Optical and Material Science Properties of Aranmula Metal Mirror from Kerala

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Abstract

Aranmula mirror is a typical speculum metal mirror, cast and polished according to traditional techniques from Kerala in Southern India. We report our experimental investigations on detailed elemental chemical compositions, chemical surface structure, surface morphology, thermal stability, and optical reflectance of Aranmula metal mirror. The results of EDS based elemental chemical composition studies at the reflecting surface of cast, thin film coated and powder form of mirror samples have revealed the use of Arsenic (As), Silver (Ag), Gold (Au), Iron (Fe), Phosphorous (P), Sulphur (S) and Zinc (Zn) as minor constituents in Aranmula mirror making. The detailed surface structure and morphology of the mirror sample is studied for the first time using XRD and AFM. The Combined use of EDS, AFM and XRD analysis of the mirror samples reveal the presence of a transparent, non-metallic, corrosion resistant, smooth, nano structured thin film layer mainly consisting of a tin enriched delta phase ($Cu_{31}Sn_8$) on the mirror surface, which is amorphous in nature. It also suggests that Aranmula metal mirror contains nano-particles that are considered to be quasi-crystalline in nature. We could prepare thin films of cast Aranmula mirror material with significantly higher optical reflectance for the first time. The average optical reflectance of the cast Aranmula mirror sample in the visible region is found to increase by 10 % when it is prepared in the form of thin film.

INTRODUCTION

The symbiotic relationship between the materials and civilizations has been receiving increasing attention in recent years. The history of metals and their shaping is an ancient as the history of civilization. Bronze, an alloy of copper and tin was the first alloy discovered during the prehistoric period now known as the Bronze Age. Aranmula mirror, a variety of cast metal mirror is made from an alloy of bronze with Cu – Sn ratio 2:1. This particular alloy is known as speculum metal and is used in reflective telescopes and other optical precision instruments from the time of Isaac Newton in 17th century and continuing up to early decades of 20th century. The tremendous increase in the number of materials available and their physical properties, coupled with demands from new applications and more severe service requirements, have brought about many changes in attitudes and viewpoints.

EXPERIMENTAL DETAILS

Aranmula metal mirror mounted on a brass handle was purchased from a reliable Govt. Agency in the year 2006. The mirror portion with an aperture of 0.05m, separated from the brass base is broken into number of fragments using diamond cutter and some fragments are grinded to powder form, which are used for experimental investigations. We could successfully make thin films of the cast mirror material for the first time using HIND High Vacuum thermal evaporation coating unit with molybdenum boat in Thin Film Lab, Department of Physics, CUSAT. The film is deposited on a glass substrate at room temperature by applying a current of about 120 A with a coating pressure of about 2 x 10^{-5} mbar in a coating time of around 5 minute. A typical Aranmula mirror brought from a commercial outlet and its thin film coated form with and without an image are shown in figure 1 and 2.

FIGURE 1. Typical Aranmula metal mirror from a commercial outlet

FIGURE 2 (a). Thin film coated Aranmula cast mirror without an image

FIGURE 2 (b). Thin film coated Aranmula cast miror with an image

EXPERIMENTAL ANALYSIS AND DISCUSSIONS

1. Identification of Elemental Chemical Composition by EDS

The identification of intermetallic compounds on the basis of composition was carried out by Bruker's XFlash- 6110 Energy Dispersive Spectrometer at an energy level of 15 keV. The normalized elemental chemical compositions at the reflecting surface of cast, thin film coated and powder form of Aranmula mirror at different locations are shown in Table 1.

