Tailored specular reflectance properties of bulk

Cu based novel intermetallic alloys

Sherine Alex^{a,d}, Kamanio Chattopadhyay^{b,d}, Bikramjit Basu^{c,d,*}

^a Centre for Nano Sciences and Engineering, Indian Institute of Science, Bangalore, India.

^b Materials Engineering, Indian Institute of Science, Bangalore, India.

^c Materials Research Centre, Indian Institute of Science, Bangalore, India.

^d Interdisciplinary Centre for Energy Research, Indian Institute of Science, Bangalore, India.

*Corresponding author: bikram@mrc.iisc.ernet.in

Key words: Solar reflectors, specular reflectance, intermetallic alloy.

Abstract

Significant research has been pursued to develop solar selective metallic coatings using a variety of coating deposition techniques, with limited attempts to assess the properties of bulk metallic materials for solar energy applications. In developing bulk solar reflectors with good reflectance in the entire solar range, we report the development of a new class of reflector materials based on Cu-Sn intermetallics with tailored substitution of aluminium or zinc. Our experimental results suggest that the arc melted-suction cast Cu (78.8 atomic %) – Al (21.2 atomic %) alloy with nanoscale surface roughness can exhibit a combination of 89% bulk specular reflectance and 83% bulk solar reflectance, together with a hardness of 2 GPa. We show that the present alloy design approach paves the way for further opportunities of tuning the spectral properties of this new class of solar reflector material.

1. Introduction

In order to meet growing energy requirements worldwide, there is a great demand for clean and affordable renewable energy sources. Sunlight provides the Earth with more energy in 1 hour than is consumed on the planet in an entire year.^{1,2} Thus, the technologies of harvesting and storing solar energy for power generation have attracted increasing attention³. Two mainstream categories of devices are currently utilized for this purpose, (a) photovoltaics⁴ (PV) and (b) concentrated solar power^{5,6} (CSP). The former (PV) involves the use of solar cells to generate electricity directly via the photoelectric effect. The latter (CSP) captures and utilizes solar thermal energy for power-producing heat processes.

Concentrated solar power^{7,8} has been under investigation for several decades and is based on a simple generic scheme. Using mirrors, the sunlight can be redirected, focused and collected as heat. This can, in turn, be used to power a turbine, heat engine or an organic rankine cycle (ORC) to generate electricity. Since lenses are unable to focus scattered light, a reflector material is preferred in a solar thermal system. Thus, developing novel materials with an optimum combination of specular reflectance, self-cleaning capabilities, and resistance to corrosion and abrasion constitute a major challenge as far as the development of new materials is concerned.

The reflector in a CSP system directly influences the amount of solar radiation that can be converted into power. The efficiency of a CSP collector is characterized by the fraction of the incident solar flux at its aperture that is absorbed and converted into heat. The net solar flux intercepting the receiver is also known to be influenced by the sun shape, concentrator quality, tracking system accuracy, and the receiver position in relation to the ideal focal position⁷. The development of reflector materials with all the

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

aforementioned properties requires a major effort, and has been the major motivation to develop new reflector materials.

In the perspective above, Ross et al. studied the possibility of using stainless steel solar mirrors for increased energy collection in thermal energy systems.⁹ A poor bulk reflectance of 67% for stainless steel was measured. Although stainless steel is mechanically strong^{10,11} and has inherent resistance to ageing, the use of stainless steel as a front reflecting surface for solar mirrors is not likely to be competitive. It has been recognized that steel as a mirror material would require at least double layer coatings to achieve sufficient solar reflectance¹². The long term stability of stainless steel for reflector purposes has not been fully investigated. Considering the superior reflectance of pure aluminium^{13,14} and silver,^{15,16} significant efforts are underway for developing front surface aluminium and silver mirrors. However, aluminium suffers from degradation, abrasion and oxidation in atmospheric conditions¹⁷ and silver suffers from photon-induced corrosion, soiling and tunneling.¹⁸ Thus, there exists a scope for developing alternative reflector materials.

In Southern India, a unique mirror-making tradition¹⁹ survives at the village of Aranmula. Here, a cast high-tin bronze mirror of 33% tin was developed with comparable specular or reflective properties²⁰, if not better than, modern mercury glass-coated mirrors. As the Cu-Sn based delta phase is a hard and silvery compound, this composition is thought to have ideal properties for a mirror. Against the backdrop above, we have attempted to develop a Cu-Sn based intermetallic mirror alloy having good reflectance and hardness to impart abrasion resistance. This class of alloys is based on an intermetallic delta phase having a composition of 78.8 atomic % Cu and 21.2 atomic % Sn. This phase has a face centered cubic structure with a space group of $F\bar{4}3m$. The inherent hardness of

such an alloy allows the alloy to be polished with the best possible uniform reflectance across the spectrum.

