely used in light weight applications i.e Aerospace (sounding rockets, launch vehicles), Aircraft (Airframe, Fuel tank) and Automotive (Extruded condenser Tubes, engine brackets) etc. The performance of lightweight materials is required to improve further to fulfill the socio-economic requirements and challenges for greater efficiency. Nevertheless, Al alloys are used partially in high performance applications due to their low mechanical properties [3]. Refining the grain size from coarser to nanostructure and alloying (substitution or interstitial solid salution) have been used in order to improve the mechanical properties [4, 5]. A number of techniques have been emerged to develop the nanomaterials materials to improve the properties of existing counterpart. These include mechanical alloying (MA) rapid solidification plasma processing, vapor deposition torsion straining under high pressure and equal channel angular pressing MA is one of the most promising techniques used to produce several advanced materials including non-equilibrium (nanocrystalline and/or amorphous materials, disordered solid solutions, other metastable phases), equilibrium and dispersion strengthened alloys where homogenous distribution of nanosize second phase particles in nanograins matrix can be achieved successfully[6, 7, 8]. In the MA process powder blends of desired nominal compositions are subjected to high energy ball milling to promote alloying/mixing at atomic level at near ambient temperature The solid solubility limit of alloying elements can also be enhanced by MA Thus, preparation of disordered solid solutions can be achieved for the system in which equilibrium solid solubility of solute elements is negligible (e.g. Y in Al matrix). The performance of these materials is expected to be enhanced, if the nanosize grains are remained stable in the bulk consolidated components. Until unless the nanocrystalline materials are stable (even at room temperature) there is no use of these for structural parts [9, 10, 11]. If the nanocrystalline powder is not stabilized, the nanofeatures cannot be retained in the consolidated components even by advanced processing techniques such as spark plasma sintering (SPS).

None of the above reports discussed the issues of thermal stabilization of nanocrystalline grains and there is no information of thermodynamics and kinetics of the stabilization.

2. Experimental details

Mechanical alloying (MA) method was used to develop the new alloy compositions of Al-Cu-X (X=0.25, 0.5 & 1 at.% Zr). The elemental powders such as Al, Cu and Zr were purchased in Alpha Aesar company with high level of purity 99.9 % and the individual particle size of 20-100 µm. Elemental powder (Al, A-Cu and Al-Cu-Zr) various compositions were milled in tungsten carbide vial and ball using SPEX 8000M high energy ball mill. The grinding media consists of 10 mm diameter balls and a ball-to-powder weight ratio of 10:1 was maintained throughout the milling time. The vial was sealed in high purity argon atmosphere prior to milling and the milling was carried out for 8h at room temperature. The as-milled powder samples were compacted as 10 mm diameter disk samples in a stainless steel die-punch at an applied pressure of 300 MPa using a hydraulic press. Then the disk samples were annealed in batches at different temperatures from 180 to 560°C under Ar. 2%H_2 atmosphere. XRD analysis of the as-milled and annealed powders was performed using Cu-Kα radiation (λ=0.154 nm) at a scan rate of 1°/min in a Rigaku X-ray diffractometer. The crystallite size of the Al- based alloys has been calculated from five major XRD peaks. After eliminating the broadening effects due to strain by using the plot between $B_r Cos\theta$ *vs.* $Sin\theta$. The disk samples were polished to a mirror finish surface and microhardness tester was employed to perform Vickers microhardness measurements. Microhardness test was carried out using 50 g load at a speed of 15 mm per second with a dwell time of 25 s for each indentation. The each reported hardness value is the average of at least 6 indentations. Transmission electron microscopy (TEM) analysis was carried out for some selected as-milled and annealed samples using a JEOL 2000FX at a beam energy of 200 keV. The TEM samples were prepared by drop cast technique using a carbon coated copper (Cu) grid.

3. Results and Discussion

3.1. XRD analysis of metastable solid solutions

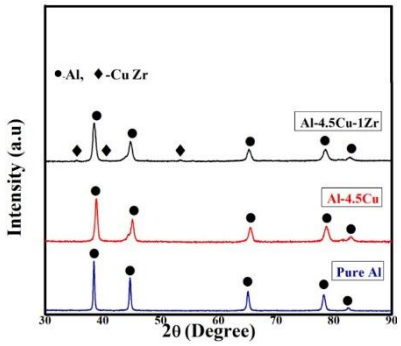

Fig. 1. XRD patterns of the as-milled samples of Al-4.5 wt.% Cu-1at.Zr in comparison with that of the Al-4.5 wt. % Cu and pure Al.