TABLE 1. **Average weight of elemental chemical compositions of the cast and thin film coated Aranmula metal mirror**

Type of Aranmula mirror	Position	Normalized weight of elemental chemical composition (Wt.%)											
		Cu	Sn	Zn	As	Ag	Au	Pb	Fe	O	P	Ni	S
Cast mirror	1.	65.97	30.22	0.71	0.08	0.85	0.23	0.14	…..	1.62	…..	0.07	0.11
	2.	67.23	29.98	0.65	0.09	0.66	0.12	…..	0.08	1.03	0.05	0.03	0.08
	3.	67.35	30.06	0.58	0.13	1.03	…..	…..	0.03	0.74	0.02	0.06	…..
	4.	67.17	30.15	0.73	0.11	0.59	0.21	…..	0.07	0.83	…..	0.05	0.09
	5.	67.04	29.90	0.62	0.15	0.87	0.18	0.09	…..	1.07	…..	0.02	0.06
	Average	66.91	29.95	0.68	0.14	0.83	0.17	0.14	0.075	0.32	0.03	0.09	0.96
Thin film coated mirror	1.	61.21	31.97	0.02	0.09	1.19	0.43	…..	0.14	4.53	0.27	0.02	0.14
	2.	62.11	31.84	…..	0.23	1.02	0.30	…..	0.09	4.07	0.19	0.03	0.11
	3.	62.64	31.60	…..	…..	0.59	0.19	…..	0.21	4.41	0.19	0.07	0.10
	4.	62.01	31.69	0.04	0.14	1.05	…..	…..	0.08	4.51	0.22	0.15	0.12
	5.	62.00	31.67	0.09	0.08	1.03	0.29	…..	0.14	4.40	0.20	0.03	0.07
	Average	61.99	31.75	0.05	0.14	0.98	0.30	…..	0.13	4.38	0.21	0.06	0.11
Powder form of cast mirror	1.	60.87	29.36	0.22	0.06	0.85	0.12	…..	…..	5.11	0.03	0.01	0.07
	2.	65.36	27.64	0.25	…..	0.66	0.25	0.11	0.09	3.21	…..	0.19	…..
	3.	61.53	30.09	0.19	…..	1.07	0.07	0.11	0.06	3.85	0.14	0.08	0.03
	4.	64.33	28.50	0.26	0.04	0.55	0.28	…..	0.01	3.52	…..	0.06	…..
	5.	61.84	29.98	0.24	…..	1.03	…..	…..	0.01	3.51	0.16	0.10	…..
	Average	62.79	29.11	0.23	0.05	0.83	0.18	0.11	0.04	3.84	0.11	0.09	0.05

EDS measurements at the reflecting surface of cast, thin film coated and powdered form of mirror indicate that the alloying system in Aranmula mirror is based on two major elements including copper (Cu) and Tin (Sn), whose concentration resembles with that of speculum metal. Observed other significant minor constituents that are included in the measurements of the reflecting surface of cast mirror are Zinc (Zn), Arsenic (As), Silver (Ag), Gold (Au), Lead (Pb) and Oxygen (O), Which constitute only about 4% of the total weight percentage of the elemental chemical composition. The mirror was also found to contain traces of Iron (Fe), Phosphorous (P) and Nickel (Ni), each in amounts less than 0.1 Wt. %.

The significant minor constituents such as Zinc (Zn), Silver (Ag), Gold (Au), Lead (Pb), Oxygen (O) and phosphorous that are observed in the measurement of the powder form constitute only 5.5% of the total weight percentage of elemental chemical composition. It also contains traces of Zinc (Zn) and Nickel (Ni), with their individual content less than 0.1 Wt. %. But in the EDS measurements of thin film coated mirror, the minor constituents such as Arsenic (As), Silver (Ag), Gold (Au), Iron (Fe), Oxygen (O), Phosphorous (P) and Sulphur (S) constitute only 6% of the total weight percentage of elemental chemical composition. It was also found to contain trace elements such as Arsenic (As), Iron (Fe), Nickel and Sulphur (S), each in amounts not exceeding 0.1 Wt. %. The minor constituent Lead (Pb) is not observed in thin film coated mirror sample, but which is included in both the reflecting surface of cast and powder form of the mirror samples. The EDS analysis reveals that the elemental chemical compositions of Aranmula mirror is not homogeneous everywhere and the addition of a small amount of minor constituents may be alter the optical and physical properties of Aranmula mirror.