Motivated with this, we report here an attempt to develop a Cu-Sn intermetallic alloy based solar reflector material. Further, alloy substitution was performed using aluminium or zinc. Aluminium¹³ is added because of its high reflectance and Zinc is chosen due to its solid solution solubility with copper²¹. Some limited literature is available for these ternary alloys^{21,22}. However, none of these studies has reported the spectral reflectance property of these alloys and the present study essentially reports the rationale of reflector alloy design from a metallurgical perspective. We will first discuss the results obtained with the baseline Cu₄₁Sn₁₁ intermetallic alloy, and, thereafter, the results obtained with other alloy compositions will be analysed to bring out the influence of Al or Zn substitution to the baseline alloy. The present work aims at establishing the suitability of the alloy design approach to obtain a new class of intermetallic reflector materials with a tailored combination of bulk specular reflectance and hardness.

2 Materials and Methods

As received shots of copper, tin, aluminium and zinc (purity 99.99%., Alfa Aesar) were used for the experiments. We first prepared a Cu-21.2 atomic % Sn²³ alloy by arc melting and chill casting. The appropriate composition of Cu₄₁Sn₁₁, that is 78.8 atomic % Cu and 21.2 atomic % Sn was weighed and melted. The alloy was remelted 4 times in a custom-designed arc melting furnace to ensure homogeneity of composition, followed by chill casting within a copper mould (2cm*2cm*0.4cm). A standard polishing procedure finishing with a diamond paste of 0.1µm was used both for metallographic examination and for reflectance studies. For the metallograph, the samples were etched using acidified potassium dichromate^{24,25} and, subsequently, colour tinted using a reagent based on a

complex thiosulphate solution. A number of $\text{Cu}_{41}\text{Sn}_{11}$ based alloys with the substitution of Al or Zn were prepared in the same way i.e. by weighing the appropriate atomic % as shown in table 1, followed by arc melting and chill casting. A summary of the alloy compositions and their properties is shown in table 1.

To identify different phases, X-ray diffraction patterns were obtained using an X-Ray diffractometer (XRD, PANalytical, Xpert pro) with Cu K_{α} radiation ($\lambda = 0.154$ nm). In general, XRD data were collected at a scan rate of $0.5^{\circ}/\text{min}$. As part of a microstructural investigation, intermetallic alloys were characterized using a SEM (FEI Corporation, Netherlands) and EPMA (JEOL-JXA 8530 field emission electron probe microanalyzer, Japan) for various structural and compositional analyse. The hardness measurement was performed using a Vickers hardness tester (Future Tech microhardness tester FM-800, Japan) and the roughness was measured using an optical profilometer (WYKO NT-1100).

The solar hemispherical reflectance of the bulk samples was measured using a UV-Visible-NIR integrating sphere spectrophotometer (Perkin-Elmer lambda 750) and the specular reflectance was measured using a UV-Visible-NIR integrating sphere spectrophotometer (Shimadzu, UV 3600). The solar reflectance²⁶ was calculated by weighting with ASTM G173 solar spectra for AM1.5

3 Results:

3.1 Phase assemblage and reflectance properties of baseline $\text{Cu}_{41}\text{Sn}_{11}$ alloy

Figure 1 shows the phase diagram of Cu-Sn system.²⁷ In the Cu-Sn binary system, the δ phase is stable under equilibrium conditions in the temperature range of 586°C - 350°C . At lower temperatures, the δ -phase exists as a line compound, while at higher temperatures it exhibits a small composition range of existence. The δ phase has a

1 metastable existence at room temperature. Against the backdrop of the Cu-Sn based
2 equilibrium phase diagram, we chose a Cu-21.2 atomic % Sn composition with the aim of
3 obtaining a single phase microstructure based on the δ phase via arc melting and chill
4 casting.
5
6
7
8
9

10 The X-ray pattern from the arc melted and chill cast samples is shown in figure 2.
11 The significant peaks match with the $\text{Cu}_{41}\text{Sn}_{11}$ intermetallic compound (Card No: 01-071-
12 0094), as indicated by the JCPDS-ICDD (Joint Committee for Powder Diffraction Studies-
13 International Center for Diffraction Data) data file. Both the patterns obtained by arc
14 melting and chill casting (using a water-cooled copper mould) can be completely indexed
15 with the reflections of the δ phase, and such an observation indicates the insignificant
16 effect of the cooling rate on the formation of the δ phase. In particular, the δ phase
17 exhibited the strongest peak at d-spacings of $2.117 \text{ \AA}^0$ ($2\theta = 42.67^\circ$), $1.222 \text{ \AA}^0$ ($2\theta = 78.15^\circ$)
18 and $3.457 \text{ \AA}^0$ ($2\theta = 25.71^\circ$), corresponding to the respective crystallographic planes of
19 planes (660), (12 6 6) and (511). The indexing of the entire pattern in terms of an fcc
20 structure is given in the supplementary data (table T1). The lattice parameter of the δ
21 phase is found to be $\sim 17.95 \text{ \AA}^0$, which is similar to the reported value of $17.96 \text{ \AA}^0$ ²⁸. The
22 retention of the δ phase (instead of the α and ϵ phase), which is metastable at room
23 temperature indicates the extremely sluggish decomposition kinetics of the δ phase. The
24 processing was performed under high vacuum conditions in the presence of an argon
25 atmosphere to prevent oxidation losses when the metal was cast. The development of the
26 $\text{Cu}_{41}\text{Sn}_{11}$ alloy with the predominant presence of a single phase δ is, therefore, established.
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50

