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# Effect of zirconium on thermal stability of nanocrystalline aluminium alloy prepared by mechanical alloying

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ABSTRACT

In the present study, a series of Al-x% Zr (x = 1–10 at.%) compositions were prepared by mechanical alloying (MA) to investigate the solid solubility extension of Zr in Al and its thermal stability. The elemental powder blends were mechanically alloyed under high purity argon atmosphere in stainless steel grinding media using SPEX 8000 M high energy ball mill. The milling was carried out for 8 h at room temperature and the ball to powder ratio was maintained at 10:1. Formation of disordered solid solutions is validated using Miedema's semi-empirical model. X-ray diffraction (XRD) analysis confirms the formation of disordered solid solution up to 1at.% Zr; whereas, $Al_3Zr$ and $Al_{9.83}Zr_{0.17}$ intermetallic phases were found to form as per the XRD pattern of 2–10% Zr alloys. Variation of lattice parameter confirmed the formation of Al-1% Zr solid solution. Crystallite size was estimated to be 41 and 30 nm, respectively, for the as-milled 1 and 10% Zr alloys. The matrix grains were found to be stabilized after annealing at 550 °C, and the XRD crystallite size of Al-10% Zr retained at ~58 nm. TEM and AFM analysis confirmed that the grain size of the as-milled as well as annealed samples was retained in the nanometre range (<100 nm), which corroborates well with the XRD crystallite size. Vickers microhardness of the as-milled 10% Zr alloy was found to be 2.4 GPa, which decreased to 1.7 GPa after annealing at 550 °C. This demonstrated that the dissolution of Zr in Al has a larger strengthening effect and Zr plausibly played a pivotal role in retaining the matrix grains size in the nanoscale range at high temperature.

## 1. Introduction

Aluminium (Al)-based alloys have a wide range of industrial applications, namely, aerospace, automobile, electronics, domestic construction and power distribution due to their high strength to weight ratio, excellent corrosion resistance, formability and thermal conductivity. In the recent years, nanocrystalline Al-based alloys have received a great attention due to their unique mechanical properties such as high specific yield strength and appreciable formability and good corrosion resistance [1]. However, the nanostructured Al alloys are often considered unsuitable for high temperature engineering applications because of instability of the grain size. Reduction of strength at elevated temperature is accounted to be the major reason behind this incompatibility [2,3]. Thus, a mechanism to strengthen the nanocrystalline Al-based alloys to make them applicable at relatively higher temperature appears to be very important.

In pure nanocrystalline metals, excess grain boundary free energy provides a huge driving force for grain growth at relatively low temperatures [4,5]. The grain growth leads to coarsening of the nanocrystalline grains and resulted in a poor mechanical strength. The grain growth becomes very serious for nanocrystalline alloys of low melting materials like Al and its alloys [6]. It is proposed that the grain size can be retained within sub-micron level by the formation of fine and homogeneous intermetallic compounds [7,8], such as in Al-Co [9] and Al-Ru [10] alloys. Various studies have been carried out to achieve grain size stabilization by the addition of small amounts of thermodynamically insoluble solute elements (oversize solute atoms) such as W (in Al) [7], which acts as a precipitation or dispersion hardening element and effectively stabilizes the grain size at high temperature [11].

Two basic approaches are used to suppress the grain growth of the nanocrystalline materials at relatively high temperatures [12]. Kinetic stabilization mechanism involves restricting the grain boundary movement by solute drag, chemical ordering and precipitation of second phase particle(s) (Zener pinning) as reported in Fe-Zr [13], Cu-Zr [14] and Pd-Zr [15] systems. The other approach to

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retain nanocrystalline grain size at high temperature is the thermodynamic stabilization. It is accomplished by reducing the excess grain boundary energy of metastable (e.g. nanocrystalline) material almost to zero by solute segregation at the grain boundary [16]. Thus, a metastable equilibrium can be achieved and no driving force would be available for further grain coarsening [16]. Zr is found to act as a good stabilizing element at high temperature as reported for Fe-Zr [13] and Pd-Zr alloys [15].

The equilibrium solubility of Zr in Al is very limited and it is only 0.083 at.%[1] at room temperature. On the other hand, non-equilibrium processing methods like mechanical alloying (MA) [17], inert gas condensation (IGC) [18] and rapid solidification processing (RSP) [19] can be used to bring thermodynamically insoluble alloying elements into the lattice of solvent up to some extent to produce disordered solid solutions [20]. Rittner et al. [18] reported a high hardness of 3 GPa of Al-Zr alloy produced through inert gas condensation technique. Al-Zr-Fe ultrafine grains (grain size ~260 nm) synthesised by physical vapour deposition technique showed a high tensile strength of 800 MPa [21]. Therefore, it is possible to produce high strength Al-Zr alloys, if the metastable nanocrystalline Al grains are stabilized by the thermodynamic and/or kinetic mechanisms. The MA is preferred among the non-equilibrium processes, because it is very effective to produce highly supersaturated solid solutions easily. The MA is also reported as a feasible solid state processing route for synthesis of large quantities of nanostructured materials [17]. Thus, it is reasonable to develop Al-Zr nanocrystalline alloys by MA and study their thermal stability. The main aim of the study is to investigate the feasibility of formation of the Al-Zr disordered solid solutions by MA and effectiveness of Zr additions on the thermal stability of such disordered alloys.

