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LLNL-PROC-790098

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September 17, 2019

Denver X-ray Conference
Lombard, IL, United States
August 5, 2019 through August 9, 2019

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X-RAY DIFFRACTION STUDY OF MECHANICAL ALLOYED Li-Sn-Zn

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I. ABSTRACT

Fusion power plants based on the deuterium-tritium (DT) fuel cycle breeds the tritium fuel by neutron reactions with lithium. Hence, Lithium has to be incorporated into the breeding blanket that surrounds the fusion source. Because of the chemical reactivity of Li with water and air, an alternative alloys based on Li was proposed for this replacement. Recent work by LLNL scientists proposed the used of an alloy of liquid Li-Sn as the breeder for the inertial fusion energy (IFE) power plant. Unfortunately, this alloy does not meet the TBR (tritium breeding ratio) and energy multiplication requirements for fusion reactors. However, based on other calculations, also done here at LLNL, it was proposed that a ternary alloy with the addition of Zn will be a good candidate and will satisfy the nuclear, thermal and chemical requirements.

To syntheses this ternary alloy, conventional melt mixing was first carried out at temperature above 800°C in argon filled glove box. Typically, binary metals can form quite easily depending on the mixing kinetics and eutectic points. However for ternary alloy, the result is not so clear because of competing kinetics and the tendency for phase separation. We report here on an alternative method of synthesize this ternary alloys by the method of mechanical alloying. Samples of $Li_{60}Sn_{20}Zn_{20}$ and $Li_{70}Sn_{20}Zn_{10}$ were prepared. The resulting powders were examined using x-ray diffraction and differential scanning calorimetry techniques and their results clearly showed that the powders are of a single FCC cubic phase. The XRD analysis also suggests that Li and Zn share occupancy in the tetrahedral sites while Sn are at the FCC 4a sites which is consistent with published powder results. From the above 2 compositions and having single phase FCC structure, it can be concluded that non-stoichiometric powders according to $Li_{(1+x)}SnZn_{(8-x)}$ where x=0 to 8 can be prepared by this technique.

II. INTRODUCTION

At present, fossil fuel which is made up of oil, coal and natural gas originated from prehistoric plants and animals died over millions of years, is the major source of power for the world. This is a non-renewable resource which is forecasted to be depleted in a couple of decades. The fossil fuel has also significant unintended effects of polluting the environment resulted in global warming and greenhouse gases. It is therefore, fitting that a new energy source for the future be found. As it is understood, nuclear energy, fission and fusion offer a solution to potentially limitless sustainable energy supply. Fission reactors are currently operated throughout the world however, there are concerns regarding their impacts on the environment in terms of radiation safety and disposal of spent fuel.

Nuclear fusion, on the other hand, can potentially provide the needed energy source and bypass the issue of radiation safety and spent fuel disposable. Fusion power is based on combining deuterium-tritium (DT), forming helium, releasing a neutron and the binding energy at

extremely high pressure and temperature are being investigated by many laboratories. The deuterium can be harnessed from seawater. Tritium can be conveniently produced by the cycling lithium during the released neutron reaction. Therefore, Lithium has to be incorporated into the breeding blanket that surrounds the fusion source.

Because of the chemical reactivity of Li with water and air, an alternative alloy base on Li-Sn was suggested but it does not meet the TBR (tritium breeding ratio) and energy multiplication requirements. Recent work by LLNL proposed the addition of Zn into Li-Zn ternary alloy to be used as the breeder in inertial fusion energy (IFE) power plant [1, 2]. It is proposed that ternary alloy with the addition of Zn will satisfy the nuclear, thermal and chemical requirements for a fusion reactor [3]. Other breeding blanket was also suggested but it involved lead which is typically considered hazardous [4].

The present work focuses and compares the synthesizing of the ternary alloy by high temperature melting and mechanical alloying (MA). As expected, melt processing resulted in phase separation upon cooling. We observed that the resulting material by MA remained single phase at all temperatures and is expected to have all the predicted thermal and chemical properties. Moreover, this single phase ternary alloy powder is more manageable than the multiple phase material synthesized by high temperature melting.