51 The stability of the δ phase was further confirmed as the heat treatment of the alloy
52 at 200°C for 3 hours could not destabilize the δ -phase, and no trace of the α or ϵ phase
53 could be recorded in the XRD spectra (figure 3). The homogenous microstructure of the
54 $\text{Cu}_{41}\text{Sn}_{11}$ alloy is characterized by a grain size of $150 \mu\text{m}$ (figure 4). The concentration
55
56
57
58
59
60
61
62
63
64
65

1 profile through repeated line scan in EPMA confirmed the presence of 78.8 atomic % Cu
2 and 21.2 atomic % Sn (figure 5). The EPMA profile does not reveal any solute segregation
3 in the single phase δ alloy. The hardness of the arc-melted single phase (δ -phase) alloy is
4 determined to be around 5 GPa ($HV_{0.2}$), which is comparatively high when compared to
5 other competing bulk metallic reflector materials²⁹.
6
7
8
9
10

11 The specular reflectance spectrum of $Cu_{41}Sn_{11}$ is shown in figure 6. The bulk
12 hemispherical reflectance of the $Cu_{41}Sn_{11}$ alloy, as measured using a UV-VIS-NIR
13 spectrophotometer, is found to be about 86% in the solar range (280-2500nm).
14 Importantly, the bulk specular reflectance and bulk solar-weighted (AM 1.5) reflectance
15 (using the standard ASTM G173-02) of the $Cu_{41}Sn_{11}$ alloy, is 77.2% and 74.5%,
16 respectively.
17
18
19
20
21
22
23
24
25
26

27 **3.2 Influence of zinc substitution on phase assemblage and reflectance properties**

28
29
30

31 In our attempt to enhance the spectral properties by refining alloy compositions,
32 we developed three different compositions of Cu-Sn-Zn bulk alloys, as shown in table 1.
33 In the case of the Cu-Sn-Zn system, the formation of the Cu_5Zn_8 compound (Card No: 04-
34 003-1988) was noticed by the substitution of ~2% to ~9% Zn. The presence of Cu_5Zn_8 is
35 confirmed from the characteristic X-ray peaks at d-spacing values of 2.090 $\text{\AA}^0$ ($2\theta =$
36 43.1 $^\circ$), 1.207 $\text{\AA}^0$ ($2\theta = 79.5^\circ$) and 2.560 $\text{\AA}^0$ ($2\theta = 35.0^\circ$), corresponding to planes (330),
37 (633) and (222), respectively. In these alloys, the intensity of the Cu_5Zn_8 peak increases
38 with Zn substitution, indicating the larger presence of Cu_5Zn_8 . Simultaneously, a decrease
39 in the intensity of the δ peak indicates a decreased amount of delta phase $Cu_{41}Sn_{11}$, as
40 shown in figure 7. The compound Cu_5Zn_8 has a body-centered cubic structure with a space
41 group of $I\bar{4}3m$. The lattice parameter of the Cu_5Zn_8 phase in our samples was found to be
42 ~8.87 $\text{\AA}^0$. This can be compared with the reported value of 8.878 $\text{\AA}^0$ ³⁰.
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

SEM microstructure confirms the presence of two different compounds as shown in figure 8. The contrast in the microstructure obtained after etching, can be well correlated with the existence of two different compounds in the as chill-casted alloy. The hardness³¹ of Cu-Sn-Zn systems was first decreased with ~2 atomic % zinc substitution from 5.1 GPa to 4.5 GPa and further increased with zinc substitution from 4.5 GPa to 5.1 GPa (the same as the parent Cu₄₁Sn₁₁ alloy).

The bulk solar specular reflectance was measured using a UV-VIS-NIR spectrophotometer with an alanod mirror (89% specular reflectance) as a standard. The bulk specular reflectance was found to increase with ~2% substitution of zinc from 77.2% to 80.7% and it decreased with the increased substitution of zinc from 80.7% to 79.6%, as shown in figure 9. The bulk solar weighted (AM 1.5) reflectance was found to decrease with substitution of ~2% zinc from 74.5% to 73.4% and it further decreased with increased zinc substitution from 73.4% to 72.5%. Importantly, it has been demonstrated that the developed novel intermetallic alloy compositions by zinc substitutions of ~2% to ~9% decreased the bulk specular reflectance by ~1% and the bulk solar reflectance by ~1%. The decrease in the amount of the δ phase in XRD can be directly correlated with the decrease in specular and solar reflections (see supplementary figure S1). All the alloys exhibited better specular reflectance than the parent Cu₄₁Sn₁₁ alloy.

