Gamma-Ray Induced Modifications in A Series of Pb-Free Sn–1.0Ag–0.5 Cu-X Solder Alloys Used for Radiation Shielding

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ABSTRACT

Irradiation effects on the mechanical properties of a series of low Ag-content Sn–1.0Ag–0.5Cu-x solder alloys (x= 2 wt. % In and Bi) have been investigated. The solder alloys were exposed to γ-rays at high doses ranging from 200 to 800 kGy. The induced modifications were studied by means of several standard experimental techniques of mechanical and structural analysis of alloy materials. An anomalous strain softening phenomenon was observed in these alloys induced by high doses of γ-radiation. It was found that the enhanced ductility with a slight decrease in strength occurs at a critical dose of 400 kGy. The mechanical response of Bi-containing solders is characterized by increased yield and ultimate tensile strengths as well as the decline in ductility with increasing dose, although the Sn–1.0Ag–0.5Cu and the In-containing alloys are slightly affected at higher doses. The impact of γ-radiation has been interpreted in terms of microscopic deformation mechanisms, since the mechanical property enhancement is caused by the cell formation and dislocation channel deformation mechanism. Such effects could assist the choice of these alloys as a new structural material design strategy in manufacturing gamma radiation shielding.

Keywords: Lead-free solders, γ-radiation softening, Microstructure, Mechanical properties.

1. INTRODUCTION

The irradiation effects on the mechanical response of metallic materials have been the subject of great importance for nuclear applications over the recent years (1-3). One crucial step towards understanding the reliability of these materials will be elucidating the deformation response of the highest densities of interfaces as these interfaces are likely to control the overall phase stability and mechanical properties (4). Hence, these studies were motivated primarily by the need to understand the microstructural evolution of structural materials for the purpose of lifetime extension of the existing fleet of nuclear reactors.

The irradiation of metallic materials by energetic particles causes significant embrittlement and degradation of their mechanical properties (5), most notably an enhanced strength with a considerable decrease of ductility, often accompanied by a severe decrease in uniform plastic flow and loss of strain hardening capacity, especially at higher irradiation doses >0.1 displacements per atom (dpa) (6). Such effects limit the lifetime of an existing flotilla of nuclear reactors. Although this has been acknowledged in a large number of reported interaction mechanism studies (7), a full measurement of the connection between irradiation-induced hardening and changes in the mechanical properties are required, particularly in commercial structural alloys used for radiation shielding applications in nuclear reactors.

In structural materials, the multiscale nature of the irradiation impairment of metallic alloys has been assessed in the literature (8). One of the few noticeable features is the self-interstitial dislocation loops and aggregated defect clusters that are responsible for the mechanical property changes. Above a critical defect concentration, the material deforms by plastic flow localization, giving rise to strain softening in terms of the engineering stress–strain response. However, the metallic materials with high strength and good ductility are critical for keeping the safe, reliable and economic operation of nuclear plants (9).
Recently, Pb and Pb-based alloys are used in manufacturing gamma radiation shielding. Owing to the environmental and health issues of Pb, a large scale lead-free solders are used as a protective materials. The Sn–Ag–Cu (SAC) alloys are very attractive candidates because of their advantages in the mechanical properties. They can also offer a decrease in the mass of garment while providing equivalent or better protection\(^{(10)}\). In this paper, we report an abnormal irradiation softening phenomenon in a series of low Ag-content Sn–1.0Ag–0.5Cu-x lead-free solder alloys (x= 2 wt. % In and Bi) irradiated with doses of gamma rays up to 800 kGy, and the physical mechanism governing irradiation softening has been discussed.

2. EXPERIMENTAL

Bulk solder specimens of Sn–1.0Ag–0.5Cu, Sn–1.0Ag–0.5Cu–2.0 wt.% In and Sn–1.0Ag–0.5Cu–2.0 wt.% Bi were fabricated using Sn, Ag, Cu, In and Bi ingots (purity 99.99\%). Their compositions are hereafter called SAC (105), SAC (105)-2In and SAC (105)-2Bi, respectively. The chemical compositions of three solder alloys are listed in Table 1.