2. Morphological Studies Using Atomic Force Microscopy

The surface morphologies of Aranmula mirror sample is monitored by AFM (Digital Instruments Nano Scope E, Si3N4 100) instrument in Contact mode at a scanning rate of 2 μm/s with bias voltage 0.5 V. The roughness of the mirror surface and mean particle size is estimated using WSxM 5.0 Develop 8.0 Analysis Software. The three dimensional AFM morphologies of cast and thin film coated mirror samples at 2 μm are shown in figure 3 (a) and 3 (b).

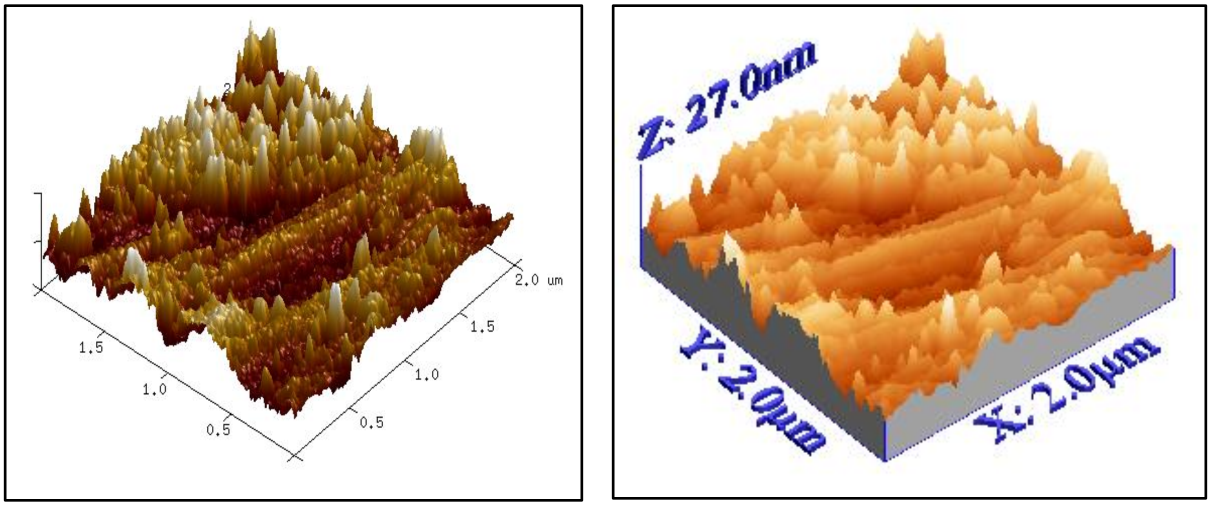

FIGURE 3. (a) 3D AFM morphology of the reflecting surface of cast mirror sample at 2 μm