3.3 Influence of aluminium substitution on phase assemblage and reflectance properties of baseline Cu₄₁Sn₁₁ alloy

Further, we developed five different compositions of Cu-Sn-Al bulk alloys and their properties are summarised in table 1. The presence of different phases in the alloys was identified using XRD. The representative XRD pattern indicated different phases as we increased the amount of aluminium as shown in figure 10 (detailed in supplementary

figure S2). The presence of the intermetallic $\text{Al}_{0.75}\text{Cu}_3\text{Sn}_{0.25}$ compound (Card No: 04-017-0545) was recorded at an aluminium substitution of ~4% to ~12% and we then noticed the predominant $\text{Cu}_{0.78}\text{Al}_{0.22}$ compound (Card No: 04-006-6355) and the Cu_3Al β_1 phase (Card No: 00-028-0005) by the substitution of aluminium in the range of ~19-21.2%. $\text{Al}_{0.75}\text{Cu}_3\text{Sn}_{0.25}$ exhibited the strongest peak at d-spacings of 2.100 Å ($2\theta = 43.01^\circ$), 1.212 Å ($2\theta = 78.9^\circ$) and 1.485 Å ($2\theta = 62.5^\circ$) indicating the presence of planes (220), (422) and (400), respectively. The presence of the $\text{Cu}_{0.78}\text{Al}_{0.22}$ compound was confirmed from the characteristic X-ray peaks at the d-spacing values of 2.119 Å ($2\theta = 42.6^\circ$), 1.835 Å ($2\theta = 49.6^\circ$) and 1.298 Å ($2\theta = 72.8^\circ$), corresponding to planes (111), (200) and (220), respectively. Also the presence of the Cu_3Al phase was evident from the characteristic X-ray peaks at d-spacing values of 2.021 Å ($2\theta = 44.7^\circ$), 1.947 Å ($2\theta = 46.6^\circ$) and 2.114 Å ($2\theta = 42.7^\circ$), corresponding to planes (1 2 10), (2 0 12) and (0 0 22), respectively. The representative SEM microstructure of Cu-Sn-Al alloys is given in figure 11. The microstructure of Cu - 21.2 atomic % Al, shown in figure 11e, indicates a eutectoid structure. The volume fraction of the $\text{Cu}_{0.78}\text{Al}_{0.22}$ compound and the Cu_3Al (β_1 phase) from SEM microstructure is calculated to be 60% and 40%, respectively.

The hardness of the parent alloy is 5.1 GPa, which was raised to a threshold value of 5.3 GPa by ~8 atomic % substitution of aluminium. Further aluminium substitutions tend to decrease the hardness value to 2 GPa. The hardness values for different alloys studied in the present investigation are listed in table 1. Figure 12 shows the variation of hardness with aluminium substitution. Since hardness is directly correlated with abrasion and scratch resistance, the present alloys are attractive for applications in reflective coating.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Importantly, it has been demonstrated that the developed novel intermetallic alloy compositions by aluminium substitution of ~4% to ~21.2% increase the bulk specular reflectance by 14% and the bulk solar reflectance by 10%. The reported specular reflectance of 89.5% is, comparatively, very high. This may be due to the presence of a eutectoid microstructure. However, the reflectance in the visible region is very low and the inclusion of some high refractive index material^{32,33} in future can improve its reflectance in the visible region. We, now, consider the effect of aluminium substitution on specular reflectance. The specular reflectance spectra by aluminium substitution are shown in figure 13. The bulk specular reflectance was found to increase from a base value of 77.3% to 89.5%, as shown in figure 13. In contrast, the bulk solar weighted (AM 1.5) reflectance was found to decrease with ~4 atomic % aluminium substitution to 72.6% and it does not exhibit any further variation till the addition of ~12 atomic % aluminium (see supplementary figure S3). The bulk solar weighted (AM 1.5) reflectance was 80.8% for ~19 atomic % aluminium substitution and 83.2% for ~21.2 atomic % aluminium substitution.

4. Discussion

In this section, we analyse the solar reflectance properties of Cu- based alloys with zinc or aluminium as alloying elements, with reference to the established theory. An attempt is also made to compare the present results with earlier literature reports based on metallic alloys (bulk and coatings).

4.1 Specular Reflectance property of Cu- based alloys

In this sub-section, we will first discuss the difference in specular reflectance properties based on plasma-edge considerations.

From the perspective of fundamental physics, the light waves incident on a material induce small oscillations of polarisation in individual atoms (or oscillation of electrons, in metals), causing each particle to radiate a small secondary wave (in all directions, like a dipole antenna). All these waves add up to give reflection and refraction. One of the most prominent optical phenomena in solids is the so-called “plasma edge”⁸, where free electrons in the material start vibrating collectively. This leads to a steep drop in reflectance for photon wavelengths to less than that associated with the onset of this oscillation (see supplementary figure S4). The drop in reflectance in different materials is associated with the plasma edge of these materials and the spectral location of the plasma edge depends on the number of free carriers. The plasma edge property is different for different alloys and it tunes the reflectance of each material. Against the backdrop above, it is evident that Al substitution can potentially shift the plasma edge wavelength to the left of that for the Cu-Sn alloy, as shown from the reflectance data (see figure 13). On the contrary, Zn substitution is expected to shift the plasma edge to the right, but to a lower extent (see figure 9).

