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Synthesis and characterization of mechanical alloyed Mg-Ni-Ca and Mg-Cu-Ca amorphous alloys

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Abstract

Magnesium and its alloys are widely recommended for automotive, electronics and biomedical industries due to their strength to weight ratio. The mechanically alloyed magnesium with Ni, Cu and Ca alloys exhibits superior properties. In this work, the ternary $Mg_{70}Ni_{10}Ca_{20}$ and $Mg_{85}Cu_{10}Ca_5$ alloys were synthesized by mechanical alloying for 10 h in SPEX mill with 10:1 ball to powder ratio under argon (Ar) atmosphere. Their structural and phase transformation with respect to milling time and composition were studied by X-ray diffraction (XRD), scanning electron microscopy and energy dispersive X-ray spectroscopy. The XRD pattern showed the formation of amorphous with nano crystalline peaks. The Mg_2Cu and CaCu intermetallic phases were identified in $Mg_{85}Cu_{10}Ca_5$ alloy and Mg_2Ni and $MgNi_2$ intermetallic compounds were identified in $Mg_{70}Ni_{10}Ca_{20}$ alloy. A crystallite size of 44.45 nm was measured from the α-Mg XRD peak in Mg-Cu-Ca alloy, and 45.59 nm was measured for the Mg_2Ni phase in Mg-Ni-Ca alloy.

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Keywords: Mechanical alloying; lightweight materials; bulk metallic glass; nano-crystalline materials; amorphous structure

1. Introduction

Magnesium and its alloys are widely used in automotive, aerospace and consumer electronics industries because they possess low density, high specific strength and stiffness. Generally, Mg-Ni binary alloys contain Mg_2Ni intermetallic compound which is widely used as a hydrogen storage material [Lee et al. (2007), Islam and Medraj

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(2005)]. Various Mg-based alloys have been developed in the recent years, which may include the Mg-Zn-Ca, Mg-Ni-Ca, Mg-Ag-Ca and Mg-Cu-Ca. Mg-based bulk amorphous alloys are of significant scientific and commercial interest because of their superior strengths, elastic limits and corrosion resistance due to their inherent glassy structure when compared with crystalline materials [Laws et al. (2014)]. The rapid quenching techniques are used to produce a few millimeters of Mg-based alloys, the mechanical alloying (MA) of elemental powder mixtures can be an alternative processing route to produce the bulk amorphous alloys without much difficulty. The Mg-Ni-Ca amorphous alloys have been studied previously by Laws et al. (2009) and showed the lowest density (~2.0 g/cc) for the highest Mg content (86 atomic %). The Mg-Cu-Ca amorphous alloys also attracted much attention due to their lower material cost, high compressive fracture strengths and good ductility [Senkov et al. (2006), kumara et al. 2006)]. The Mg-Cu-Ca amorphous alloys have been studied previously by Faqiang Guo et al. and showed the lowest density ~1.8 g/cc fracture strengths of ~570 MPa for the high magnesium content [Hino et al. (2000), James et al. 2007), Xin wang (2014), Senkov et al. (2007)]. This study focuses on the production of high-strength, low-density Mg–Ni–Ca and Mg-Cu-Ca amorphous alloys through mechanical milling techniques. A comparison of the microstructural characterization and thermal stability of milled powders is presented.

2. Experimental procedure

Elemental powders of Mg (99.9%, -50 mesh), Ni (99.9%, -100 to +325 μm), Cu (99.9%, +72 μm) and Ca (99.9%, -8 mm to 3.25 mm), were weighed to yield the desired compositions of $Mg_{70}Ni_{10}Ca_{20}$ and $Mg_{85}Cu_{10}Ca_5$. The weighed powders were filled in the high speed steel vial together with the high carbon steel balls in an argon-filled glove box equipment. The ball to powder ratio (BPR) was maintained as 10:1. 4% of stearic acid was added as lubrication to the powders. The SPEX shaker ball mill was employed for the mechanical alloying process. The powders were milled 10 h by following the cycles of 10 min-OFF and 15 min-ON in SPEX mill. Then the resultant powders were carefully removed from the vial for the scanning electron microscopy (SEM), x-ray diffraction (XRD) and energy dispersive spectrum (EDS) analysis. SEM analysis was performed to understand the size and morphology of milled powders. EDS analysis was used to find out the distribution and influence of alloying elements in the milled powders. XRD characterization was used to verify the amorphous state and to identify the formation of intermetallic compounds with respect to the milling time. The XRD patterns were obtained using PANalytical X'pert Pro powder X-ray diffractometer with a CuKα radiation and were acquired from 20° to 120° 2θ with a 0.02° step size and 7 s of a point scan time. The analysis of the XRD patterns was carried out using X'Pert HighScore Plus software. The crystallite size was calculated using the Scherrer equation. The thermal stability of the samples was investigated by differential scanning calorimetry (TA instruments, USA) at a heating rate of 10 °C/min.