Fig. 1 shows the XRD patterns of the Al-4.5 wt.% Cu-1at.% Zr, Al-4.5 wt. % Cu and pure Al samples milled for 8 h. Formation of any inter- metallic phase(s) or presence of free element is not detectable from the phase analysis of the XRD pattrns of Al-4.5 wt.% Cu and pure Al. As per the XRD phase analysis, it can be observed that the complete dissolution of 4.5 wt.%Cu in Al has occurred after 8 h of MA. But, in Al-4.5 wt.% Cu-1at.% Zr alloy, Zr is found not to dissolve completely in Al-Cu matrix and formation of intermetallic phases like $Cu_{10}Zr_7$, Cu_5Zr could be observed as per the XRD phase analysis of the alloy. It can be noticed that the intensity of Al peaks gradually decrease and width of the peaks (FWHM) increases due to addition of 4.5 wt.% Cu and Zr in the Al alloys. The decrease in the peak intensity and increase in the peak width is due to the decrease in the crystallite size and increase in the lattice micro strain. As the XRD is known to be a weak technique and has its own limitation of detect ability, the limit of formation of the disordered solid solutions has been analyzed by precise lattice parameter variation of the Al-based solid solutions. The precise lattice parameter of Al-based alloys (a_{Al}) has been calculated from the five major XRD peaks to confirm the limit of dissolution of 4.5 wt.% Cu and Zr in Al-matrix.

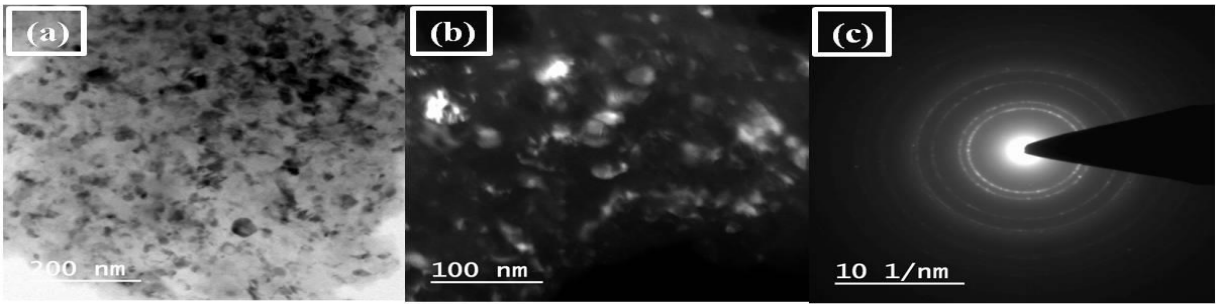

Fig. 2. TEM micrographs and SAED patterns of 8 h milled samples: (a) Bright field image, (b) Dark field image and (c) SAED pattern of Al-4.5 wt.% Cu-1at.%Zr.

Fig. 2 shows TEM micrographs and corresponding SAED pattern of the as-milled (a-c) Al- 4.5 wt.%Cu-1at.%Zr sample. From TEM imaging analysis, it can be noticed that the dark field imaging is found to be more prominent because of more contrast difference as compared to that of bright imaging mode. It can be observed from the TEM images, especially from the dark images (Fig. 2b) that the morphology and distribution of the grains are almost similar irrespective of the composition and the grain sizes are well within the nanometric range. It can be noticed from the SAED patterns (Fig. 2c) that all the major peaks of Al, i.e. (111), (200), (220), and (311) are present. This indicates that neither interme tallic phase nor any free elements are present in the solid solutions. The almost continuous rings clearly showed that the grain sizes are extremely fine and within the nanometric level. While, the presence of extra diffracted rings, which are identified as $Cu_{10}Zr_7$ (622), Cu_5Zr (220) & $Cu_{10}Zr_7$ (239), confirms the evolution of Cu-Zr intermetallic phases along with the formation of Al-based solid solution. The corresponding XRD pattern also revealed the same fact (as discussed earlier) (Fig. 1).

3.2. Thermal stability and mechanical properties

The as-milled samples of Al-4.5 wt.% Cu-1at.% Zr were annealed in batches at 180, 280, 380, 480 and 560°C under controlled Ar 2%H_2 atmosphere for 1 h, and then their respective XRD data were recorded to detect the microstructural phase changes, if any. The annealed samples were examined by rigorous microhardness measurements, the variation of crystallite size to evaluate their thermal stability.

