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Mechanical Characterisation of Cast Sn-XFeO-0.2Cu Solder Alloy

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Abstract
The act of soldering that is devoid of any debilitating health hazards is a global concern necessitating the development of varied lead-free solders exhibiting desirable solderability. In this study, a lead-free solder composed of tin-iron millscale-copper (Sn-FeO-0.2Cu) alloy was fabricated by casting and characterised for mechanical properties critical to its functionality while the iron millscale (IMS) varied from 1-5 wt.%. The cast alloy samples were evaluated for microstructure and mechanical properties (elastic modulus, yield strength, ultimate tensile strength and hardness) using optical microscope and relevant state of the arts mechanical characterisation tools respectively. Results show positive comparison with established solders mechanical properties. This is attributed to the coherency of IMS with the tin matrix on one hand and the role of dislocation motion impediment played by the Fe-Cu intermetallic formed within the relatively soft tin matrix on the other. The solder melts in the range of 245-255^{0}C suggesting its suitability for soldering electric motors, car radiators and other high melting point (HMP) soldering.

Keywords: Solder alloy, iron millscale, copper-tin, characterisation, mechanical properties

1.0 INTRODUCTION

The drive for the development of lead-free solder materials for varied applications is an active research concern globally. This has become more imperative in the light of stringent legislations against the use of leaded solders coupled with the ever increasing challenge of joining critical electrical and electronic components in hi-tech structures (Leads Direct, 2006, Warren, 2004, Anderson, 2007). Currently, the tin-silver-copper (SAC) alloy systems have emerged as one of the effective and reliable lead-free solder composition in micro-electronics applications (Caro *et al.*, 2007, Alan, *et al.*, 2002). However, based on factors such as cost, processing flexibility and peculiarity of area of application, researchers by way of innovation have introduced different elements as replacement for silver in comparable SAC composition designs. This effort has widened the latitudes and availability of reliable and cost competitive lead-free solders. The current study aims at using iron millscale (IMS) innovatively in place of silver within the Sn-Cu system that is devoid of drossing phenomenon.

Iron millscale is usually formed on the surfaces of hot rolled profiles such as plates, sheets and bars. On the basis of the best rolling practice adopted, between 35 and 40 kg of IMS is produced per metric ton of hot rolled steel bar (IISI, 1987). This represents about 4 % yield loss to steel millers thereby reflecting a huge difference between input stock and final output tonnages (Danlov, 2003). The accumulation of IMS on the shop floor over time usually creates handling and disposal challenges.

Consequently, researchers have proposed various efficient methods and possible areas of its application in different engineering materials as value addition. These may also contribute to a boost in cleaner environment (Seok-Heumbaek *et al.*, 2010, Gaballahi *et al.*, 2013, Saberifar *et al.*, 2014, Mamdouh *et al.*, 2015).

Enhancement of solders performance and solderability is known to be impacted by physical, electrical and thermo-mechanical parameters (Yee and Haseeb, 2016). All of these parameters are influenced by the solders' microstructures induced sequel to compositional design that might have been executed to influence these properties (McCormack *et al*., 1994, Zhou, *et al*., 2007, Ervina *et al*., 2017). However, the current study focuses on the mechanical characteristics critical to the solder's functionality which include; elastic modulus, hardness, yield strength, fatigue-life among others. The addition of IMS particles into Sn-Cu system in this study is meant to trigger the formation of a type of eutectic phase that solidifies over a range of temperatures. This solidification regime can be taken advantage of such that during soldering, the cooling rate of the liquid|molten solder is controlled to obtain varied microstructures that enhance the desired mechanical properties. For example, Chawla, *et al*. (2004) obtained significant improvement in the Young's modulus of Sn-3.5Ag solder as the cooling rate was controlled resulting in desirable Ag_3Sn morphology. The information obtain from this study will therefore provide the scientific basis for the use of IMS waste in the production of lead-free solders.

2.0 MATERIALS AND METHOD

2.1 Materials

The three major materials used in this study are tin (Sn), copper (Cu) and iron millscale (FeO). Tin (Plate 1a) in powder form was procured through the Federal Institute of Industrial Research, Oshodi, (FIIRO) Lagos, Nigeria, copper (Plate 1b) foils were obtained commercially while iron millscale (Plate 1c) was supplied by Federated Steel Mill, Ikeja, Nigeria. The iron millscale composition (Table 1) was obtained through x-ray fluorescence (XRF) analysis with the loss on ignition (LOI) observed to be 0.001.


