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Alloy Nanoparticle Fabrication by Mechanical Approach

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Abstract

This paper reports the results of preparing alloy nanoparticles by mechanical grinding followed by filtration to sort the particles according to size. Although the long-term goal of this work is to prepare icosahedral quasicrystalline nanoparticles, the alloy used in this study is of $Al_{65}Cu_{25}Fe_{15}$ composition and multi phases, under the assumption that the established procedure is applicable to future quasicrystalline nanoparticle fabrication. The obtained particle size and elemental information were investigated using scanning electron microscopy and energy dispersive x-ray spectroscopy. Problems with filter fragment fall-out and salt contamination were encountered and procedures to address the problems have been suggested and tested. The study is successful in obtaining alloy particles with reduced sizes.

INTRODUCTION

The end goal of this study was the preparation of quasicrystalline nanoparticles from alloys. For the atomic configuration in solids, crystal and amorphous stand in the two extremes. In crystalline structure, atoms are arranged according to predefined rules while in amorphous structures atoms are packed in a completely random fashion. Crystalline structure possesses both translational and rotational symmetries, while amorphous structure presents none of these. Quasicrystalline structure can be considered as a state between the two; it has rotational symmetries and lacks translational symmetries.

Among the three structures, quasicrystalline structure was the latest to be found [1]. Since its discovery, many researchers have dedicated their efforts to studying this field, which

has resulted in significant progress in the understanding of the properties of this structure. For example, alloys of quasicrystalline structure are found to be hard and brittle compared to regular crystalline alloys of similar composition, and they typically have lower electrical conductivity. It has also been revealed that there are two types of quasicrsytals, polygonal and icosahedral. Among these discoveries, finding alloys with stable pure icosahedral quasicrystalline phase is directly related to our present work [2, 3].

Material property is affected by size, which is especially true when the size is of the nanometer scale [4]. For example, it is known that the melting point of gold nanoparticles is significantly different from that of bulk. The emission spectrum of Cadmium Selenite quantum dot can be controlled simply by adjusting the size. Though nanoparticles with crystalline or amorphous structure have been reported and applied, there are no reports concerning the fabrication of icosahedral quasicrystalline nanoparticles. Because of the novel structure and nano size, icosahedral quasicrystalline nanoparticles are expected to show improved performance in many applications [5, 6]. The lack of reports in regard to nanoparticle preparation is likely due the fact that well-used nanoparticle fabrication approaches, such as the solution-based method, do not work in this case. Alloy of pure icosahedral quasicrystalline phase can only be prepared by standard alloy preparation methods, which are not suitable for nanoparticle preparation.

The long-term goal of this study was to prepare icosahedral quasicrystalline nanoparticles, by mechanically crushing pure stable icosahedral quasicrystalline alloy, followed by filtering to sort particles according to their size [7, 8]. The results of our attempt to establish an effective protocol using an alloy of $Al_{65}Cu_{25}Fe_{15}$ nominal composition and multi phases are reported here [9-12]. It should be noted that $Al_{65}Cu_{25}Fe_{15}$ alloy used in the present study is not pure icosahedral quasicrystalline phase, though it is closely related. This test alloy was used because of the limited supply of alloy with pure icosahedral quasicrystalline phase. It is assumed that any established procedure that was effective for the $Al_{65}Cu_{25}Fe_{15}$ alloy, would also be applicable to future work on alloys of pure icosahedral quasicrystalline phase.

EXPERIMENTAL

The as-prepared alloy was cut to the desired size with a diamond saw. The piece of alloy obtained was grinded with a mortar and pestle for forty hours in methanol. The particles were then suspended in methanol at a concentration of one milligram of alloy per milliliter of methanol for subsequent usage. This is referred to as the raw solution for the rest of this manuscript.