Fig.3, respectively, show the XRD patterns along with the phase analysis of the annealed samples. The phase analysis revealed the formation of intermetallic phases such as Al_3Zr, Cu_5Zr, $Cu_{10}Zr_7$, Cu_5Al_4 and $AlCu_3$ during the annealing of the samples. It can be noticed from Fig. 8 that the annealing at 280-560°C, more number of minor peaks of inter- metallic phases were evolved. The XRD analysis clearly shows that the width (FWHM) of (e.g. Al 111 reflection) the peaks decreased with increase in the intensity as the annealing temperature increases (Fig. 3). It is important to note that the formation of intermetallic phases in Al-4.5 wt.% Cu-1at.% Zr alloy has been discussed through XRD phase analysis in the earlier section (Fig. 1). The intermetallic phases are expected to play an important role to stabilize the matrix grains by Zener pinning at higher temperature.

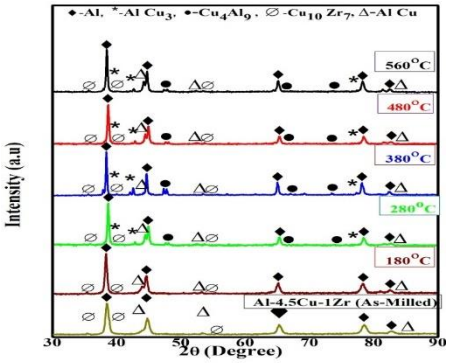

Fig. 3. XRD patterns of Al-4.5 wt.% Cu-1at.% Zr samples annealed up to 550°C.

Fig. 4 shows the variation of crystallite sizes of the Al-4.5 wt.% Cu- 1at.% Zr alloys as a function of annealing temperature. It can be observed from the (Fig. 4) that Al- 4.5 ¼t.% Cu alloy retained the crystallite size around ~73 nm after annealing at 250°C, and thereafter, grain growth occurred significantly. The crystallite size of the Al-4.5 wt.% Cu- 1 at.% Zr samples after annealing at 150℃ was found to be 35 nm. On the other hand, the Al-4.5 wt.% Cu-1at.% Zr sample after annealing at 550 °C to maintain the crystallite sizes within ~60 nm only, which ascertains their significantly high thermal stability. The grain growth is found to be very slow and stabilizes in small range (i.e. less grain growth) with increase in the annealing temperature. Many researchers [7, 8,9,10] reported that the suppress the grain growth at higher temperature possibly is due to the segregation of larger size (over size) solute elements (Nb, Y and Zr) along the grain boundaries, i.e., over size solute element acts as a good stabilizing agent. Therefore, it can be concluded that the solute segregation of Zr along the grain boundaries (thermo- dynamic mechanisms) and/or Zener pinning by second phase particles such as Al_3Zr, Cu_5Zr, $Cu_{10}Zr_7$, Cu_5Al_4 and $AlCu_3$ led to the development of superior thermally stabilize Al-based alloys.

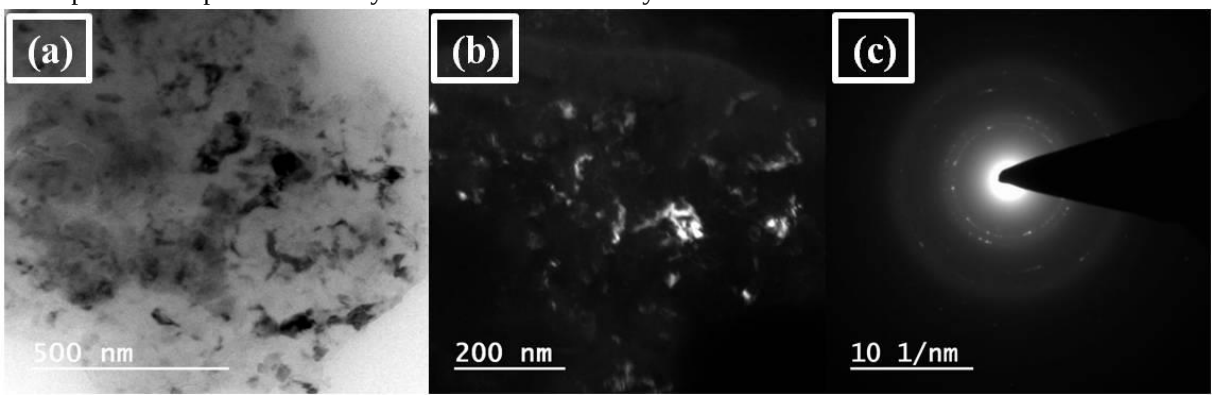

Fig. 5. TEM micrographs and SAED patterns of annealed at 550°C samples: (a) Bright field image, (b) Dark field image and (c) SAED pattern of Al-4.5 wt.% Cu-1at.%Zr.