(a)


(b)


(c)

Plate 1: Experimental materials (a) Tin (b) Copper (c) Iron millscale

Table 1: Chemical composition of iron millscale by XRF analysis

Compounds	FeO	Fe_2O_3	Fe_3O_4	SiO_2	MgO	CaO	MnO
Weight (%)	68.809	24.735	6.184	0.011	0.016	0.220	0.024

2.2 Method

The materials design in the solder consists of iron millscale (IMS) particles varied from 1-5 wt. % while the copper concentration was fixed at 0.27 wt. % and tin filled up the balance. The corresponding mass of each material was also computed for the alloy samples (Table 2). Justification for this alloy ratio stems from literature which stipulates that addition of copper in tin-based lead-free solder alloys should be restricted to 0.1 – 0.5 wt. % due to the tendency of copper to cause adverse reflow of joint produced by the solder (Carol, *et al.,* 2007). Moreover, tin being the base material is normally present between 95 wt. % and 98 wt. % while both Cu and IMS are usually in trace amounts to effect microstructure modifications and prevention of undesirable dross formation (Qing, *et al.,* 2005).

Table 2: Experimental materials formulation matrix

	FORMULATION MATRIX									
SAMPLES	**1**		**2**		**3**		**4**		**5**	
Alloy Elements	Conc (wt. %)	Mass (g)	Conc (wt. %)	Mass (g)	Conc (wt. %)	Mass (g)	Conc (wt. %)	Mass (g)	Conc (wt. %)	Mass (g)
Tin	98.80	133.38	97.80	132.03	96.80	130.68	95.80	129.33	94.80	127.98
Copper	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
IMS	1.00	1.35	2.00	2.70	3.00	4.05	4.00	5.40	5.00	6.75

Iron millscale was oven dried, ground in a ball mill and sieved to 106 µm particle size while tin was also pulverized and copper foils were mechanically sized into tiny pieces chargeable into a small crucible pot. The melting of the charges in a pit furnace was carried out according to the alloy design whereby five melting cycles were carried out sequentially with regard to the varied mass of tin and IMS particles. Although the charges theoretical melting temperature varies; tin, 232^0C, copper, 1083^0C and IMS, 1377^0C, it was observed that the mixture melted at 450^0C. This is attributable to established principle melting temperature depression due to mixing of alloy elements (Oh, *et al.,* 1996, Askeland, 1989, Lewis, *et al.,* 2002). According to Bradley and Hranisavlevic (2001), the mixing of 96.5%Sn with 3.5%Ag depressed the liquid temperature of the solid to 221^0C compared with the theoretical melting temperature of pure silver and tin which is 961^0C and 232^0C respectively. The charges became molten at 350^0C, homogenised to 355^0C and cast in a cylindrical metal mould (Plate 2a) with three slots to cast three samples for each melting cycle. Some of the cast alloy samples are shown in Plate 2b while the chemical composition of the cast solder alloy is presented in Table 3.

Plate 2a: Metal mould with inscribed three slots

Plate 2b: Cast solder bar samples

Table 3: Composition Analysis Result of Cast Sn-xFeO-0.2Cu Solder Alloy

Elements	Sn	Al	Si	Cu	Fe	Sb	Ti	P	Pb	Ni
Wt. %	91.78	2.15	1.88	0.16	3.32	0.28	0.13	0.07	0.14	0.09

2.3 Microstructural Analysis

The microstructural integrity of the cast solder alloy was examined using an optical microscope (OM). The preparation of samples for the analysis involved mechanical cutting of samples into appropriate sizes at ambient temperature and grinding to obtain smooth surfaces. Further preparation involved polishing of samples using emery papers of grits 400, 600 and 800 in succession until mirror-like surfaces were obtained. The mirror-like surfaces were then washed under a running tap water and dried. This was followed by etching using a solution containing nitric acid in 125 ml of distilled water after which the microstructural features were viewed under an OM (Magnification: 200x).