Table (1): Chemical composition of the lead-free solders studied (wt. %)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu</th>
<th>Ag</th>
<th>Fe</th>
<th>As</th>
<th>Bi</th>
<th>Sb</th>
<th>In</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC(105)</td>
<td>0.502</td>
<td>1.005</td>
<td>0.002</td>
<td>0.001</td>
<td>0.000</td>
<td>0.014</td>
<td>0.001</td>
<td>Bal.</td>
</tr>
<tr>
<td>SAC(105)-2In</td>
<td>0.504</td>
<td>1.004</td>
<td>0.002</td>
<td>0.001</td>
<td>0.000</td>
<td>0.014</td>
<td>2.001</td>
<td>Bal.</td>
</tr>
<tr>
<td>SAC(105)-2Bi</td>
<td>0.503</td>
<td>1.006</td>
<td>0.002</td>
<td>0.001</td>
<td>2.008</td>
<td>0.014</td>
<td>0.006</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

The melting process was carried out under a KCl LiCl (1.3:1) atmosphere in a ceramic crucible and kept at 700 °C for about 1 h to achieve the homogeneous characteristics. The melt was poured into a steel mold to prepare the chill casting ingot with a diameter of approximately 10 mm. A cooling rate of 6–8 oC /s was achieved, so as to create fine microstructure typically found in small solder joints in microelectronic packages. Because of different approaches in the specimen design, test setups and experimental methodology are necessary to investigate solder tensile behavior at different volumes. Therefore, the homogenized cast ingots were then mechanically machined into a wire samples with gauge length marked 4 x 10-2 m for each samples and 1.2 mm diameter. Details are described elsewhere.\(^{(11-13)}\). The microstructure was examined by scanning and transmission electron microscopy (SEM JSM-5410 and TEM JEOL 3010, Japan). A solution of 2%HCl, 3%HNO3 and 95% (vol.%) Ethyl alcohol was used to etch the samples. Phase identification was carried out by Energy Dispersive X-ray Spectrometry (EDS). Before tensile testing, the specimens were annealed at 120 °C for 45 min to reduce the residual stress induced during sample preparation. Then, the samples were irradiated by the \(^{60}\)Co gamma cell irradiation facility (type MC-20 Russian Atomic Energy) at different gamma doses ranging from 200 to 800 K Gy. These irradiations were performed at the Gamma Division, Atomic Energy Authority, Cairo. The dose rate was 1.2kGy/h. The samples were positioned at the center of the drivingbelt and the irradiation process was achieved automatically. Tensile properties were characterized using a computerized tensile testing machine.\(^{(14)}\) The tensile tests were carried out at various doses ranging from 0.0 to 800 K Gy and constant temperature of 25 oC. The axial strain is measured in accordance with the ASTM: E83-10a, and ASTM D767/D767M-11 standard practices for force verification. Then, the mechanical properties were obtained by averaging three testing data.
3. RESULTS AND DISCUSSION

3.1. Microstructure of Alloys

As shown in Fig. 1 (a), the microstructure of unirradiated SAC (105) solder with a fully dendritic microstructure consists of (i) β-Sn dendritic phase and (ii) eutectic region surrounding interdendritic regions of β-Sn phase. High-magnification FE-SEM observations in Fig. 1(b) and EDS analysis revealed that the eutectic region consists of two types of contrast IMC particles: One is the fine needle-like Ag3Sn precipitates with a length of 2–13 µm. Another is a circular or plate-like Cu6Sn5 particles with a size of 2–4 μm. In contrast, the solidification morphology associated with unirradiated SAC (105)-2In alloy does not appear dendritic structure, definitely with any extended Sn-rich phase formed, as seen in Fig. 2a and b. The rather coarse IMC particles in SAC (105) solder with a small fraction, can be compared to the extremely wide area of fine IMC, with a size of about 2–4 µm in SAC (105)-2In solder.

![Fig (1): Low and High-magnification backscattered scanning electron micrographs of unirradiated: (a and b) SAC (105) solder and EDS analysis of Ag₃Sn and Cu₆Sn₅ IMC phases.](image)

Moreover, the large aspect ratio of needle-like Ag₃Sn changes into a small one (a more round cross-section) with In doping. This can be ascribed to the higher affinity between Sn and In and the redistribution of alloying elements with respect to that of SAC (105) solder. The presence of In element promotes the nucleation of Cu₆(Sn,In)₅ IMC as confirmed by EDS analysis, which may be due to the high solubility of In in Sn, and providing more heterogeneous nucleation. The fine structure observed in Fig. 2 could result in creating high densities of interface boundaries to offer impartial sinks for point defect annihilation. However, it is difficult to distinguish and characterize the microstructure of Cu₆Sn₅ and Cu₆(Sn,In)₅ IMCs shown in Fig. 2b, since they possess the same morphology with a similar bright and contrast. In order to explicate the distribution of In element in the alloy matrix, element mapping analysis (EPMA) was carried out on the inset of the lower right of Fig. 2(b).
As can be seen in Fig. 2, the white phase composed of Ag and In, while Cu element was found in the white and gray phase. A large amount of In element was found to be distributed in the Sn-rich phase. In the case of unirradiated SAC (105)-2Bi alloy, three types of phases, named needle and rod-like Ag3Sn precipitates (gray phase), circular and rod-like Cu6Sn5 particles (dark phase), white fine Bi particle (phase) and Bi-rich phase, were found in the solder matrix as indicated in Fig. 3a and b. Bi element was found to be uniformly distributed in the β-Sn matrix solder, especially around Ag3Sn precipitates. This statement can be confirmed by EDX analysis, which shows that the fraction of Bi particle in Sn-rich phase was about 88.4 wt% for the bright colored phase. Fig. 3 provides an additional evidence for the formation of micro-voids on the surface of unirradiated SAC (105)-2Bi microstructures, which may affect the ductility of Bi-containing solder. In addition, Bi element was found to change the large dendritic structure of β-Sn phase into fine grains with average size of 3 µm as seen in Fig. 3c.
Fig (3): Low and High-magnification backscattered scanning electron micrographs of unirradiated: (a-c) SAC(105)-2Bi solder and EDS analysis of Bi.