Filtering was used to sort particles by size according to the following procedures. 2 millilitres of solution were gravity fed though a syringe filter of 5, 1, and 0.45 μm pore size. To compensate for volume loss and to ensure that we obtained filtrate through each filter, extra methanol was added to maintain the total volume at 2 millilitres before subsequent filtering. At each step, 100 microliters of the filtrate was sampled and prepared for examination by scanning electron microscopy (SEM). These samples of filtrate were left in air so that the methanol could evaporate allowing the concentration of the particles to double. Finally, a drop of 10 microliter concentrated solution was dispersed on a silicon wafer to prepare SEM specimens. The two types of filters tested were made of polypropylene and glass fibre respectively.

SEM examination was carried out on a SEM of TESCAN VEGA-3 XMU equipped with STD X-MAX50 energy dispersive x-ray spectrometer (EDS) detector operated on an Aztec HKL system. The acceleration voltage used was 20 kV.

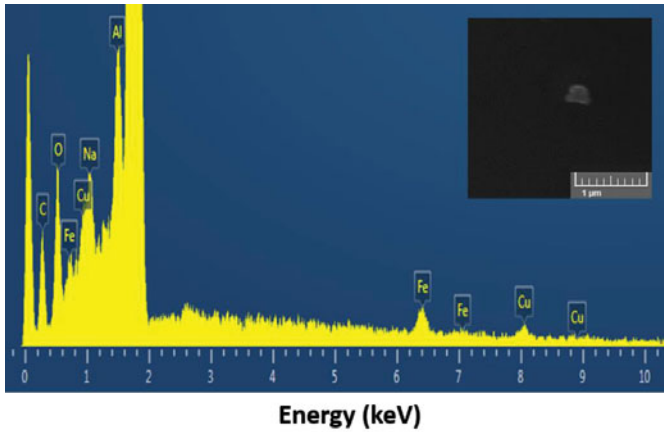

Figure 1 SEM image (inset) and EDS spectrum of an obtained nanoparticle.

RESULTS AND DISCUSSION

While further efforts should be made to perfect the procedure, it has been proven that nanoparticles can be obtained through sequential filtering of the prepared solution by using glass filters of 5, 1, and 0.45 um pore sizes. This procedure is currently considered to be optimum. Fig. 1 shows an EDS spectrum with the inset SEM image of one such nanoparticle. As shown in the SEM image, the particle size is smaller than that of the filter pore, demonstrating the effectiveness of grinding and filtering protocol. Peaks corresponding to Al, Cu, and Fe elements on the EDS spectrum prove that the particle is from the original alloy. Other peaks correspond either to the substrate silicon wafer or contamination. It is acknowledged that the EDS spectrum is not suitable for quantitative analysis because: (a) the hundred nanometer sizes of the particles are smaller than the penetration depth of the electron beam (estimated as 1 µm for 10 kV acceleration voltage [13]), and (b) the surface of the particles are not flat as required for quantitative analysis.

The optimum procedure was established based on the following experimentations. First, the effectiveness of grinding in reducing particle size was examined. Typical SEM images of particles obtained by grinding for 2, 10, and 16 hours are shown in Figs. 2(a), 2(b), and 2(c), respectively. While particle size reduction is obvious from 2 to 10 hours grinding, no obvious difference is observed in particle size from 10 to 16 hours grinding, though it was assumed that the longer the grinding time is the smaller the particle size is. It was determined that 40 hours grinding was a good compromise between the need for reducing particle size, and the physical limitations on laboratory time. The size distribution of the obtained particles was investigated using SEM, where the particles are assumed to be spherical in shape and the diameters are measured from the SEM image. The top histogram

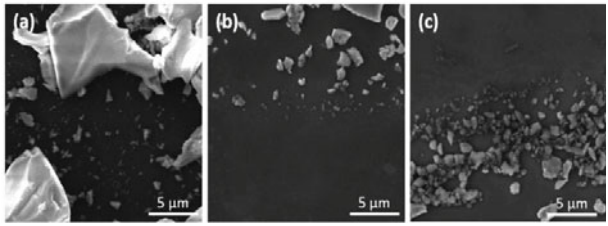

Figure 2 SEM images of obtained particles after grinding for (a):2, (b):10, and (c): 16 hours.