2.4 Mechanical Properties Evaluation

The cast solder alloy bars were thoroughly fettled then standard tensile and hardness properties test samples were prepared. The tensile test was carried out according to ASTM E8 standards using Instron electromechanical testing machine model 3369, USA. Three different points on the samples surfaces where subjected to hardness test using the Vickers scale.

3. 0 RESULTS AND DISCUSSION

3.1 Microstructure

The solder alloy's microstructural features as shown in Plates 3 (a – e) are generally influenced by the varied volume fractions of IMS particle addition, which manifest in terms of colour, grain size and their distribution within the matrices. The micrographs display three major phases namely; tin matrix, IMS particles dispersed evenly within the matrices and Sn/Cu intermetallic appearing as spheroids at the grain boundaries. Grain coarsening is observed in Plate 3e due to the relatively higher IMS particles at 5wt. %. Variation in colour of the micrographs can be attributed mainly to the overriding influence of ferric oxide which IMS approximates in the alloy composition. All these features acted in concert to affect the alloy's mechanical properties to varying degree. The copper content, though very low, serves the purpose of structure modification. This is demonstrated in term of grain size control, which appears to corroborate the report from the work of Chen, *et al*., (2012).

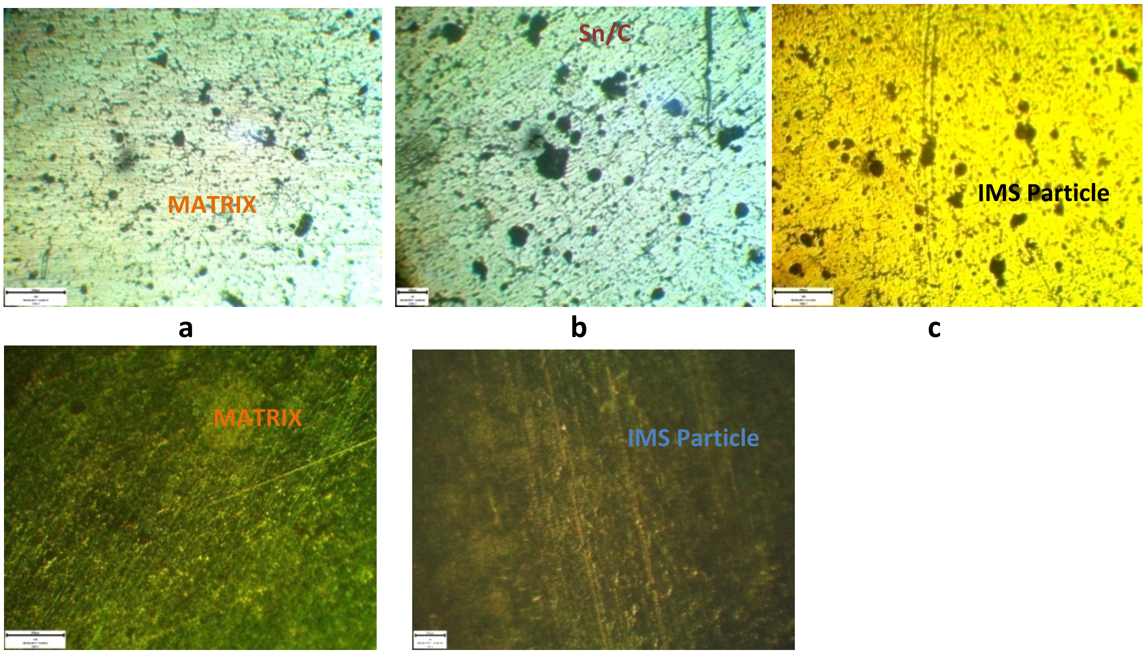

Plate 3: Optical micrographs of tin-copper solder at varied IMS addition (a) 1 wt. %, (b) 2 wt. %, (c) 3 wt. %, (d) 4 wt. % and (e) 5 wt. % (Magnification: 200x).

3.2 Mechanical Properties

The results of both hardness and tensile properties are shown in Table 4 for the purpose of panoramic comparison.