3.2. General tensile tests

Fig. 4 shows the comparative tensile curves of the alloy materials, unirradiated and irradiated at γ-doses of 400 and 800 kGy. Tensile tests were carried out at room temperature and a constant strain rate of 2.9 x10-3s-1. To rationalize this behavior, the ultimate tensile strength (UTS), yield stress (0.2% YS), Young’s modulus and elongation (El.%) were assembled in a histogram (Fig. 5) and Table 2. The baseline alloy behavior was characterized by an initial elastic stage followed by the appearance of a yield point at 0.2% strain and subsequent pronounced plateau region, where the plateau region increases with the In and Bi additions. Notably, the highest UTS and Young’s modulus of unirradiated samples are that of the SAC (105)-2Bi alloy (of about 50.3 MPa and 27.5 GPa, respectively) with higher gains in ductility than the SAC (105) as seen in Fig. 5. The enhancement in both strength and ductility of SAC (105)-2Bi is basically due to the solid solution effect and precipitation hardening of Bi [13]. The intermediate values are those of the SAC (105)-2In solder, which are associated with higher elongation (about 63.7 %,) than the other two alloys (i.e., higher drop resistance).
Fig (4): Comparative tensile curves of unirradiated and irradiated SAC(105), SAC(105)-2In and SAC(105)-2Bi solder alloys at doses of 400 and 800 kGy

The higher ductility in SAC (105)-2In solder could be ascribed to the formation of small sub-grain size of primary β-Sn (1-2 µm) and eutectic area. Besides, the formation of fine IMC particles (~200 nm) at the sub-grain boundaries could affect the tensile strength. Such IMC particles could contribute to some intergranular embrittlement and hardening. However, the SAC (105) alloy showed the lowest UTS and Young’s modulus with small elongation values, although the work hardening capacity is slightly enriched in the initial stage of deformation. Nevertheless, the elongation increased while UTS, 0.2%YS and Young’s modulus of SAC (105) and SAC (105)-2In solders decreased with γ-doses of 400 kGy, in contrast to the SAC (105)-2Bi alloy. When the γ-doses reached 800 kGy, the opposite behavior was observed for the three alloys, revealing that irradiation effects on the mechanical response of metallic materials depend on the alloy composition and radiation doses. Depending on the energy transmitted to a lattice atoms by gamma rays, the damage produced by γ-doses can produce a fine-scale features such as dislocation loops (excess concentrations of vacancies and self-interstitial atoms). Unfortunately the present technique does not approve the vacancy-interstitial character, leaving a substantial part of clarification lacking. The dose dependence of the tensile properties is summarized in Fig. 6 and Table 2. Post-irradiation tensile properties were measured at room temperature at a strain rate of 2.9x10^-3 s^-1.
Fig (5): Histogram of: ultimate tensile strength (UTS), yield stress (YS), young modulus and elongation (El %) for SAC(105), SAC(105)-2In and SAC(105)-2Bi solder alloys at doses of 0.0, 400 and 800 kGy at $\varepsilon_{\gamma}=2.9 \times 10^{-3}$ s$^{-1}$