III. MELT PROCESSING

The most convenient method of synthesizing an alloy is by melt processing. The neat elements or compounds of the elements are brought together and heated to above their melting points. In the liquid state, the atoms are free to move around and well mix. When the atomic potentials and the kinetics are favorable, they tend to interact with each other and upon cooling, crystalline phases are formed. These resulting phases are somewhat controlled by the kinetics, according to the atomic species and concentration, temperature and cooling rates as pointed out in the thermodynamic calculations [5]. Unfortunately, for ternary alloys, the kinetics is more complex. Very often, binary phases occur much easier than ternary. They tend to form multiple phases at specific compositions at their eutectic points. In some cases, ternary alloys can be formed at specific concentrations.

IV. MECHANICAL ALLOYING

Mechanical alloying (MA) also refers to as high energy ball-milling is a powder metallurgy methodology widely used to synthesize metal alloys which otherwise are not possible. Generally, it consists of applying high energy ball collisions to the sample in a confined space. This is accomplished by mixing the powder samples with hardened steel balls in a steel container. The container is then made to vibrate resulting in a series of collisions between the balls and/or the wall of the container.

There are still no clear agreements on the mechanistic behavior during the MA process (for review articles see [6]). At times, it is also used to pulverize chucks of material into powders and intimately mixed the neat materials and improving mixing properties. It can also be viewed as localized high pressure and high temperature mixing. At the atomistic level, it is also generally

thought of as a process through the accumulation of structural defects in crystalline lattices, intimate mixing of elemental species at interfaces, hot spot theory, defect enhanced diffusion, shear-induced mixing, interface roughening and contact melting. In many instances, amorphous structures can also be formed [7].

V. SAMPLE PREPARATION

High purity neat elemental samples of Li, Sn and Zn were purchased from commercial supplier (Alfa Aesar). The materials are weighed using precision microbalance according to the atomic ratio and placed in a Ta crucible and placed in a furnace which was heated up to 900 °C for 3 hours. The experiment was carried out in an argon filled glove box.

MA of the powder was carried out using the commercial SPEX 8000D mixer. The cover was removed so that the vials can be exposed to a stream of cooled air from a portable laboratory air-conditioner using two large air hoses. The temperature at the end of the air hoses was measured to be 9 °C. Stainless steel (316L) balls (1/4 inch diameter) were used. The vials are also made of hardened steel.

VI. EXPERIMENTAL

The resulting sample removed from the furnace after high temperature melting and then cooling to room temperature is shown in Figure 1a. Unfortunately, the sample was stuck to the Ta crucible and also observed to show domains which are probably crystalline. After considerable amount of scrapping, the sample was removed and loaded onto the NETZSCH's STA 449 ***F1*** *Jupiter*®, High-Temperature DSC instrument, which is also located inside the glove box to avoid air contamination.

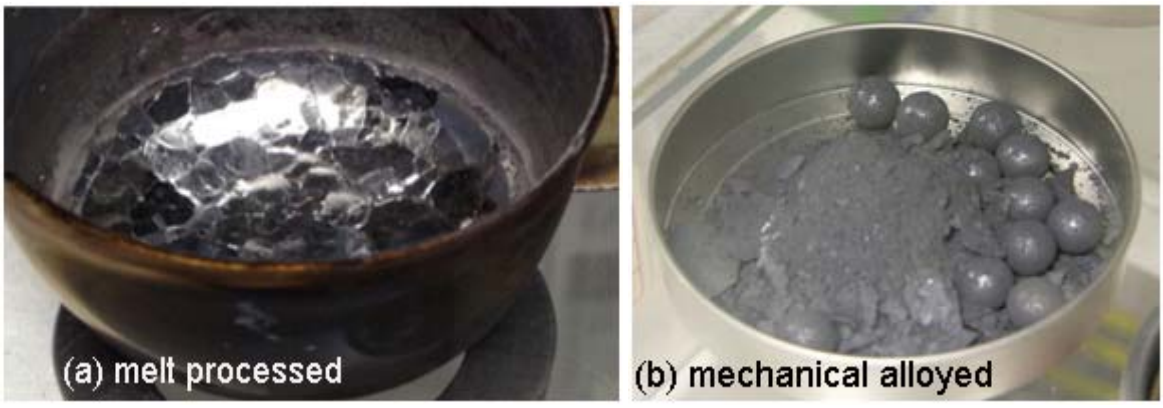

Figure 1: Resulting material after (a) melt processed (b) mechanical alloyed

For MA process, the sample, after carefully weighed and loaded into the machine hardened steel vial in the glove box. The vials can be sealed using 'o' rings. Samples of neat Li, Sn and Zn in the atomic ratio of $Li_{60}Sn_{20}Zn_{20}$ and $Li_{70}Sn_{20}Zn_{10}$ (refer to as 622 and 721) were prepared. MA was carried out in the duration of 6, 24 and 36 hours and typically resulting powder was shown in Figure 1b. The powders were loaded onto a sealed sample holder and examined using Bruker

Discover XRD instrument, utilizing CuKa radiation. Step scans were performed from 10 to 80° (2θ) at 4 seconds acquisition time per step. The x-ray generator was set at 40KeV and 40 mA.