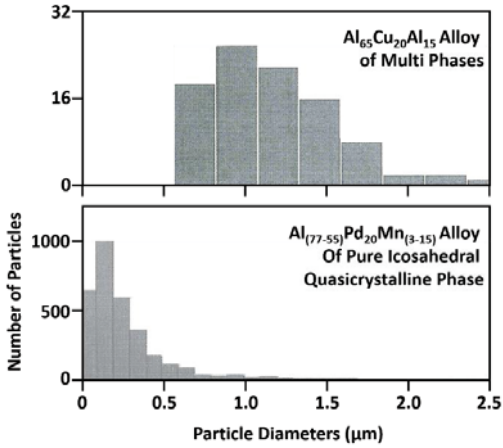

Figure 3 Histograms showing particle size distribution of obtained particles after grinding for 40 hours of (a) Al65Cu20Al15 and Al(77-55)Pd20Mn(3-15) alloys.

of Fig. 3 shows the size distribution of particles obtained from the $Al_{65}Cu_{20}Al_{15}$ alloy of multi phases. The histogram is peaked at a particle diameter of 0.80 μm. As a comparison, results for particles prepared the same way from $Al_{(77-55)}Pd_{20}Mn_{(3-15)}$ alloy of pure icosahedral quasicrystalline phase is shown in in the lower part of Fig. 3, which has a peak around 0.15 μm. While it is acknowledged that size investigation by SEM suffers the drawback of inaccuracy in measuring smaller particles and a limited sampling population, this primary result indicates a difference between the two cases. With the same preparation procedure, alloy of pure icosahedral quasicrystalline phase tends to produce particles of smaller sizes, which is in agreement with previous reports that icosahedral quasicrystalline alloy is brittle [14]. The filtering process was additionally optimized. It was found that diluting the original 1 milligram per milliliter solution to half the concentration is effective in increasing the particle population in the filtrate, probably due to a reduction in clogging caused by larger particles. The effectiveness of filtering with filters of 5 μm pore size is demonstrated in the SEM images of Figs. 4(a) and 4(b). Fig. 4(a) shows the particles in the filtrate. Particles trapped on the filter were back-pushed off the filter, and used to prepare the specimen shown in Fig. 4(b). The effectiveness of size sorting by filtering is obvious. Better methods for SEM specimen preparation were also established. Initially it was found that simply dispersing the solution onto a wafer and waiting for it to dry does not produce an ideal specimen. As shown in the SEM image of Fig. 5(a), thus obtained specimen tends to have particles agglomerated as the methanol vaporizes and recedes. Several trials lead

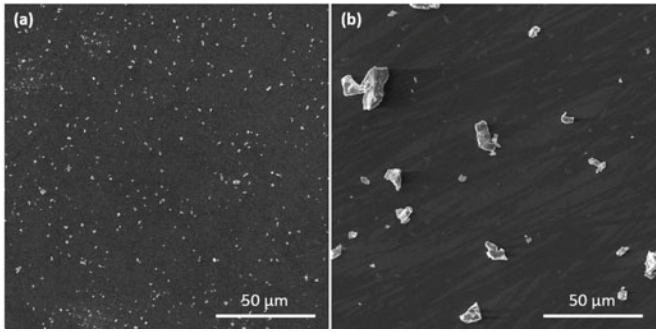

Figure 4 SEM images showing particles through (a) and caught (b) on a filter of 5 um pore size.