As far as the various factors influencing spectral properties are concerned, Davies’ theory^{34,35} predicts the surface roughness dependent on the specular reflectance at normal incidence by the following equation,

$$R_s = R_o \exp(-4\pi\sigma^2/\lambda^2) \quad (1)$$

Where R_s is the specular reflectance of the rough surface, R_o that of a perfectly smooth surface of the same material (specular reflectance of unity for perfectly smooth surface), σ is the surface roughness and λ is the appropriate wavelength in microns. From equation (1), the specular reflectance of the rough surface is expected to decrease with surface roughness. The roughness values of the investigated alloys are listed in table 1.

Since the roughness values obtained from an optical profilometer lie in the nanometer range with a narrow variation, the effect of surface roughness on the variation of specular reflectance can be ignored. Thus, we estimate that the specular reflectance of the investigated materials is an intrinsic material property, independent of the surface roughness.

The surface roughness of the parent Cu₄₁Sn₁₁ alloy was measured to be 17.4±7.8 nm. The nanoscale roughness indicates the extreme surface flatness of the sample. The roughness values were increased from 12 nm to 55 nm by aluminium substitution. As explained previously, since the surface roughness value lies in the nanometer range, it will have only a negligible effect on specular reflectance.

4.2 Comparison with earlier literature reports:

Based on extensive literature analysis, the reflectance property of various metallic materials are summarized and compared with the representative results obtained in the present work (see table 2). Most of the coatings are fabricated using either vacuum evaporation or magnetron sputtering techniques. Depending on the thickness as well as the composition of various layers, the different coatings are reported to exhibit solar specular reflectance in the range of 80% - 98.8%. The highest spectral reflectance of 98.8% has been achieved using silver thin film with a silica protective layer, fabricated using the magnetron sputtering route³³. Overall, the reflective metallic coating developed so far exhibits a specular reflectance of more than 85% in the entire solar spectral range. Two important design parameters are critically considered while developing solar coatings- the first one is the rationale of having successive layers of different compositions and the second is the thickness of the different layers. While optimizing solar reflectance, one has to tailor both these parameters over a close window and, accordingly, the process

parameters are to be optimized in the magnetron sputtering or vacuum evaporation route to meet the desired reflectance properties.

From the perspective above, we have presented a novel alloy design approach to develop bulk solar reflective material with more specular reflectance properties. We have made an attempt to substitute single phase intermetallic $\text{Cu}_{41}\text{Sn}_{11}$ material with zinc or aluminium, respectively. After extensive experiments involving systematic compositional variations, we observed that the complete substitution of tin with aluminium (Cu- 21.2 atomic % Al) can result in 90% specular reflectance, which is much higher than that of bulk stainless steel and some of the metallic coatings developed earlier (see table 2). Since thickness and material purity can affect the reflectance, we believe that if we deposit Cu- 21.2 atomic % Al as coatings with tailored thickness using electrodeposition or sputtering techniques, we would be able to achieve more than 95% specular reflectance. However, the electrochemical bath composition and other parameters for thickness tailoring need to be optimized. This aspect is currently under investigation. Nevertheless, the alloy design approach reported in the present work was never investigated before.

It is worthwhile to mention further that comprehensive property measurement in terms of surface roughness, hardness or detailed phase assemblage have not been reported with most of the earlier investigated metallic coatings. In the present work, we have reported both the surface roughness and hardness, in addition to reflectance and microstructure. It is interesting to note that while pursuing higher reflectance by aluminium substitution, one has to compromise on the hardness. For example, the hardness of 2 GPa is measured with a Cu- 21.2 atomic % Al alloy. Also, nanoscale roughness can be achieved with a simple metallographic polishing technique for the alloys investigated in the present work. It, therefore, appears that the conventional metallurgical

processing route together with an alloy design approach can be adopted as a new route to develop solar reflector material.

5. Conclusions

We have developed a Cu-Sn based intermetallic alloy using conventional processing routes, i.e. arc melting and chill casting. The as cast single phase bulk alloy of the Cu-21.2 atomic % Sn composition exhibited a bulk specular reflectance of 77.2% and a bulk solar reflectance of 74.5%, together with a hardness of 5 GPa. The developed alloy exhibited a grain size of 150 μm without any solute segregation. Further, we fabricated Cu-Sn based intermetallic alloys with tailored substitutions of aluminium or zinc. It was noted that the substitution of ~8% aluminium has a hardness of 5.3 GPa. Importantly, we demonstrated that the developed novel intermetallic alloys with an aluminium substitution of ~4% to ~21.2% increased the bulk specular reflectance by 14% and the bulk solar reflectance by 10%. In contrast, a zinc substitution of ~2% to ~9% decreased the bulk specular reflectance by 1% and the bulk solar reflectance by 1%. Moreover, the Cu-21.2 atomic % Al alloy composition exhibited 89.5% specular reflectance and 83% solar reflectance with nanoscale roughness and a hardness of 2.1 GPa. In summary, the present work for the first time presents a new alloy design approach and demonstrates the use of the conventional metallurgical processing route to develop bulk materials with good solar/specular reflectance, which are even better than some of the earlier developed multilayer solar reflective coatings.