VII. RESULTS AND DISCUSSIONS

(a) MELT PROCESSING

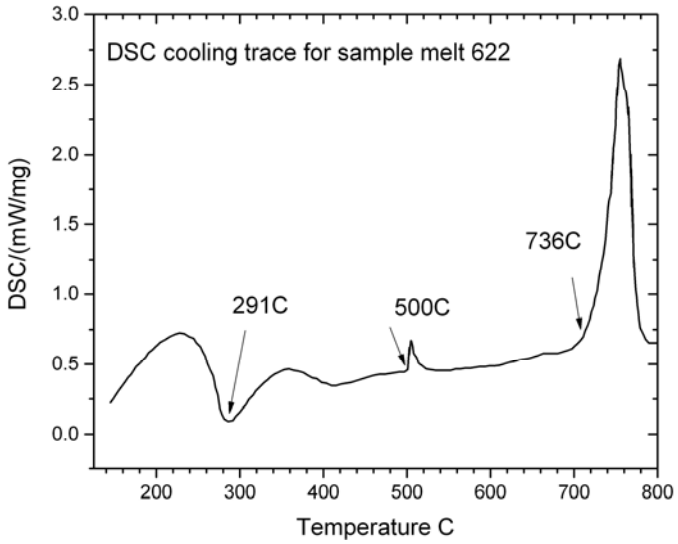

Figure 2: DSC trace for melt process $Li_{60}Sn_{20}Zn_{20}$

Figure 2 shows the resulting cooling DSC traces for melt process for sample 622. A series of broad/sharp peaks can be observed which indicates the formation of multiple phases of either Li-Sn or Li-Zn as previously as pointed out [5].

(b) MECHANICAL ALLOYING

Figure 3a shows the heating and cooling DSC traces for the mechanical alloyed powder 622 when the sample was milled for 6 hours. Clearly only one peak can be observed which indicates that the materials is made up of a single phase which melts at about 715 °C. The peak at roughly 500°C is probably due a small amount of contaminant detected during the heating cycle. The lower temperature DSC peaks as observed in Figure 2 are not observed here.

The XRD results for MA 622 sample is shown in Figure 3b, along with the ICDD listings for neat Li, Zn, Sn and the ternary alloy of Li-Zn-Sn [8]. The strong partial broad peak at lower 2θ angle is due to the sample holder window. Clearly, the initial powder shows the presence of neat Li, Sn and Zn, indicated in the lower curve as expected. After 6 hours of mechanical alloying, the XRD result is also shown on the top plot indicating the presence of the FCC cubic phase, consistent with the published result for $Li_{7.72}Sn_4Zn_{4.28}$[9]