Table 4: Results of hardness and tensile properties tests

		Tensile Properties		
IMS addition (wt. %)	**Hardness (Hv)**	**Ultimate tensile strength (MPa)**	**Yield strength (MPa)**	**Elastic modulus (GPa)**
1	11.3	409.4	270.2	44.7
2	16.6	456.3	311.5	42.3
3	18.1	517.6	342.7	39.8
4	20.5	524.5	365.1	37.2
5	21.7	533.1	377.3	35.4

3.2.1 Hardness

The hardness of the cast solders were observed to increase as IMS addition increases while the highest hardness of 21.7 Hv is demonstrated at 5 wt. % IMS addition (Figure 1). The IMS particles appear to be coherent with the tin matrix and being a harder phase it effectively enhance inter facial cohesion, which resulted in the observed increase in hardness. This behaviour was found to subsist as the volume fraction of IMS particles increase within the matrix. It is observed from Figure 1 that hardness values range from 11.3 – 21.7 Hv. This level of hardness appears to be sufficient to prevent any form of damage to soldered joints after solidification. Moreover, the hardness value range obtained in this study compared well with the report of Yee and Haseeb (2016) for solders meant for car radiator and similar automotive components.

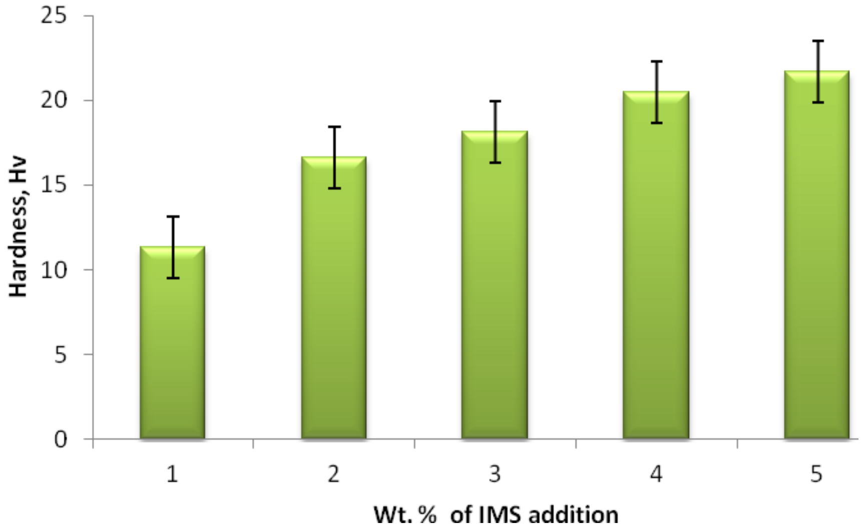

Figure 1: Effect of IMS particles addition on hardness of Sn/Cu solder

3.2.2 Ultimate tensile strength

As shown in Figure 2, the solder alloys were found to exhibit steady increase in ultimate tensile strength (UTS) as the volume fraction of IMS addition increases. The UTS values range from 409.4MPa and peaked at 533.1MPa corresponding to the minimum (1 wt. %) and maximum (5 wt. %) IMS additions respectively. This behaviour can be ascribed to the resistance to dislocation motion provided by IMS particles within the matrices. Thus, the more of IMS particle in the matrix, the higher the resistance to dislocation motion on application of force, hence the steady rise in the UTS. This level of UTS demonstrated by the solder alloy compares well with similar work by Thomas *et al*., (2002).