## 2. Experimental

Elemental powders blends of aluminium (Alfa Aesar −325 mesh, 99.9% purity) and zirconium (Hi-Media, −200 mesh, 99.7% purity) were mechanically alloyed in 440 stainless steel grinding media using SPEX 8000 M high energy ball mill. The grinding media consists of 8 mm (17 in numbers) and 6 mm (16 in numbers) 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 (purity <10 ppm $O_2$) prior to milling and the milling was carried out for 8 h at room temperature. The as-milled powder samples were compacted as disks specimens in a tungsten carbide die-punch using a pressure of 300 MPa by a hydraulic press. Then, the disk samples were annealed in batches at different temperatures from 150 to 550 °C for 1 h under (Ar + 2% $H_2$) atmosphere. X-ray diffraction (XRD) study was performed using a Cu K$\alpha$ radiation ($\lambda = 0.154$ nm) at a scan rate of 1°/min in a Rigaku X-ray diffractometer. The average crystallite size was calculated from the broadening of 3 major peaks after eliminating the broadening effects due to strain by using the plot between $B_r\text{Cos}\theta$ *vs*. $\text{Sin}\theta$ [22]. The precise lattice parameter of the Al-based alloys ($a_{Al}$) was calculated from 3 major XRD peaks by the extrapolation of $a_{Al}$ *vs*. $(\cos^2\theta/\sin^2\theta)$ plot to $\cos\theta = 0$ [23]. The samples were polished to achieve mirror finished surface and Buehler Microhardness (Model: UHL Technische Mikroskopie VMHT) tester was employed to perform Vickers microhardness measurements. The microhardness test was carried out using 50 g load at a speed of 15 μm per second with a dwell time of 15 s for each indentation. Atomic force microscopy (AFM) analysis was performed on the disks samples using a silicon nitrate probe in VECCO di Innova atomic force microscope (Model: TS-150). Transmission electron microscopy (TEM) analysis was carried out for some selected as-milled and annealed samples using a JEOL 2000FX electron microscope at a beam energy of 200 keV. Sample preparation for TEM analysis was carried out by drop cast technique using carbon coated copper (Cu) grid.

## 3. Results and discussion

### 3.1. Effect of Zr concentration

Fig. 1a shows the XRD patterns of the as-milled Al-Zr alloys. It can be noticed that the Zr peak is not detectable from the XRD patterns of any compositions. The XRD phase analysis also reveals that plausibly a disordered solid solution is formed up to 1% of Zr alloy. This is so as only Al peaks are detected from the relevant XRD pattern (if any dilute quantity of intermetallic phase(s) formed in 1% Zr alloy, it is not possible to detect by XRD technique due to its limited detectability for the second phase. Beyond 1% of Zr, probability of formation of intermetallic phases such as $Al_3Zr$ and $Al_{9.83}Zr_{0.17}$ increased with increase in Zr concentration (2–10% Zr alloys). This clearly indicates that the solid solubility of Zr in Al plausibly could not be enhanced beyond 1 at.% by MA due to the formation of the intermetallic phases (as detected from the XRD patterns of 2–10% Zr alloys). It can be noticed, especially from the high angle peaks, that the peak intensity gradually decreased and peak width at FWHM increased with the increase in the Zr content. This is due to the combined effect of grain size refinement (finer crystallite size) and increase in the residual strain [24].

As the sensitivity of XRD to determine the presence of secondary phases has a limit of 1–2 wt%, the limit of formation of disordered solid solution has been analyzed by precise lattice parameter measurement of Al-based solid solutions. The magnified view of (111) peak in Fig. 1b indicates that there is a peak shift towards lower 2θ position with respect to the standard peak position of pure Al (111). It is to be noted that the peak shift is very small and it can be detected only for the 1% Zr alloy. The peak shift for the alloys containing more than 1% Zr is not detectable as per the XRD analysis. It should be remembered that the peak shift towards the lower diffraction angles is an indication in the increase in the lattice parameter [23], which is possible only due to the formation of solid solution, i.e. Zr atoms dissolved in Al lattices. The variation of lattice parameter (calculated from the XRD analysis) of the Al-rich solid solution ($a_{Al}$) can be a very useful tool to predict the solid solubility of a solute [14,23,25]. Fig. 2 shows the variation in the $a_{Al}$ for all the compositions. The $a_{Al}$ was calculated from 3 major XRD peaks to reveal the dissolution of Zr in Al during MA. The refined values of $a_{Al}$ were calculated from the plot of $a_{Al}$ *vs*. $(\cos^2\theta/\sin\ \theta)$ after extrapolation of $\cos\theta = 0$ [22]. It is observed that initially the $a_{Al}$ increased slightly from 4.0495 Å (pure Al) to 4.0592 Å corresponding to Al-1% Zr alloy. After that there is almost no significant change in the $a_{Al}$ even after addition of more Zr (Fig. 2), which indicates no further dissolution of Zr in Al occurred in the same conditions of MA. The initial increase in the $a_{Al}$ indicates the dissolution of larger in size Zr atoms (atomic radius = 0.158 nm) into the lattice of Al (atomic radius = 0.143 nm) [26]. And thereafter, the added Zr mostly converted to intermetallic phases as indicated in the XRD plots (Fig. 1a). The temperature rise during milling possibly played an important role leading to the formation of intermetallic compounds, especially in the high stacking fault energy Al alloys [17]. It is well known that the alloying elements which are forming intermetallic phases do not play any role in the variation of lattice parameter of matrix phase; only the alloying content which dissolves in the lattice of solvent can change the lattice parameter of solvent [27].

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[1] Hereafter, at.% will be written as %, unless it is indicated.