3. Results and discussion

High energy ball milling (BM) or MA is able to produce the amorphous phase [Suryanarayana (2001), Murty and Ranganathan (1998), Datta et al. (2000)], but the system must satisfy the well-known Inoue´s empirical guidelines to form an amorphous phase. So as per the Inoue´s empirical guidelines, the proposed elements in our system display a large difference in atomic radius between each constituent element of at least 20% (Cu-128 pm, Mg-160 pm Ni-125 pm and Ca-197 pm), and all of which display negative heats of mixing with one another. In addition, the relatively large atomic radius of the solute elements (Cu, Ni, Ca) in these systems enhances the glass forming ability (GFA). Fig. 1 shows the composition ranges to form the amorphous or crystalline phase in Mg-Cu-Ca and Mg-Ni-Ca system.

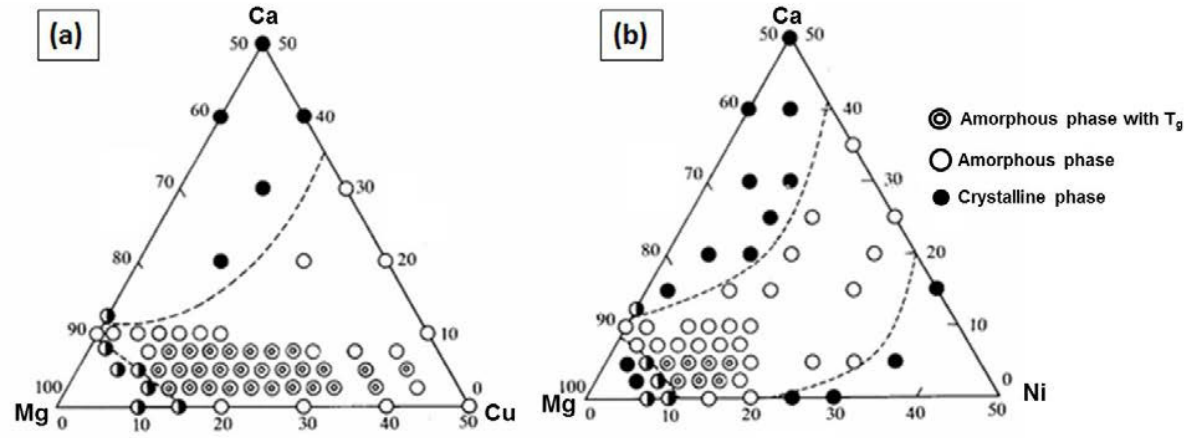

Fig. 1. Composition ranges for the formation of amorphous phase in (a) Mg-Cu-Ca; (b) Mg-Ni-Ca system [Toshisuke et al. (1993)].

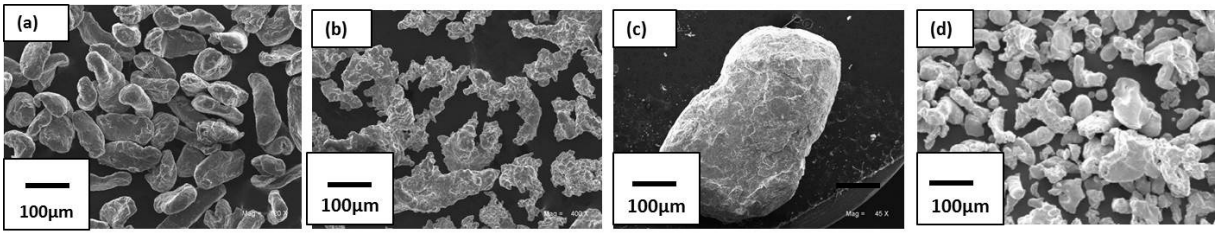

Fig. 2. SEM images of (a) Mg; (b) Ni; (c) Ca; (d) Cu powders - As received.