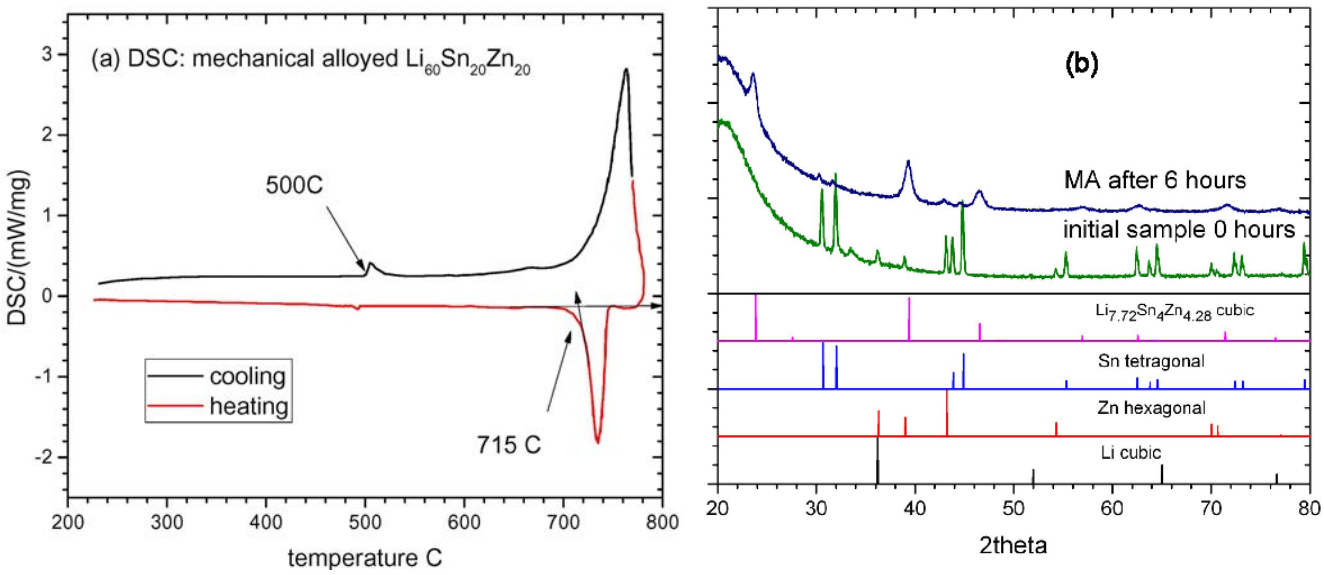

Figure 3: (a) DSC traces (b) XRD traces for MA - $Li_{60}Sn_{20}Zn_{20}$ powder

Two additional samples with milling times of 24 and 36 hours were prepared and the XRD results are shown in Figure 4a and again, single cubic phase is observed. The contaminant as mentioned in Figure 3 is not observed for the 24 and 36 milling times samples. A sample 721 was also prepared by similar high energetic ball milling. The XRD results (not shown here) also show similar behavior. The spectra are evaluated and the crystallite sizes are found to be ~ 7 nm with the lattice spacing of 6.510A. The crystallite size and the lattice parameter do not appear to change significantly with increasing milling time.

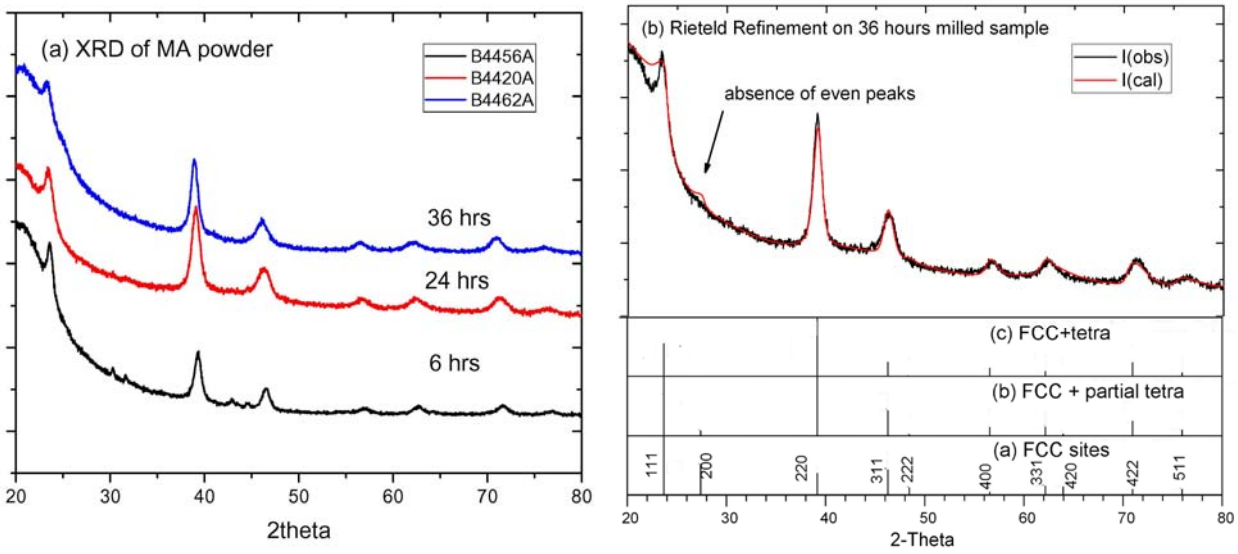

Figure 4: (a) Comparison of XRD spectra for MA of 622 powder at different milling times and (b) Rietveld analysis fitting