Fig. 5. shows TEM micrographs and corresponding SAED patterns of the sample annealed at 550°C (a-c) Al-4.5 wt.% Cu-1at.% Zr. It can be observed especially from the dark TEM images (Fig. 5b) that the distributions of the grains are well within the nanometric range. It can be noticed from the SAED patterns (Fig. 5c) that all the major peaks of Al, i.e. (111), (200), (220) and (311) are present. The extra faint rings/spots indicate that the formation of intermetallic phases such as Al_3Zr (008), Cu_9Al_4 (611) and Al_3Zr (105) in the alloy. The continuous rings clearly showed that the grain sizes are extremely fine and within the nanometric range even after annealing at 550°C. Formation of the intermetallic phases has also been confirmed by the XRD phase analysis as discussed earlier (Fig.2a, b and c). The intermetallic compounds enhanced the strength of the Al-4.5 wt.% Cu based alloys by two ways: through precipitation hardening and by stabilization of the matrix grains well within the nanometer level. TEM grain size analysis corroborates well with the XRD crystallite size values of the corresponding samples.

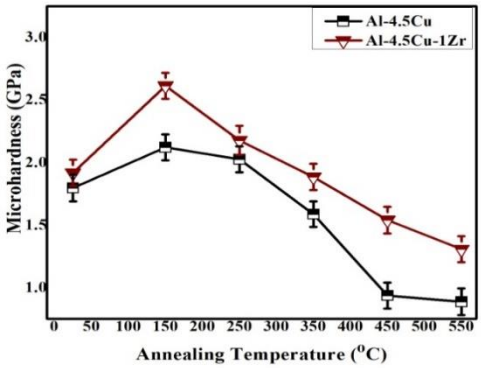

Fig. 6. Variation of hardness as a function of annealing temperatures.

Fig. 6. shows the variations of hardness for Al-4.5% Cu alloy system with the addition of Zr solutes as a function of annealing temperature. The microhardness value of the as-milled sample of Al-4.5 wt.% Cu alloy was found to be 1.75 GPa. It is gradually increased due to the addition of solute in the order of Cu — Cu+Zr in the as-milled condition. The maximum hardness values of the as-milled samples of Al-4.5% Cu alloy was estimated to be and 1.91 GPa, for the 1 at.% Zr addition. It is important to note that initially, the hardness value increased up to the annealing temperature of 150°C and then it showed a decreasing trend at higher annealing temperature. The maximum hardness values of the annealed sample was measured to be 2.61 GPa for the Zr alloys after annealing at 150°C as compared to 2.12 GPa for the Al- 4.5 wt% Cu alloy without the stabilizing agent (Zr). Therefore, improvement of the hardness occurred mainly due to the two reasons: through precipitation hardening because of the formation of fine intermetallic phases and by stabilization of the matrix grains well within the nanometer level through segregation and/or Zener pinning by the intermetallic phases[12]. Thermodynamic mechanism of the solute Zr segregation along the grain boundaries as well as the kinetic mechanism of Zener pinning by second phase particles stabilized the matrix grains in the nanometer range (<100 nm). The decrease in the hardness at higher temperature is due to the coarsening of the precipitates as well as matrix grains. The variation of hardness values and grain size analysis is found to be directly related as per the Hall-Petch relationship.

4. Conclusions

Al-4.5 wt.% Cu alloys with addition of 0.25, 0.5 and 1 at.% Zr were prepared by mechanical alloying from the elemental powder blends under inert gas atmosphere and their thermal stability, mechanical property and microstructural features were investigated in details.

1. The XRD analysis, variation of lattice parameter and TEM analysis of the as-milled samples showed the formation of intermetallic compounds was detected by both XRD and TEM analysis in the Al-4.5% Cu-1at.% Zr alloy.
2. Maximun values of values of hardness were obtained for the 150°C annealed samples, and the estimated value was found to be 2.61 GPa, for the Zr added alloys as compared to 2.12 GPa for the Al-4.5 wt.% Cu alloy without any stabilizing agent Zr.
3.Thermodynamic mechanism of the over-size solute Zr segregation along the grain boundaries as well as the kinetic mechanism of Zener pinning by the second phase particles played the pivotal role in the stabilization of the matrix grains in the nanometer range (<100 nm).

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