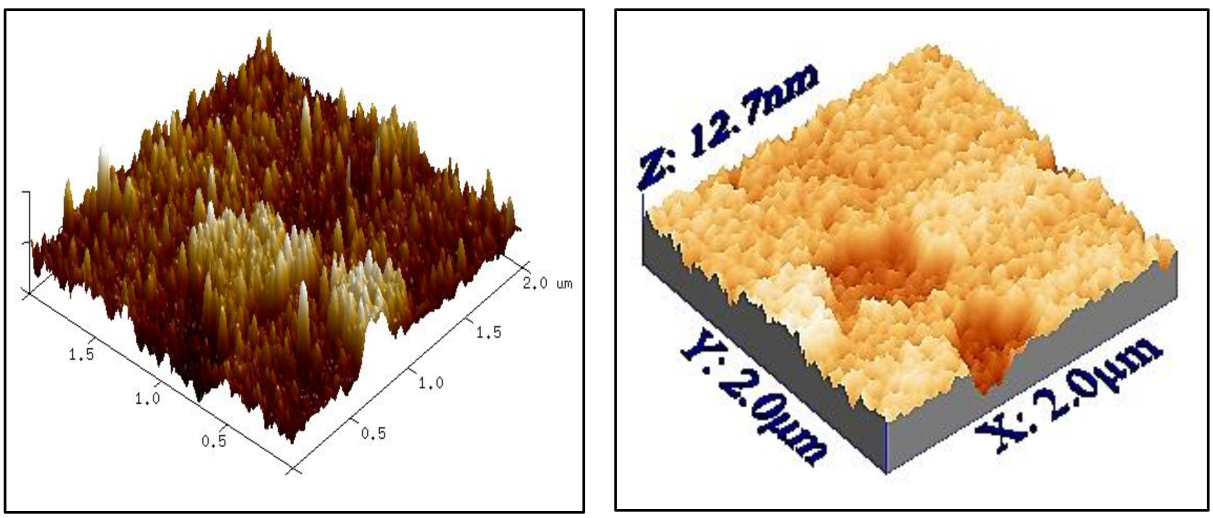

FIGURE 3. (b) 3D AFM morphology of the thin film coated mirror sample at 2 μm

The three dimensional AFM morphology of the reflecting surface of cast mirror sample at 2 μm shows a streak or texture pattern with porous structure. It also consists of many fine grains and each grain consists of elongated rulings with crystals arranged in a uniform pattern with RMS roughness of about 3.38 nm. The average particle size estimated is about 65.27 nm. The 3D AFM morphology of the thin film coated mirror sample at 2 μm shows dense particles with porous structure. There is no distinct particle distribution on the surface of the mirror. The estimated value of average size of the particle and RMS roughness of thin film coated mirror are about 29.21 nm and 1.61 nm respectively, which indicates that the surface of thin film coated mirror is highly smooth. Thus AFM morphology of the reflecting surface of cast and thin film coated mirror shows a texture pattern with porous structure with a small value of roughness, which is the direct evidence for high value of smoothness of the surface.

3. Structural Evaluation by means of X-Ray Diffraction

X-Ray diffraction patterns were recorded directly on the mirror sample by using XPERT PRO - 83005153 diffractometer with copper anode and irradiated with monochromatic A_1K_α X-rays at a wave length of 1.54060 Å. The identification of the species was carried out by using XPERT PRO Software Index. The XRD spectra of the reflecting surface of cast, thin film coated and powdered Aranmula mirror samples are shown in figure 4 (a), (b) and (c).