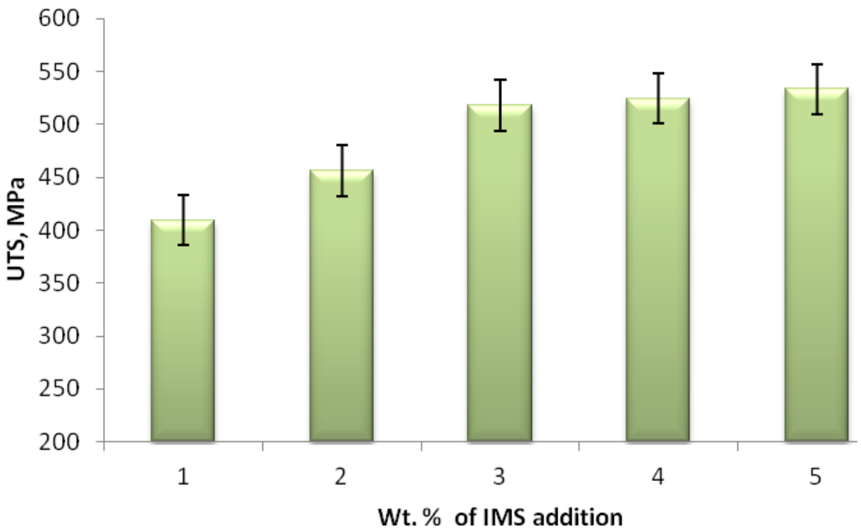

Figure 2: Effect of IMS particles addition on UTS of Sn/Cu solder

3.2.3 Yield strength

Figure 3 shows the ductility of the solder alloys, which is observed to be significantly influenced by IMS addition. It was found that the ductility of the solder alloys increased in tandem with increase in IMS addition. It had been established that enhancement of ductility often stems from the introduction of an interstitial element (Carol, *et al*., 2007), which is the purpose IMS particles serve in this study. Enhancement in yield strength may also be due to increase in grain boundaries, as the copper in the alloy composition modifies the structure giving rise to fine grain size. These two factors namely; interstitial element and fine grains, impede dislocation motion within alloy system, which appear to be the case in this study. Thus, the solder alloy samples exhibited minimum yield strength of 270.3 MPa corresponding to 1 wt. % IMS addition and demonstrated the peak value of 377.2 MPa at 5 wt. %.

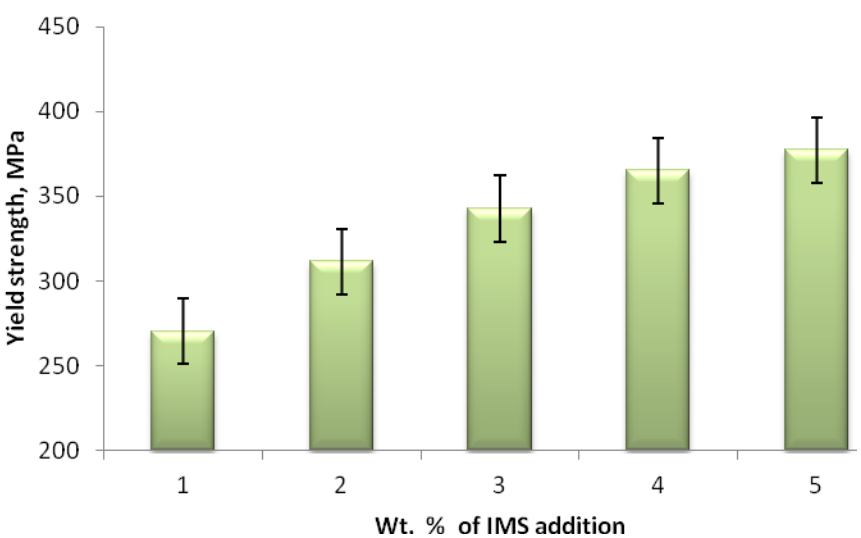

Figure 3: Sn/Cu solders ductility variation with IMS addition

3.2.4 Elastic modulus

The elastic modulus is the measure of stiffness behaviour of a material required to prevent permanent warpage in service. In this study, the solder alloys exhibited sustained marginal increase in elastic modulus as IMS addition increases. This can be explained by the fact that elastic modulus is an intrinsic property which is not dependent on processing parameters but seldom influenced by composition change and size of test sample. The marginal variations noticeable in Figure 4 might have arisen from different degree of coherency of constituent phases in the solder alloy due to IMS addition which affect resistance to inter-atomic bond stretching.