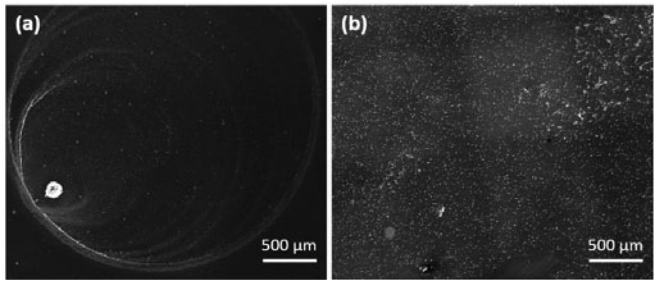

Figure 5 SEM images showing particle distribution on (a) as-prepared and (b) pre-wetted wafers. Alloy particles appear with bright contrast.

to the following approach: pure methanol was dispersed on the surface of the substrate before dispersing the solution containing the particles. This is referred to as pre-wetting in the rest of the paper. As shown in the SEM image of Fig. 5(b), pre-wetting results in a more desired, even and single particle dispersion, which is adopted in subsequent experiments.

Two problems were encountered in filtering the particles. First, it was found that the strength of the filter affects the result. The polypropylene filter, which was used in the initial stage of the experiment, appeared to fall-out and contaminate the specimen. Figs. 6(a) and 6(b) are SEM images with the suspected filter fall-out marked by arrows. This speculation was confirmed by the following experiments. First, SEM examination of specimens prepared from the raw solution without going through the filter did not display such features. Second, the concentration of this suspected filter fall-out increased as the number of the filters the solution was put through increased. Third, EDS spectrum from these features registers a very strong carbon peak as shown in the EDS spectrum of Fig. 6(c), where an enlarged fall-out SEM image is inserted to show where the spectrum was collected from. The carbon peak is consistent with a polypropylene make-up. Of note is the fact that the filter fall-out was not detected when the raw solution containing alloy particles was replaced with pure methanol. This demonstrates that the fall-out from the filter is directly related to the presence of the particles. This fall-out obscures the SEM observation of the desired particles. Fortunately, switching from the polypropylene filter

to the glass one made a significant improvement, as shown in the SEM image of Figs. 6(d) and 6(e), and was adopted for the rest of the experiment.

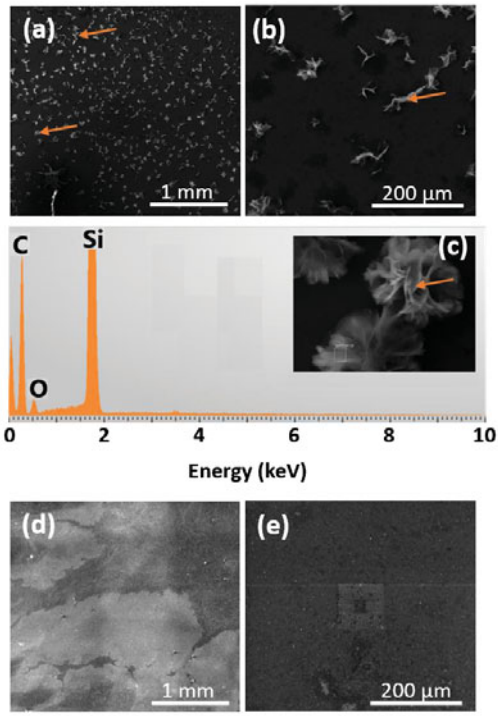

Figure 6 Fall-out from polypropylene filter is marked with arrows on the SEM images of (a) and (b). A strong carbon peak on the EDS spectrum in (c) supports the assumption of filter fall-out. Filter fall-out is significantly reduced when a glass filter is adopted as shown in the SEM images of (d) and (e).