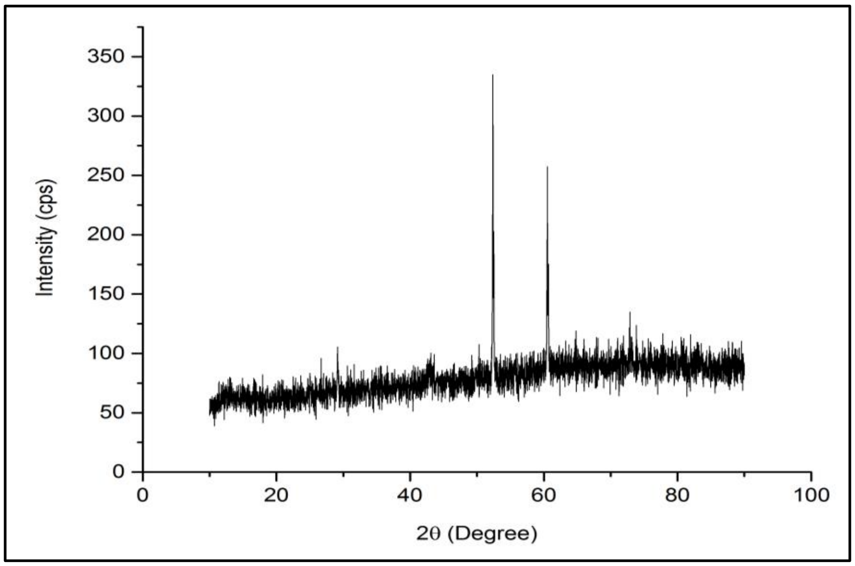

FIGURE 4. **(a) XRD spectrum of the reflecting surface of cast Aranmula mirror**

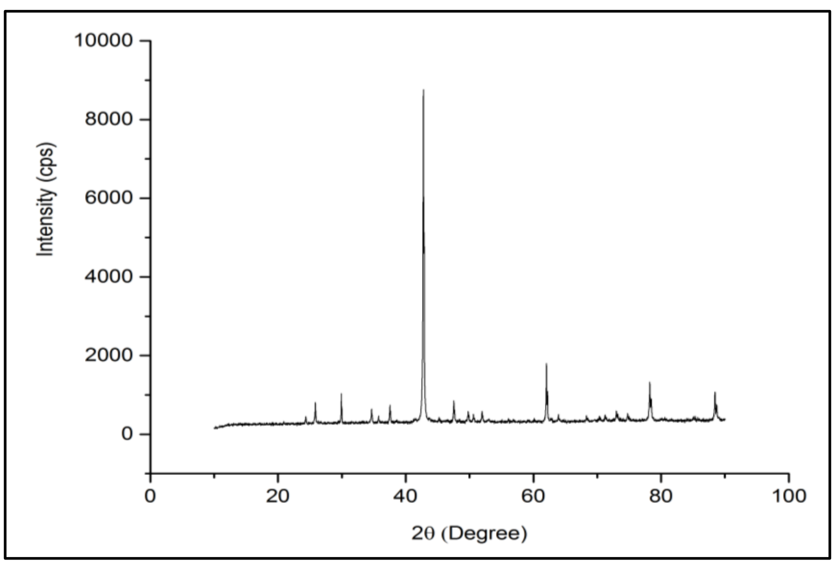

FIGURE 4. **(b) XRD spectrum of powdered form of cast Aranmula mirror**

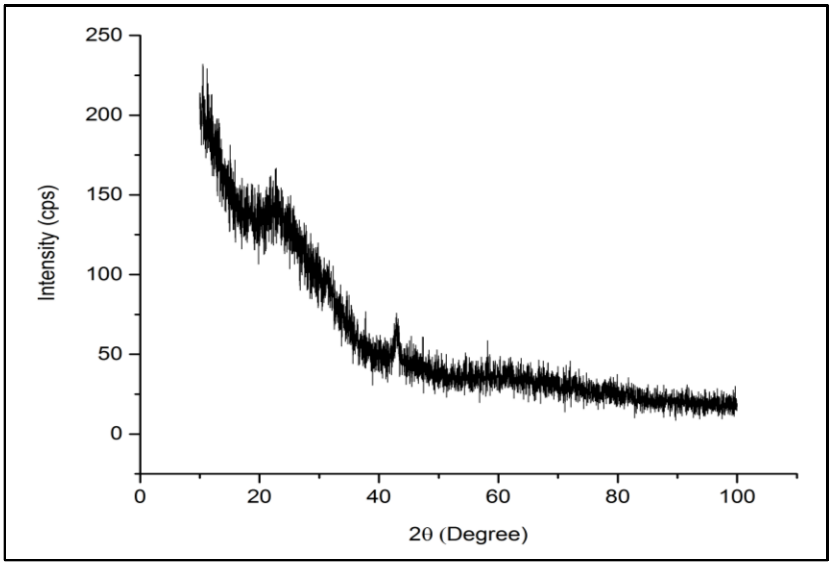

FIGURE 4. **(c) XRD spectrum of the reflecting surface of thin film form of cast mirror**

The XRD pattern of the reflecting surface of cast Aranmula mirror shows an amorphous nature with two intense peaks at the positions 52.4° and 60.5° respectively, which confirms that both copper and $Cu_{6.25}Sn_5$ phases present in the as synthesized material. This pattern of the mirror sample also contains a line broadening, which may be due to lattice parameter changes associated with relative diffusional growth of adjacent intermetallic layers. The average crystallite size estimated from Scherer formula is found to be about 72.1 nm. The XRD pattern of the powdered form of the mirror sample consist one intense peak at the position 42.94°, which confirms the presence of $Cu_{6.25}Sn_5$ phase of the Cu- Sn alloy system. The other phases that are included in this XRD pattern are the intermetallic phase $Cu_{41}Sn_{11}$ and the oxides of copper and tin such as Cu_2O and SnO_2, which indicates that the material is not purely crystalline in nature. The average crystallite size estimated from Scherrer formula is found to be about 75.2 nm.