As can be seen, the relationship between the tensile parameters and irradiation doses is complicated by the fact that resolved tensile parameters will vary from one dose to another as well as with the alloying element additions. To clarify these effects on the tensile parameters, the tensile parameters were extracted from the stress–strain curves and elucidated in Fig.7. For SAC (105) and SAC (105)-2In solders, the most notable finding is the slight increase of UTS, 0.2% YS, Elastic modulus with small decrease in elongation at low dose irradiations $\leq 400$ kGy, which reveal that irradiation with low doses did not modify the work hardening behavior. At the higher doses ($\geq 400$ kGy), the tensile strength is reduced a little bit by the irradiation, but the elongation is slightly enhanced, suggesting that a slight radiation-induced defect structure was evident for the high $\gamma$ radiation doses. A recent publication by Uosif (9) reported that the degree at which $\gamma$ radiation is attenuated in SAC alloys is dependent on the energy of the incident $\gamma$ radiation, the thickness of the shielding, the atomic number and density of the elements in the shielding material. In this respect, it was found that these SAC lead-free solders can be positively utilized as a new structural material design strategy in a light weight multifunctional shielding materials. Moreover, the enhanced ductility of SAC (105)-2In solder has thoughtful implications for improving the bulk compliance and plastic energy dissipation ability of solder joints, which enriches the drop impact reliability in electronic packages (16).
In contrast to these results, and surprisingly, the main feature of irradiated SAC (105)-2Bi samples is the tensile strength was decreased and the ductility increased up to 400 kGy, which in turn advances the bulk conformity and plastic energy dissipation ability of Bi-containing solder joints. Such drop impact energy could diminish the dynamic stresses dispersed at the interface boundary. At the higher doses ≥ 400 kGy, significant degradation of the mechanical properties was observed, where the flow stresses increased and the ductility dropped. The change in flow stresses correlates well with the changes in dislocation structure of the alloy sample with the highest doses. Such effects constrain the choice of this alloy as a radiation shielding, and limit their lifetime at the higher doses. Therefore, in the following, we present irradiation-related microstructures to discuss the deformation mode in the three alloys.

### Table (2): Mechanical property data for different solders at constant strain rate $2.9 \times 10^{-3} \text{s}^{-1}$ and various doses

<table>
<thead>
<tr>
<th>Alloy/D</th>
<th>UTS (MPa)</th>
<th>YS (MPa)</th>
<th>Elongation (%)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC (105)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 kGy</td>
<td>28.1</td>
<td>25.8</td>
<td>39.5</td>
<td>12.9</td>
</tr>
<tr>
<td>200 kGy</td>
<td>29.2</td>
<td>26.1</td>
<td>36.2</td>
<td>13.1</td>
</tr>
<tr>
<td>400 kGy</td>
<td>32.0</td>
<td>28.3</td>
<td>28.5</td>
<td>14.2</td>
</tr>
<tr>
<td>600 kGy</td>
<td>31.0</td>
<td>28.0</td>
<td>40.3</td>
<td>14.0</td>
</tr>
<tr>
<td>800 kGy</td>
<td>27.9</td>
<td>23.6</td>
<td>43.5</td>
<td>11.8</td>
</tr>
<tr>
<td>SAC (105)-2In</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 kGy</td>
<td>29.6</td>
<td>26.1</td>
<td>63.7</td>
<td>13.1</td>
</tr>
<tr>
<td>200 kGy</td>
<td>31.4</td>
<td>28.6</td>
<td>60.3</td>
<td>14.3</td>
</tr>
<tr>
<td>400 kGy</td>
<td>35.5</td>
<td>31.6</td>
<td>57.4</td>
<td>15.8</td>
</tr>
<tr>
<td>600 kGy</td>
<td>24.7</td>
<td>22.0</td>
<td>64.5</td>
<td>11.0</td>
</tr>
<tr>
<td>800 kGy</td>
<td>22.8</td>
<td>20.1</td>
<td>65.7</td>
<td>10.1</td>
</tr>
<tr>
<td>SAC (105)-2Bi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 kGy</td>
<td>50.3</td>
<td>46.9</td>
<td>45.1</td>
<td>23.5</td>
</tr>
<tr>
<td>200 kGy</td>
<td>45.7</td>
<td>41.7</td>
<td>46.3</td>
<td>20.9</td>
</tr>
<tr>
<td>400 kGy</td>
<td>41.0</td>
<td>35.7</td>
<td>51.6</td>
<td>17.9</td>
</tr>
<tr>
<td>600 kGy</td>
<td>57.0</td>
<td>53.5</td>
<td>47.1</td>
<td>26.8</td>
</tr>
<tr>
<td>800 kGy</td>
<td>58.2</td>
<td>54.3</td>
<td>41.3</td>
<td>27.2</td>
</tr>
</tbody>
</table>
Fig (6): Tensile properties of SAC(105), SAC(105)-2In and SAC(105)-2Bi solder alloys with different γ-radiation doses at room temperature and $\varepsilon^* = 2.9 \times 10^{-3}$ s$^{-1}$