Acknowledgement

This paper is based upon work supported in part under the US-India Partnership to Advance Clean Energy-Research (PACE-R) for the Solar Energy Research Institute for

1 India and the United States (SERIUS), funded jointly by the U.S. Department of Energy
2 (Office of Science, Office of Basic Energy Sciences, and Energy Efficiency and
3 Renewable Energy, Solar Energy Technology Program, under Subcontract DE-AC36-
4 08GO28308 to the National Renewable Energy Laboratory, Golden, Colorado) and the
5 Government of India, through the Department of Science and Technology under
6 Subcontract IUSSTF/JCERDC-SERIUS/2012 dated 22nd Nov. 2012.
7
8
9
10
11
12
13

14 The authors also appreciate the help rendered by Thermax, Pune for the
15 measurement of specular reflectance and solar reflectance. Sherine Alex is thankful to Mr
16 Surendrakumar Makineni for assisting in performing casting and other metallurgical
17 work.
18
19
20
21
22
23
24
25

26 **References**

-
- 27
28
29
30
31 1 R. Almanza, C. Jiefeng, G. Correa, M. Mazari, Further option for solar concentrators:
32 Aluminium first surface mirrors, *Solar Energy* 54, 5 (1995) 333-343.
33
34
35
36
37 2 D. Barlev, R. Vidu, P. Stroeve, Innovation in concentrated solar power, *Solar Energy*
38 *Materials & Solar Cells*, 95 (2011) 2703–2725.
39
40
41
42 3 D. Barlev, R. Vidu, P. Stroeve, Innovation in concentrated solar power, University of
43 California Davis Solar Energy Collaborative Workshop, Davis, CA, May 11, 2010.
44
45
46
47
48 4 H. J. Hovel, Photovoltaic materials and devices for terrestrial solar energy application,
49 *Solar Energy Materials*, 2 (1980) 277-312.
50
51
52
53 5 S. A. Kalogirou, Solar thermal collectors and applications, *Progress in Energy and*
54 *Combustion Science*, 30 (2004) 231–295.
55
56
57
58
59
60
61
62
63
64
65

-
- 6 T. Fend, B. Hoffschmidt, G. Jorgensen, H. Kuster, D Kruger, R. Pitz-Paal, P. Rietbrock,
K. J. Riffelmann, Comparative assessment of solar concentrator materials, Solar energy,
74 (2003) 149-155.
- 7 Guidelines, Measurement of solar weighted reflectance of mirror materials for
concentrating solar power technology with commercially available instruments, Solar
PACES interim Version 1.1, May 2011.
- 8 A. E. Dixon and J. D. Leslie, Solar energy conversion- An introductory course, 10 287-
329.
- 9 A. Ross, C. G. Ribbing, Stainless steel solar mirrors- a material feasibility study, Solar
Energy Materials, 18 (1989) 233-240.
- 10 M. Brogren, A. Helgesson, B. Karlsson, J. Nilsson, A. Roos, Optical properties,
durability, and system aspects of a new aluminium-polymer-laminated steel reflector for
solar concentrators, Solar Energy Materials and Solar Cells, 82 (2004) 387-412.
- 11 P. Nostell, A. Ross, B. Karlsson, Ageing of solar booster reflector materials, Solar
Energy Materials and Solar cells, 54 (1998) 235-246.
- 12 A. Ross, C. G. Ribbing, Stainless steel solar mirrors- A material feasibility study, Solar
Energy Materials, 18 (1989) 233-240.
- 13 R. Almanza, P. Hernandez, I. Martinez, M. Mazari, Development and mean life of
aluminium first-surface mirrors for solar energy applications, Solar energy materials and
solar cells, 93 (2009) 1647-1651.

-
- 14 B. A. Benson, Acrylic solar energy reflecting film 3M brand ECP-244 (formerly FEK-244), Proc. Annu. Meet. - Am. Sect. Int. Sol. Energy Soc, 6 (1983).
- 15 R. O. Adams, C. W. Nordin, F. J. Fraikor, Co-sputtering of aluminium-silver alloy mirrors for use as solar reflectors, Thin Solid Films, 63 (1979) 151-154.
- 16 R. O. Adams, C. W. Nordin, Al-Ag alloy films for solar reflectors, Thin Solid Films, 72 (1980) 335-339.
- 17 T. Fend, B. Hoffschmidt, G Jorgensen, H. Kuster, D. Kruger, R. Pitz-Paal, P. Rietbrock, K. Riffelmann, Comparative assessment of solar concentrator materials, Solar Energy, 74 (2003) 149-155.
- 18 P. Schissel, G. Jorgensen, C. Kennedy, R. Goggin, Silvered-PMAA reflectors, Solar Energy Materials and Solar Cells, 33 (1994) 183–197.
- 19 Srinivasan. S, Glover. I, Skilled mirror craft of intermetallic delta high-tin bronze ($\text{Cu}_{31}\text{Sn}_8$, 32.6% tin) from Aranmula, Kerala, Current Science, 93 (2007) 35-40.
- 20 Sekhar. J. A, Mantri. A. S, Yamjala. S, Saha. S, Balanuralikrishnan. R, Rama Rao. P, Ancient Metal Mirror Alloy Revisited: Quasicrystalline Nanoparticles Observed, The Minerals, Metals & Materials Society, 40 (2015) 1-8.
- 21 Vilarinho. C, Soares. D, Castro. F, Contribution to the knowledge of the Cu–Sn–Zn system for compositions close to brass alloys, Journal of Alloys and Compounds, 379 (2004) 161–165.