The XRD pattern of thin film coated mirror sample suggests an amorphous nature with one peak at the position 43.02°, which indicates the presence of the intermetallic phase $Cu_{6.25}Sn_5$ of bronze alloy system. This pattern also contains a line broadening, which may be due to lattice parameter changes associated with relative diffusional growth of adjacent intermetallic layers. The average particle size obtained from Scherrer formula is found to be about 18.65 nm. We could find a distinct transition from crystal to amorphous phase as the material is polished in cast mirror or made in the form of thin film. The nature of decreasing crystallinity for different cases is shown in figure 5.

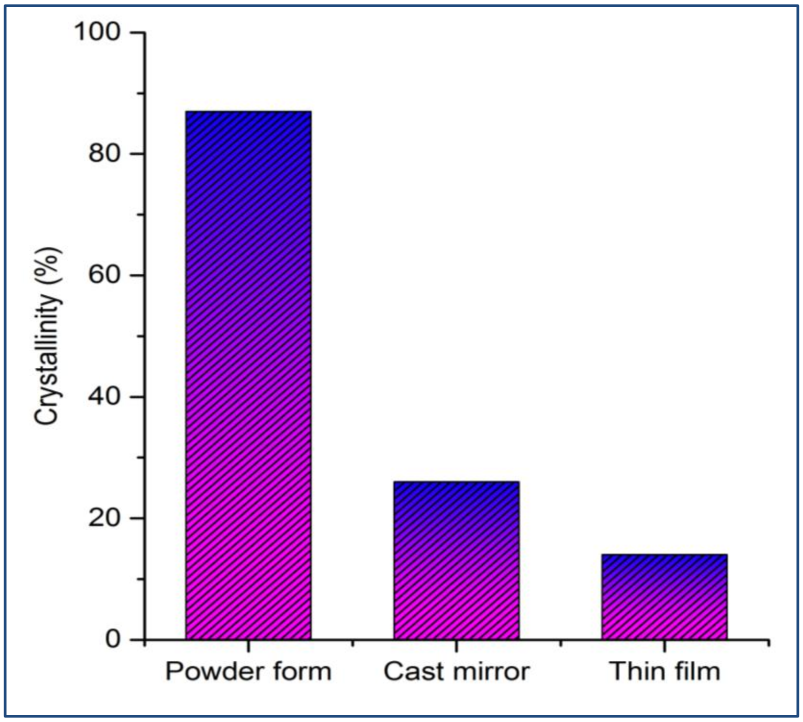

FIGURE 5. Nature of decreasing crystallinity in different cases

The amorphous nature found in the XRD pattern of the reflecting surface of cast and thin film coated mirror indicates the presence of a non-metallic, thin film layer mainly consisting of a tin enriched delta phase ($Cu_{31}Sn_8$), which is an intermetallic compound of fixed composition of 32.6 % tin. The presence of this delta phase is optimized and its high brittleness offset by a clever casting and polishing process [1]. Delta phase is not formed on normal tinned surfaces, but it can occur on heat- treated tinned surfaces. However it does normally occur in the body of a cast or worked bronze as the eutectoid and has a characteristic microstructure, which is only derived from cooling the bronze through the 520℃ isothermal temperature [2]. Moreover, the delta phase, being a stable compound, does not corrode or tarnish easily [1]. The XRD data obtained from mirror samples were compared with the data in the JCPDS reference file available in IIT Madras, but it does not give a pattern specifically for the delta phase suggested in early literature [1,3]. Thus in general, the combined use of EDS, AFM and XRD analysis of the reflecting surface of cast and thin film coated mirror suggest that on the mirror surface, there exist a transparent, non- metallic, highly corrosion resistant, smooth and nano-structured thin film layer of amorphous nature mainly consisting of a tin enriched delta phase($Cu_{31}Sn_8$) . It also concluded that Aranmula mirror contains nano-particles that are considered to be quasi-crystalline in nature. These results are broadly in agreement with the report of early literature [4,5].