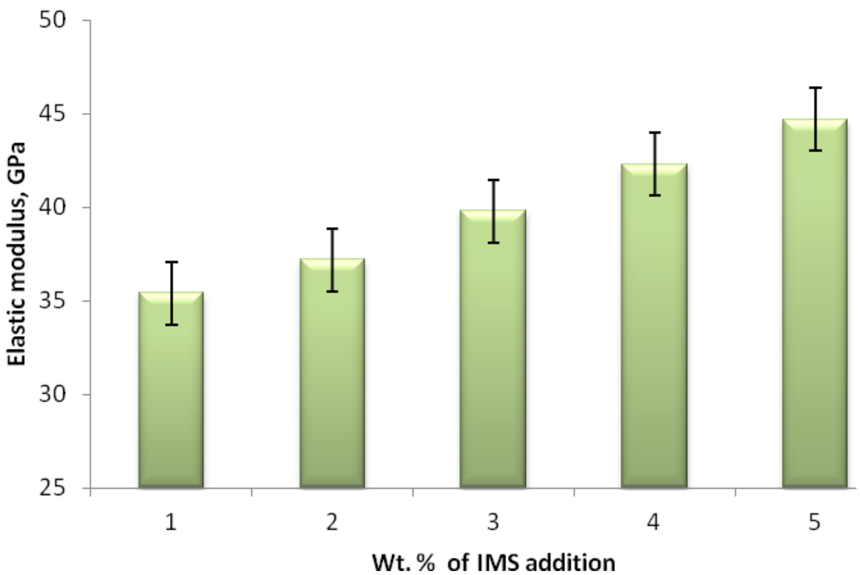

Figure 4: Sn/Cu solders elastic modulus variation with IMS addition

According to Bhagava and Sharma (2011), extensive alloying is often required to produced appreciable improvement in elastic modulus hence, the relatively compact range of 35.4-44.7GPa resulting in a marginal variation of 2.3GPa obtained in this study. This notwithstanding, the range of elastic modulus values obtained in the current study agrees well with the values reported (Lau and Pao, 1997, Hiroyuki *et al*., 2005) in literature which is 39-53 GPa.

4.0 CONCLUSIONS

The fabrication and evaluation of the mechanical properties of Sn/Cu lead-free solder with varied iron millscale (IMS) addition have been carried out. Results and their analyses gave rise to the following deductions:

(a) Addition of varied 106 µm IMS particles act in concert with the copper content modified the solders' microstructures, induced fine grains that are dispersed homogeneously within the tin matrix. These impacted significantly the solders' mechanical properties.

(b) The best mechanical properties were obtained at 5 wt. % IMS addition namely; hardness, 21.7 Hv, UTS, 533.1 MPa, yield strength, 377.7 MPa and elastic modulus, 44.7 GPa.

(c) Given this level of performances, it is concluded that the solder fabricated can be categorized as a heavy-duty solder suitable for soldering electric motors and car radiators.

REFERENCES

Anderson, I. E. (2007). "Development of Sn–Ag–Cu and Sn–Ag– Cu–X alloys for Pb-free Electronic Solder Applications". *.Journal of Material Science and Material Electronics, Vol. 18, pp 55-76.*

Alan, B., Christopher. H., Milos, D. and Jaspal, N. (2002). "Reliability of Joints Formed with Mixed Alloy Solders". Materials Centre, National Physical Laboratory, pp. 1-18.

Askeland, D. R. (1989). "The Science and Engineering of Materials". Second Edition, PWS-KENT Publishing Company, USA, pp. 68-75.

Bhagava A. K. and Sharma, C. P. (2011). "Mechanical Behaviour and Testing of Materials". PHI Learning Private Limited, Eastern Economy Edition, New Delhi, pp. 105-107.

Bradley, E. and Hrenisavljevic, J. (2001). "Characterisation of the Melting and Wetting of Sn-Ag-x Solder". *IEEE Transactions on Electronics Packaging Manufacturing, Vol. 24, No. 4, pp. 255-259.*

Carol, H., Ursula, K. and Kil-Won, M. (2007). "Fundamental Properties of Pb-free Solder Alloys". Bath J. Edition, p. 299.

Chawla, N., Ochoa, F., Ganesh, V., Deng, X., Koopman, K. and Scarritt, S. (2004). "Measurement and Prediction of Young's Modulus of a Lead-free Solder". *Journal of Materials Science: Materials in Electronics,* Vol. 15, pp. 385-388.

Chen, H. T., Ya, B. B., Yang, M., Ma, X. and Mingyu, L. (2012). "Effect of Grain Orientation on Mechanical Properties and Thermo-mechanical Response of Sn-based Solder Interconnects". *Journal of Material Characteristics.* Vol. 8, pp 64-72.

Danlov, E. V. (2003). "Economic Method of Recycling Metallurgical and Millscale by Sitfer Technology in an Arc Steelmaking Furnace". *Metallurgist,* 47, 5-6, pp. 197-205.