-
- 22 Leach. J. S. L, Raynor. G. V, The Constitution of the Copper-Rich Copper-Aluminium-Tin Alloys, with Special Reference to Ternary Compound Formation, Proceedings A, 224 (1954) 251-259.
- 23 N. N. Acharya, Thermal analysis of slow cooled copper-tin alloys, Journal of materials science, 36 (2001) 4779-4795
- 24 N. N. Acharya, P. G. Mukunda, Metallography of copper-tin alloys, Metallography, 21 (1998) 137-150.
- 25 Standard practice for microetching metals and alloys, designation E407-07, 1-23.
- 26 Standard Tables for reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface, designation G173-03 (Reapproved 2013) 1-21.
- 27 ASM Metals Handbook, Volume 03 - Alloy Phase Diagrams, 1-1741.
- 28 Furtauer. S, Li. D, Cupid. D, Flandorfer. H, The Cu–Sn phase diagram, Part I: New experimental results, Intermetallics, 34 (2013) 142-147.
- 29 Tabor. D., The hardness of metals, Oxford university press, (1951) 155-168.
- 30 Bayer. A. E, Determination of lattice parameters, diffracting crystallite size, and thermal stability in mechanically alloyed Cu-Zn solid solutions, Journal of Materials Engineering and Performance, 6 (1997) 149-152.
- 31 Hung. Fei. Yi, Lui. Truan. Sheng, Chen. Li. Hui, You. Ji. Ge, The Effect of Electrical Current on Tensile Properties and Vibration Characteristics of Sn-9Zn-1Cu Lead-Free, Solder Materials Transactions, 47 (2006) 2935-2941.

32 Y. J. Xu, J. X. Liao, Q. W. Cai, X. X. Yang, Preparation of a highly reflective
TiO₂/SiO₂/Ag thin film with self-cleaning properties by magnetron sputtering for solar
front reflectors, Solar Energy Materials & Solar Cells, 113 (2013) 7-12.

33 Y. J. Xu, Q. W. Cai, X. X. Yang, Y. Z. Zuo, H. Song, Z. M. Liu, Y. P. Hang,
Preparation of novel SiO₂ protected Ag thin films with high reflectivity by magnetron
sputtering for solar front reflectors, Solar Energy Materials & Solar Cells, 107 (2012)
316–321.

34 H. E. Bennet, J. O. Porteus, Relation between surface roughness and specular
reflectance at normal incidence, Journal of optical society of America, 51 (1961) 123-129.

35 C. A. Depew, R. D. Weir, Surface roughness determination by the measurement of
reflectance, Applied optics, 10 (1971) 969-970.

Table 1 The reflectance properties of Cu-Sn based alloys and summary of the newly developed Cu-Sn based alloys

Alloy composition	Elemental composition (atomic %) before melting				Phases assemblage (XRD results)	Absolute specular reflectance %		Vickers Hardness (GPa) HV _{0.2g/10s}	Surface roughness R _a (nm)
	Cu	Sn	Zn	Al		Weighted average, 1.5 AM, 300-2400nm	Normal average 280-2500 nm		
Cu ₄₁ Sn ₁₁	78.8	21.2	-	-	$\delta\text{-Cu}_{41}\text{Sn}_{11}$	74.5	77.2	5.1±0.06	17.4±7.8
CuSnZn-1	75	21.2	4	-	$\delta\text{-Cu}_{41}\text{Sn}_{11}, \text{Cu}_5\text{Zn}_8$	73.4	80.7	4.5 ±0.06	21.6±3.9
CuSnZn-2	71	21.2	8	-	$\delta\text{-Cu}_{41}\text{Sn}_{11}, \text{Cu}_5\text{Zn}_8$	73.3	80.4	4.8 ±0.06	25.4±1.7
CuSnZn-3	67	21.2	12	-	$\delta\text{-Cu}_{41}\text{Sn}_{11}, \text{Cu}_5\text{Zn}_8$	72.5	79.6	5.1 ±0.02	17.6±1.7
CuSnAl-4	78.8	17.2	-	4	$\delta\text{-Cu}_{41}\text{Sn}_{11}, \text{Al}_3\text{Cu}_{12}\text{Sn}$	72.6	75.7	5.1 ±0.04	12.1±1.7
CuSnAl-5	78.8	13.2	-	8	$\delta\text{-Cu}_{41}\text{Sn}_{11}, \text{Cu}_3\text{Al}_{0.75}\text{Sn}_{0.25}$	72.2	77.3	5.3 ±0.06	14.7±2.4
CuSnAl-6	78.8	9.2	-	12	$\delta\text{-Cu}_{41}\text{Sn}_{11}, \text{Cu}_3\text{Al}_{0.75}\text{Sn}_{0.25}$	74.6	81.1	3.9 ±0.04	22.3±2.6
CuSnAl-7	78.8	1.9	-	19.3	$\text{Al}_{0.05}\text{Cu}_{0.9}\text{Sn}_{0.05}, \text{AlCu}_3$	80.82	88.0	2.9±0.04	29.6±2.9
CuAl-8	78.8	-	-	21.2	$\text{Cu}_{0.78}\text{Al}_{0.22}, \text{AlCu}_3$	83.20	89.5	2.1 ±0.06	54.2±6.7