To understand the Mg-Cu-Ca and Mg-Ni-Ca ternary systems and its phases, it is necessary to understand its binary system effectively. The Mg-Cu-Ca ternary system comprises the three Mg-Cu, Mg-Ca and Ca-Cu binary systems. The following phases are calculated as stable as per the stoichiometry: Mg, Cu, Mg_2Cu and $MgCu_2$ phases in the Mg-Cu system; Cu, Ca, Ca_2Cu, CaCu, $CaCu_5$ phases in the Cu-Ca system; Mg_2Ca phase in the Mg-Ca system. The Mg-Ni-Ca ternary system comprises the three Mg-Ni, Mg-Ca and Ni-Ca binary systems. The following phases are identified: Mg, Ni, Mg_2Ni, and $MgNi_2$ for the Mg-Ni system; Ca, $CaNi_2$, $CaNi_3$, Ca_2Ni_7 and $CaNi_5$ for the Ni-Ca system; Mg_2Ca for the Mg-Ca system. Fig. 2 shows the SEM images of Mg, Zn and Ca powders used in the milling process. The shape factors for the Mg, Ni, Cu and Ca are different from each other. The Ni powder exhibits a very irregular morphology. The Ca powder particles revealed bigger in size than the other particles.

Figs. 3(a) and (b) shows the SEM images and XRD spectrum details of Mg-Ni-Ca and Mg-Cu-Ca powders milled for 10 hours. Both milled powders exhibited agglomerated particles. The agglomeration may happen due to the occurrence of a cold welding phenomenon during ball milling. Due to the effect of agglomeration, the powder particles are welded with other particles, resulting that the particle size becomes enlarged after milling. So it is difficult to find out the particle size of milled powders from the observed SEM images.

Fig. 3(c) shows the comparison of the EDS distribution (atomic percentage) between as-mixed and 10h milled powders of both Mg-based systems. A reasonable level of oxygen was detected in the EDS analysis of milled powders. This could happen due to the formation of oxides. The reduced atomic percentage values of milled powders compared with the as-mixed condition, revealed the formation of intermetallic compounds.