Ervina, E. M., Nur, F. M. and Mohd, M. A. (2017). "Influence of Dopants on Lead-free Solder Alloy". American Institute of Physics (AIP), Vol. 1835, doi.org/10.1063/1.5012611.

Gaballahi, N. M., Zikry1, A. F., Khalifa, M. G., Farag, A. B., El-Hussin, N. A. and Shalabi, M. E. (2013). "Production of Iron from Mill Scale Industrial Waste via Hydrogen". *Journal of Inorganic Non-metallic Materials,* Vol. 3 No. 3, pp. 34-42.

Hiroyuki, T., Lang, F. Q., Osamu, M. T. and Toshio, N. (2005). "Elastic Properties of Sn-Based Solder Alloys Determined by Ultrasonic Pulse Echo Method". *Japan Institute of Metals: Materials Transactions,* Vol. 46, No. 6, pp. 1271-1273.

International Iron and Steel Institute-IISI (1987). "The Management of Steel Industry By-Products and Waste". Report of Committee on Environmental Affairs, pp. 1-21.

Lau, H. John and Pao Yi-Hsin (1997). "Solder Joint Reliability of BGA, CSP, Filp Chip and Fine Pitch SMT Assemblies". Mc-Graw Hill, pp. 132-147.

Leads Direct (2006). "Soldering Regulations". www.leadsdirect.co.uk/technical-library/soldering. Retrieved on 8th October, 2017.

Lewis, D., Allen, S., Notis, M. and Scotch, A. (2002). "Determination of the Eutectic Structure in the Sn-Ag-Cu System". *Journal of Electronic Materials,* Vol. 31, No. 2, pp. 161-167.

Mamdouh, E., Azza, A. and Mohammed, E. (2015). "Conversion of Millscale Waste into Valuable Products via Carbothermic Reduction". *Journal of Metallurgy,* Vol. 2015, pp. 1-9.

McCormack, M, Jin, S. and Kammloth, G. W. (1994). "Enhanced Solder Alloy Performance by Magnetic Dispersions". Packaging and Manufacturing Technology: Part A-IEEE Transactions on Components, Vol. 17, Issue 3, pp. 452-457.

Oh, C. S., Shim, J. H., Lee, B. J. and Lee, D. N. (1996). "Thermodynamic Study on Ag-Sb-Sn System". *Journal of Alloys and Compounds,* Vol. 238, Issues 1-2, pp. 155-166.

Qing, W., William, F. and Johnson, R. (2005). "Mechanical and Microstructure Investigation of Lead-Free Solder". NASA and Allied Aerospace Research, pp. 83-95.

Saberifar, S., Jafari, F., Kardi, H., Jafarzadeh, M. and Mousavi, S. (2014). "Recycling Evaluation of Millscale in Electric Arc Furnace". Journal of Advanced Materials and Processing, Vol. 2, No. 3, pp. 73-78.

Seok-Heumbaek, S. H., Seok-Swoocho, D. J. and Won, S. (2010). "Optimisation of Process Parameters for Recycling of Millscale Using Taguchi Experimental Design". Journal of Mechanical, Science and Technology, Vol. 24, Issue 10, pp. 2127-2134.

Thomas, S. Stephen, L., David, S. and Juan, C. (2002). "Database for Solder Properties with Emphasis on New Lead-free Solders". National Institute of Standards and Technology, Colorado School of Mines Release 4.0, pp. 8-27.

Warren H. H. (2004). "Global Perspectives on Electronic Materials: Challenges and Opportunities". TMS Proceedings of the 46th Electronic Materials Conference (EMC). www.tms.org/pubs/journals/JOM/0406/. Retrieved on 7th December 2017.

Yee, M. L. and Haseeb. A. S. (2016). "Soldering Characteristics and Mechanical Properties of Sn-1.0Ag-0.5Cu Solder with Minor Aluminum Addition". *Journal of Materials,* 9, 522, pp. 1-17.

Zhou, Y. C., Pan, Q. L. and He, Y. B. (2007). "Microstructures and Properties of Sn-Ag-Cu Lead-free Solder Alloys Containing La". *Transactions of Nonferrous Metals Society of China,* Vol. 17, No. 1, pp. 1043-1048.