Rietveld analysis (using Jade 9 software) was performed on the sample milled for 24 hours using the model of Pobitschka et. al. and fixing the concentrations at $Li_{1.93}Zn1_{.07}Sn$. Sn occupies the

4a sites (0, 0, 0), Li resides on the 4b sites (½, ½, ½) and Zn/Li shares the 4c sites (¼, ¼, ¼) and 4d (¾, ¾, ¾) sites. The fit was observed to be reasonably good with an R-factor of 3.72% as plotted in Figure 4b. However, it is difficult to refine the concentrations of Li/Zn at the 4c sites due to the large difference in atomic structure factors between Zn and Li, and the data quality.

The lower plots in Figure 4b compares the simulated XRD peaks for the FCC structure at just the (a) 4a and 4b sites, (b) 4c and 4d partially filled and (c) fully filled. As expected, the result indicates that "even" peaks (002), (222), (400) diminish in intensity with increasing filling of the 4c and 4d tetrahedral sites. This proves that in these samples, the tetrahedral sites are filled and shared by the Zn and Li atoms. The above results also indicate that non-stoichiometric ternary alloy can be synthesized by the method of mechanical alloying. Since in the FCC structure, there are 4 atoms at the 4a and 4b sites, and 8 atoms at 4c sites, the composition range can varies according to $SnLi_{(1+x)}Zn_{(8-x)}$ where x=0 to 8.

In summary, it can then be concluded that at the instantaneous high energy ball collision, the crystalline phases of Li, Sn and Zn are melted down to form the FCC cubic structure with Sn atoms situated at the 4a sites of the lattice. Li/Zn atoms are then forced into the tetrahedral sites and that the atom at the tetrahedral site is trapped by 4 Sn atoms. The fact that Li/Zn remains in the tetrahedral site and do not phase separate upon cooling suggest that chemical order is likely present in the liquid state where 3 Sn atoms encompassed either a Zn or Li atom.

VIII. REFERENCES

1. Dunne, M., et al., "Timely Delivery of Laser Inertial Fusion Energy (LIFE)", *Fusion Sci. Tech.* **60**, 19 (2011)
2. Latkowski, J. F., et al., "Chamber design for the Laser Inertial Fusion Energy (LIFE) engine." *Fusion Sci. Tech.* **60**, 54 (2011),
3. Jolodosky, A., and M. Fratoni, "Neutronics evaluation of lithium-based ternary alloys in IFE blankets. (2014)". *LLNL-SR-664710*
4. L. Gaincarli, M. Ferrari, M.A. Futterer, S. Malang, "Candidate blanket concepts for a European fusion power plant study", *Fusion Engineering and Design* 49-50 (2000) 445-456
5. Turchi, P. E., *Thermodynamic assessment of the ternary alloy system Li–Sn–Zn.* (2014). LLNL-TR-653675
6. P.S. Gilman, J,S.Benjamin, :Mechanical Alloying", Ann. Rev., Mater., Sci., 1983, 13 (279-300), C. Suryanarayan and Nasser Al-Aqeeli, 'Mechanically Alloyed Nanocomposites", *Prog. In Mat. Sci.* 58 (2013) 383-502
7. R.B. Schwarz, R.R. Petrich and C.K. Saw, "The Synthesis of Amorphous Ni-Ti Alloy Powders by Mechanical Alloying" *J.of Non-cryst. Solids, 76 (1985) 281-30*
8. ICDD listings PDF#00-015-0401 (Li), PDF#00-004-0831 (Zn), PDF#00-004-0673 (Sn)
9. PDF#00-031-0762 (Li7.72Sn4Zn4.28), PDF#04-015-4321(RDB) (Li1.93 Zn1.07 Sn), Pobitschka W., Schuster, U.,Z. Naturforsch., B: Anorg. Chem., Org. Chem., v33 p115,1 (1978), PDF#04-015-4889(RDB), Katscher H., Hahn H.U.,Z. Naturforsch., B: Anorg. Chem., Org. Chem., 33 p115,1 (1978), PDF#04-015-4889(RDB), Katscher H., Hahn H.,Naturwissenschaften, v53 p361 (1966)

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-PROC-790098