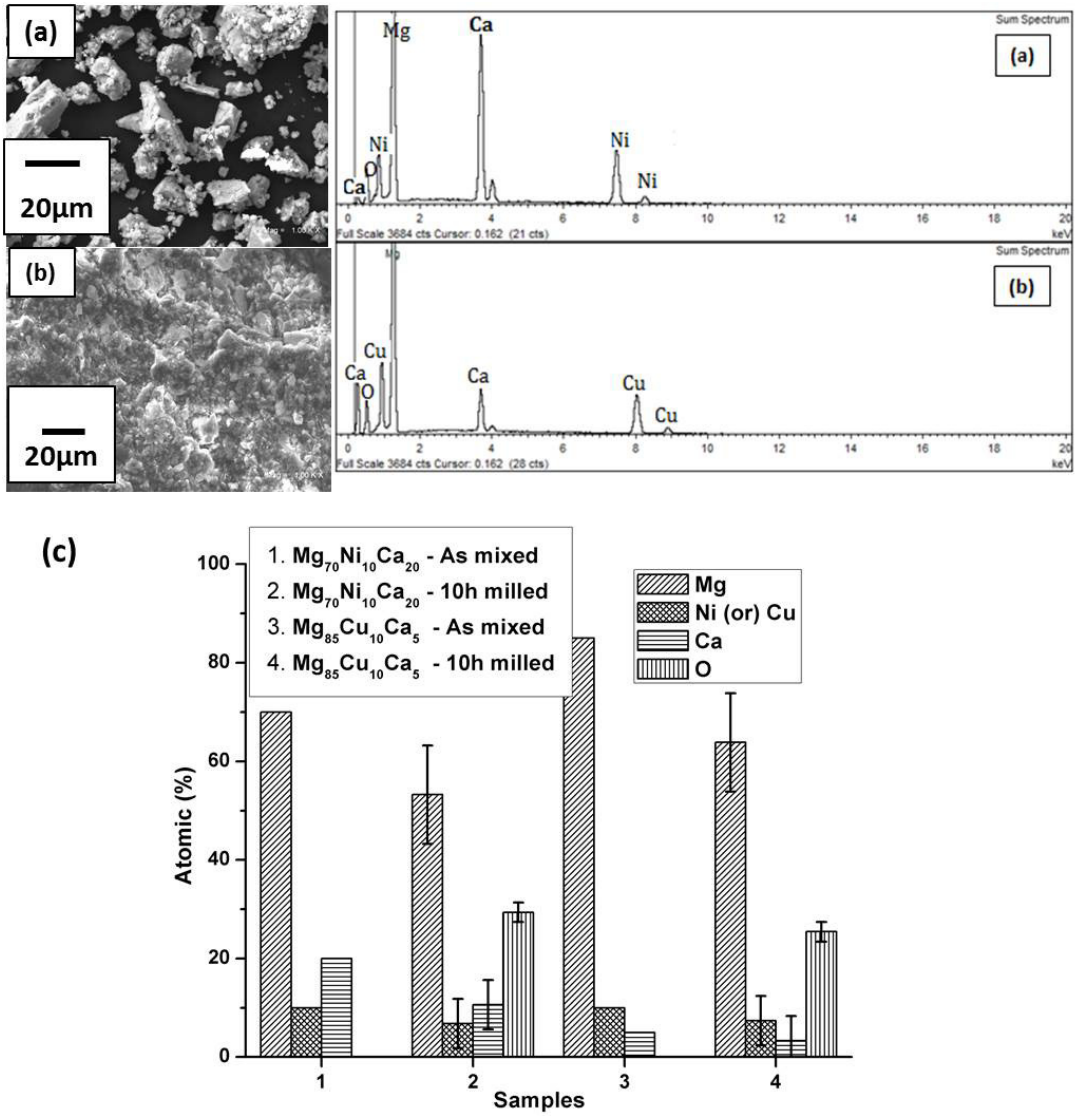

Fig. 3. SEM images and spectrum analysis of milled powders (a) $Mg_{70}Ni_{10}Ca_{20}$; (b) $Mg_{85}Cu_{10}Ca_5$; (c) EDS bar chart to compare the as-mixed and milled powders.

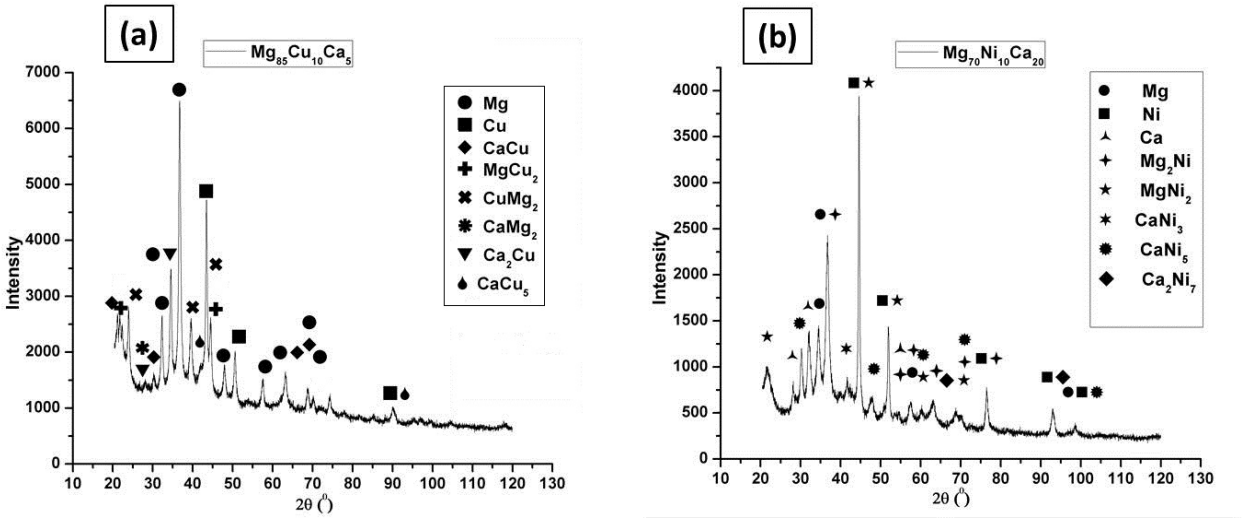

Fig. 4. XRD patterns of powders milled for 10 h (a) $Mg_{70}Ni_{10}Ca_{20}$; (b) $Mg_{85}Cu_{30}Ca_5$.