4. Thermal Characterization by means of TG/DTA

Thermal properties of Aranmula mirror in the form of powder is studied up to 1000℃ in Nitrogen atmosphere at a rate of 20℃ /min by means of Perkin Elmer, Diamond TG/DTA flexible axial and radial view instrument with TG sensitivity 0.2 mg and DTA sensitivity 0.06 mV. TG/DTA curve for mirror sample up to 1000℃ in Nitrogen atmosphere is shown in figure 6.

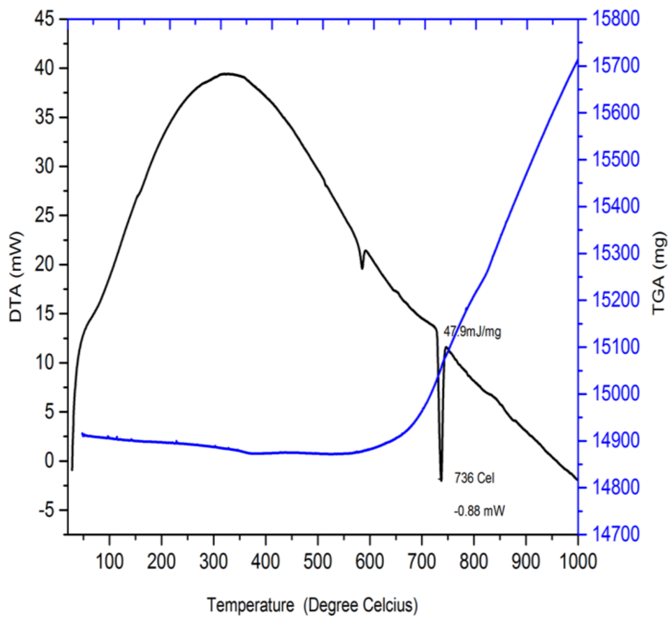

FIGURE 6. TGA and DTA curve of mirror sample

The material is found to be thermally stable up to a temperature of 600℃ and notable mass loss is observed afterwards. To confirm this feature we have carried out DTA analysis and clear discontinuity is observed at a temperature of 736℃ , which is very close to the melting point of the mirror sample reported in early literature [6].

5. Optical Reflectance Studies by UV- Visible Spectroscopy

The optical reflectance of the cast and thin film coated mirror samples are measured in a region of wave length ranging from 200 nm to 900 nm using JASCO - 550V UV- Visible Double Beam Spectrophotometer. The reflectance spectra for cast and thin film form of the mirror samples are shown in figure 7.

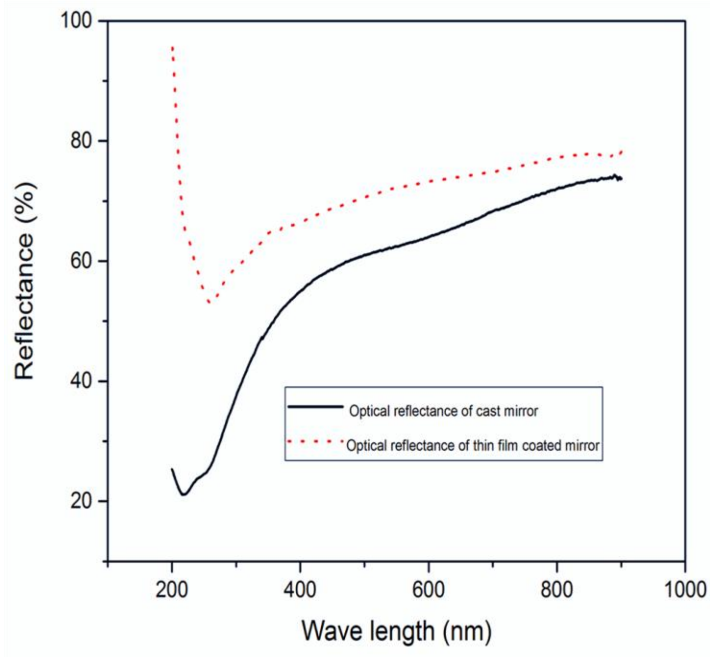

FIGURE 7. **Optical reflectance spectra of cast and thin film form of Aranmula mirror sample**