The major microstructural mechanisms responsible for the changes in mechanical behavior of metallic materials (whether irradiated or not) at room temperature are: dislocation tangling and cell formation; dislocation banding or planar deformation; dislocation channel deformation (DCD); and micro twinning deformation. Nonetheless, in most unirradiated alloys, deformation by dislocation tangling and cell formation is the normal mode. Microscopic observation of unirradiated and irradiated SAC(105)-2In solder have been performed in order to assist in the identification of the various deformation modes that occur in this sample. As seen, the set of micrographs shown in Figs. 8 and 9 present and confirm the typical cell formation and DCD profiles in SAC (105)-2In solder before and after irradiation. Besides, the precipitation of small IMC particles are realized only at the sub-grain boundaries of irradiated sample, which lead to some sort of hardening. However, finding a threshold dose at 400 kGy (Fig.7) should be a crucial strategy to demonstrate the mechanisms underlying plastic flow deformation for the three alloys. We consider two cases of interaction of dislocation with irradiation-induced clusters of defects. The first regime is at low doses ($\leq 400$ kGy), where the radiation induced defects and dislocation loops. It has been reported that the size of dislocation loops increases with irradiation dose, which could act as obstacles to dislocation motion and increased matrix hardness. As the material hardens, a small increase in YS, UTS and elastic modulus with minor reductions in ductility was observed in SAC (105) and SAC (105)-2In solders. In this case, the deformation mode is the same as that of unirradiated alloys, where the work hardening rate is modest.
Fig (7): Effect of γ-radiation doses on: ultimate tensile strength (UTS), yield stress (YS), Young modulus and elongation (El. %) for SAC(105), SAC(105)-2In and SAC(105)-2Bi solder alloys

The second regime is at high doses (≥ 400 kGy), where the YS, UTS and elastic modulus are decreased and the ductility increased. Deformation by cell formation and/or dislocation planar deformation mechanism is promoted, and the alloy samples exhibit strain softening. Besides, the alloying by In addition and impurity elements in these solders may create high densities of interfaces that can offer neutral sinks for point defect annihilation, thereby reducing the development of tensile strength. The presence of grain boundary cavities and dislocation channeling could impact the mechanical properties near the grain boundaries at higher doses, since it can produce a very low macroscopic value for uniform elongation. However, opposite finding was observed for irradiated SAC (105)-2Bi solder. The deformation mode in SAC (105)-2Bi solder is notable in that it underwent a transition from work softening at low doses to enhanced work hardening at high doses. The work softening associated with strain localization includes subsequent unpinning and rapid release of dislocations from locked sources, in which all plastic activity is assumed to occur. The enhanced work hardening at high doses is possibly accompanied with dislocation pinning by irradiation-induced clusters of precipitates, which may have formed initially at dislocation loops, and subsequently collected at the grain boundary. Such effect limits the lifetime of SAC (105)-2Bi solder in nuclear shielding, and constrains their choice at high doses.
Fig (8): Dislocation channels, cell formation and sub-grain boundary precipitates in (a, b and c) unirradiated and (d) irradiated SAC(105)-2In solder specimen at 800 kGy dose.

Fig (9): Cell formation and sub-grain boundary precipitates in irradiated SAC(105)-2In solder specimen at 800 kGy dose. Cell formation; dislocation banding.

4. CONCLUSIONS

In this study, we have examined γ-radiation-induced softening and hardening in the low Ag content SAC (105) lead free alloys with In and Bi additions (2 wt.%). The addition of certain alloying elements induces numerous effects, including high densities of interface boundaries to offer impartial sinks for point defect annihilation; however, the mode of deformations are indefinite in many cases. The following conclusions were obtained:

The doses of γ-radiation ranging from 200 to 800 kGy are found to induce modifications in the mechanical properties of three solders, where the transition between softening and hardening occurs at a critical does of 400 kGy. At low doses (≤ 400 kGy), SAC (105) and SAC (105)-2In solders exhibited a slight increase in strength with low ductility, whereas the SAC (105)-2Bi solder showed small decrease in strength with high ductility. These modifications in ductility and strength maintain high bulk compliance and plastic energy dissipation ability in these solders, where the drop-impact energy can be dissipated through bulk solder deformation. At high doses (≥ 400 kGy), the SAC (105) and SAC (105)-2In the solders showed enhanced ductility with low elastic modulus in contrast to the SAC (105)-2Bi solder, which showed high strength with low ductility. Such effects could assist the choice of these alloys as a new structural material design strategy in manufacturing gamma radiation.
shielding. The experimental observations clearly demonstrate that the mechanical property enhancement is caused by the cell formation and dislocation channel deformation mechanism.

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5-REFERENCES