Fig. 4 shows the XRD patterns of Mg-Cu-Ca and Mg-Ni-Ca milled powders. The Mg-Cu-Ca milled powders revealed the amorphous-like halo regime with nano-crystalline peaks. The ball milling technique can produce the equilibrium intermetallic phases, amorphous compounds, nano-crystalline materials, or metastable crystalline phases of various materials. However, the formation of phases and nanoscale microstructure is still confusing during the ball milling process due to the complex mechanism involved in ball milling, especially in the field of solid-state amorphization caused by ball milling. The 10 h of ball milled Mg-Cu-Ca powders revealed the Mg, Cu, $CuMg_2$, CaCu phases and few other compounds ($MgCu_2$, $CaMg_2$,Ca_2Cu and $CaCu_5$) as shown in Fig. 4(a). The compounds of $MgCu_2$, $CaMg_2$ and $CaCu_5$ are identified as lower intensity levels in the XRD analysis. Zongqing Ma et al. (2012) investigated the Mg-Cu alloy and found that Mg firstly reacts with Cu, forming the Mg_2Cu alloy in the primary stage of ball milling. The XRD results of Mg-Cu-Ca milled powders also confirmed the formation of Mg_2Cu phases [Tanaka et al. (2008)]. The 44.45 nm of crystallite size was calculated for higher intensity of α-Mg peak. The Mg-Ni-Ca milled powders expressed the better amorphous-like halo regime with nano-crystalline peaks than Mg-Cu-Ca milled powders (Fig. 4(b)). Predominantly the Mg, Ni, Ca, Mg_2Ni and $MgNi_2$ phases were appeared in the XRD analysis. The other compounds of $CaNi_3$, $CaNi_5$ and Ca_2Ni_7 revealed as lower intensity levels and distributed as random in the whole Mg-Ni-Ca XRD spectrum. The formation of Mg_2Ni phase occurs after 4 hours of ball milling as per the results reported previously [Moomen et al. (2013), Jose et al. (2010)]. 45.59 nm of crystallite size was calculated for the Ni contained $MgNi_2$ compounds.

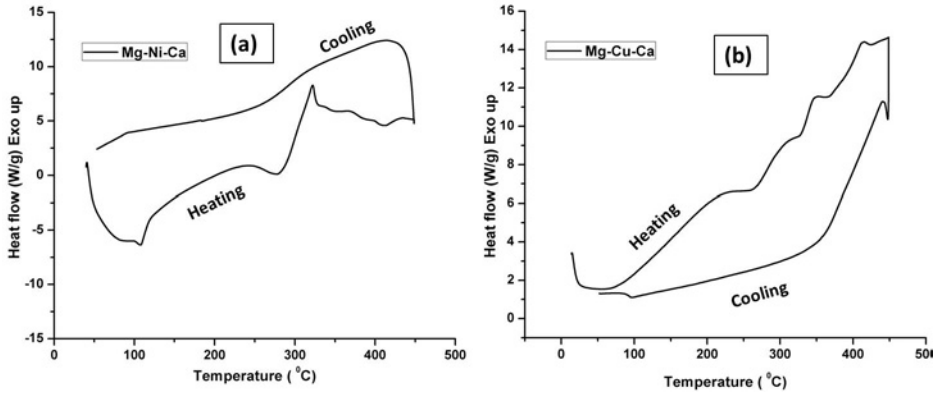

Fig. 5. DSC analyses of 10 h milled powders (acquired at 10 °C/min) (a) Mg-Ni-Ca; (b) Mg-Cu-Ca.

Fig. 5 shows the DSC curves of milled Mg-Ni-Ca and Mg-Cu-Ca powders. An enthalpy relaxation corresponding to the glass transition (T_g or T_x=109 °C) and following three unclear transitions are the characteristics of Mg-Ni-Ca alloy. The unexpected transitions indicate the presence of multiple phases (Mg, Mg_2Ni) and abnormal crystallization. Similar DSC results have been obtained by Laws et al. (2009). The endothermic reaction (270 °C) and following two exothermic reactions (344 °C and 411°C) are characteristics of Mg-Cu-Ca alloy.

4. Conclusion

The microscopic examination of both milled powders reveals agglomeration which is attributed to domination of cold welding events during mechanical alloying. A reasonable level of oxygen and the variation of atomic percentile values (deviation from the as-mixed values) were found in the EDS analysis of milled powders. The Mg-Cu-Ca milled powder revealed the Mg, Cu, $CuMg_2$, CaCu phases and the Mg-Ni-Ca milled powder revealed the Mg, Ni, Ca, Mg_2Ni and $MgNi_2$ phases. The crystallite size of Mg in the Mg-Cu-Ca system was calculated as 44.45 nm, whereas the crystallite size of $MgNi_2$ compound in the Mg-Ni-Ca system was calculated as 45.59 nm. Further studies with higher milling time will probably be able to produce the amorphous phase without crystalline compounds.

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