The optical reflectance values for thin film form of the Aranmula mirror material is shown as dotted line and its higher optical reflectance is clearly seen in figure. Optical spectra of cast and thin film form of Aranmula mirror showed more uniform reflectance across the entire visible region. Both spectra give a maximum value of reflectance in the IR region and absorption is observed in the lower wave length region, which results in a significant loss of reflection. The average optical reflectance of the cast Aranmula mirror sample in the visible region is found to increase from 61.35 % to 71.02 % when it is prepared in the form of thin film. The reflectance spectrum of Aranmula mirror obtained matches with that of speculum metal mirrors reported in literature [7, 8]. Tolansky obtained thin film form of speculum metal mirror for the first time, which also had enhanced optical reflectance [9].

CONCLUSIONS

1. The EDS based elemental chemical composition studies of the reflecting surface of cast, thin film coated and powdered form of mirror samples provide for the first time evidence for the presence of minor constituents such as As, Ag, Au, Zn, P and S in Aranmula mirror making. Arsenic was used in early telescope mirrors made from speculum metals. The chemical composition of the mirror is not to found change significantly when the mirror materials are made in the form of thin films. The EDS analysis reveals that the elemental chemical compositions of Aranmula mirror is not homogeneous everywhere and the addition of small amount of minor constituents may be alter the optical and physical properties of Aranmula mirror.

2. The nano structure as revealed from XRD and AFM analysis of the reflecting surface of cast, thin film coated and powdered form of mirror samples are not reported previously in the case of Aranmula mirror. Combined use of EDS, AFM and XRD analysis of the mirror sample reveals the presence of a transparent, non-metallic, corrosion resistant, smooth, nano structured thin film layer mainly consisting of a tin enriched delta phase ($Cu_{31}Sn_8$) on the mirror surface, which is amorphous in nature. These results also suggest that Aranmula mirror contains nano-particles, which are considered to be quasi-crystalline in nature. But the specific pattern of delta phase ($Cu_{31}Sn_8$) suggested in the Aranmula mirror making by earlier studies is not conformed by JCPDS analysis of the XRD data of the mirror sample.

3. The thermal stability of Aranmula mirror sample up to 600℃ as evident from TGA analysis, clearly rules out earlier speculations of herbs and the presence other organic materials in the traditional Aranmula mirror making. The melting point of the cast Aranmula mirror is found to be 736℃ , which is very close to the reported value in early literature.

4. The optical reflectance of the cast Aranmula mirror material is found to increase by about 10 % on an average in the visible region of the spectrum when it is prepared in thin film form in glass substrate.

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REFERENCES

[1] Sharada Srinivasan, Ian Glover, Current Science, 93, No. 1, 10, July (2007)

[2] N.D. Meek, Archaeometry 28, No. 2, 133- 162 (1986).

[3] S. G. K. Pillai, R. M. Pillai, A. D. Damodaran, T. R. Ramachandran, JOM. 59 – 62, (1994)

[4] G.M. Ingo, P. Plescia, E. Angelini, C. Riccucci, T. Decaro, Appl. A 83,611- 615 (2006)

[5] J. A. Sekhar, A. S. Mantri, S. Yamjala, Sabyasachi Saha, R. Balamuralikrishnan, P. Rama Rao, JOM, Vol. 67, No. 12, 2976- 2983 (2015)

[6] Takekazhu Nagee, Sharada Srinivasan, Srinivasa Ranganathan, R. M. Pillai, Yasuji Shimizu, ISIJ International, 54, No. 5, 1172 - 1176 (2014)

[7] T. E. Girish, Proc Int. Conf. Solar Cells, CUSAT, Extended Abstracts, 199- 200 (2008)

[8] A. A. Mills, R. Hall, Notes Rec. Roy, Soc. Lond. 37, 149 (1983)

[9] S. Tolansky, W. K. Donaldson, J. Sci. Instrum. 24, 248 - 249 (1947)