The second problem encountered with the filtering process was contamination of particles by salt, as shown in the EDS spectrum of Fig. 7 and the corresponding inset SEM images. The salt contained elements such as Na, Mg, Ca, and Cl. As revealed by the SEM images, sometimes the salt showed typical nanocrystal morphology with distinguished facets, a square-like shape in the present case. Other times these salt particles displayed an irregular shape, where Al, Cu, and Fe elements corresponding to the starting alloy was detected, in addition to salt elements. It is likely that features with distinguished facets are single crystals of pure salt while those with irregular shapes have alloy particles embedded inside. To trace the origin of the salt, wafers at different steps of SEM specimen preparation were examined. No salt was detected on the original clean wafer or on the wafers with pure methanol dispersed, implying that both the wafer and the methanol were not the source of the salt. However, when the specimen was prepared with methanol that went through the filter, salt was detected. The detection of salt is independent from the filter types used. It is speculated that trace amounts of salt on the filter were washed out with the filtrate. Since methanol was left to evaporate during the specimen preparation, the salt was concentrated and its negative effect amplified, presenting a challenge for SEM characterization.

Efforts were made to remove the salt. Initially an attempt to rinse the filters before use was made with the simple aim of washing away the residual salt. However, this was found to weaken the filters significantly, causing an increased amount of filter fall-out and allowing larger particles to pass through. The second experiment involved scratching the silicon wafer with diamond paper, causing grooves to form in the wafer which the nanoparticles

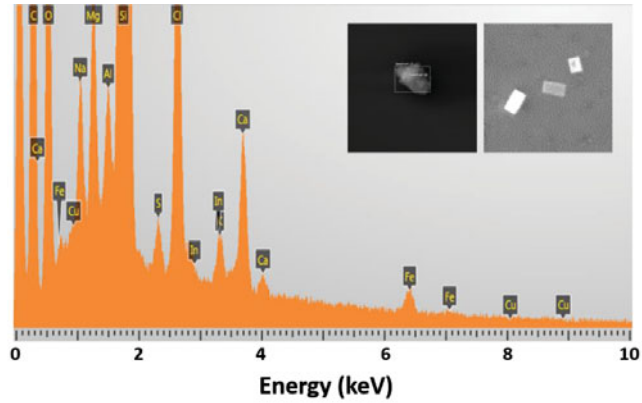

Figure 7 EDS spectrum of the salt contamination. The inset SEM images show two types of salt morphologies.

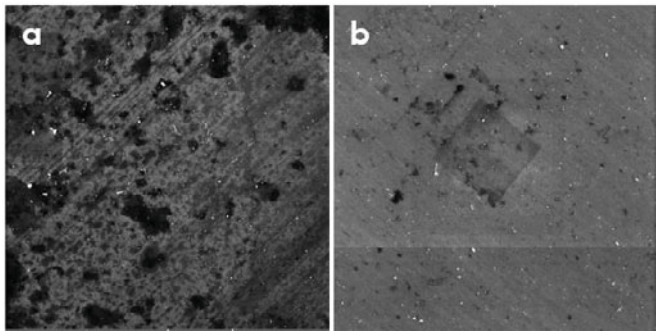

Figure 8 SEM images of the as-prepared (a) and rinsed (b) wafers.

could stick to. Then, once the SEM specimen was prepared, the wafer was rinsed with water while retaining the desired alloy particles. Fig. 8(a) shows the SEM image of a specimen prepared in this manner prior to the rinse, here the salt appears as stain. This stain is largely removed on the SEM image of Fig. 8(b) corresponding to the same specimen following rinsing.

CONCLUSION

Preparing brittle alloy nanoparticles by mechanical grinding followed by filtering has been demonstrated to be possible. This is significant since there is currently no established protocol for fabricating this type of alloy into nanoparticles. Pre-wetting silicon wafers is recommended for preparing SEM specimens in order to obtain a uniform and single particle distribution. Fall-out of the filter material was encountered and can be minimized by adopting a glass filter, instead of a polypropylene type. Salt contamination in the

prepared SEM specimen was observed and found to be directly related to the filter. Using relatively rough silicon wafers in preparing SEM specimens of filtered particles, and rinsing the wafer with water following preparation, was demonstrated to be effective measure for reducing this salt contamination.

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