Table 2 Comparison of reflectance property measured with Cu-Sn based alloys (present work) with those reported in previous work

Alloy composition	Bulk/ coating	Fabrication condition	Normal specular reflectance % (280-2500 nm)	Reference
78.8% Cu and 21.2% Sn	Bulk	Arc melting and suction casting	77.2	Present work
78.8% Cu and 21.2% Al	Bulk	Arc melting and suction casting	89.5	Present work
Aluminized acrylic film (Commercial ECP-244 grade)	Coating	-	86	14
Silvered PMMA reflectors (Commercial ECP-305 grade)	Coating	-	96	18
Stainless steel	Bulk	-	51	11
Anodized Al	Coating	Anodisation	80	
Al-foil	Coating	Vacuum evaporation	85	
Laminated Al on steel reflector with PET protective layer	Coating	Vacuum evaporation	77	10
Aluminium solar mirrors	Coating	Magnetron sputtering	85	13
SiO ₂ protected Ag thin films	Coating	Magnetron sputtering	98.8	33
Reflective TiO ₂ /SiO ₂ /Ag thin film	Coating	Magnetron sputtering	96	32

Figure 1 (a) Phase diagram of Cu-Sn Alloy systems demonstrating various phase stability regions, (b) narrow region of Cu₄₁Sn₁₁ alloy composition.²⁷

Figure 2 XRD pattern of (a) arc melted and (b) chill casted ingots of $\text{Cu}_{41}\text{Sn}_{11}$ alloys confirming the presence of δ phase. Reference peaks of $\text{Cu}_{41}\text{Sn}_{11}$ are indicated by red lines.

Figure 3 XRD pattern confirming the presence of delta phase $\text{Cu}_{41}\text{Sn}_{11}$ alloy, heat treated at 200°C for 3 hours. Reference peaks of $\text{Cu}_{41}\text{Sn}_{11}$ are indicated by red lines.

Figure 4 Representative SEM image of $\text{Cu}_{41}\text{Sn}_{11}$ alloy (Cu-21.2 atomic % Sn): (a) as arc melted and (b) as chill cast.

Figure 5 EPMA measured concentration profile confirming the homogeneity in copper and tin, acquired across δ - phase grain. SEM image of the grain along which the composition scan was performed, is shown in the inset.

Figure 6 Specular reflectance of as cast $\text{Cu}_{41}\text{Sn}_{11}$ parent alloy.

Figure 7 XRD patterns acquired from various Zn-substituted Cu-Sn baseline alloy (as chill casted). Reference peaks of Cu₄₁Sn₁₁ and Cu₅Zn₈ are indicated by red and blue lines, respectively.

Figure 8 SEM microstructure of as cast Cu-Sn-Zn alloys. (a) CuSnZn-1 (b) CuSnZn-2 (c) CuSnZn-3, the alloy compositions are shown in table 1.

Figure 9 Specular reflectance of the newly developed $\text{Cu}_{41}\text{Sn}_{11}$ baseline alloy as well as the Zn substituted alloy.

Figure 9 XRD pattern revealing phase stability due to Al- substitution to baseline Cu-Sn alloy.

Reference peaks of $\text{Cu}_{41}\text{Sn}_{11}$ and $\text{Cu}_{0.78}\text{Al}_{0.22}$ are indicated by red and blue lines, respectively.

Figure 10 SEM microstructure of as cast aluminium substituted Cu₄₁Sn₁₁ alloy system. (a) CuSnAl-4, (b) CuSnAl-5, (c) CuSnAl-6, (d) CuSnAl-7 and (e) CuAl-8, the alloy compositions are shown in table 1.

Figure 12 Plot of hardness variation with Aluminium substitution to baseline Cu₄₁Sn₁₁ alloy

Figure 13 Specular reflectance of the newly developed $\text{Cu}_{41}\text{Sn}_{11}$ baseline alloy as well as the Al substituted alloy.