Rare-earth Information Center

Insight

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Strengthening Pb – Sn Solder

Common Pb–Sn solder dates back at least to the Romans who used alloyed lead and tin to join the pipes in their aqueducts. Despite the current concern about Pb in the environment, Pb-Sn is still extensively used. The performance of Pb-Sn solder is particularly important in electronic applications where changes in joint performance with aging under thermal cycling can result in circuit board failure. The thermal cycling behavior of Pb-Sn solder is determined by the eutectic microstructure that forms during solidification. The desired uniform microstructure is difficult to obtain in the binary composition since the solidification conditions usually vary across a solder joint. It is therefore desirable to add constituents to refine the microstructure. Ag, Sb and Cu have all been used. However for electronics applications, there are severe limits on the melting temperature of the solder, and these additions test these limits. Recently, X. Ma et al. {*Mater. Lett.*, **52**, 319-22 (2002)} have investigated Pb-Sn alloys with trace amounts of La (0.05 wt%), which have a melting point 1 to 2 degrees higher than the 183°C eutectic temperature. Tensile test samples aged for 1 h at 125°C showed a 70% increase in tensile strength at 125°C compared to the standard Sn_{60}-Pb_{40} composition. The authors also thermally cycled a simulated surface mount assembly between 218K and 398K. The joints were considered to have failed when a visible crack formed through the surface. The 60/40 samples averaged 132 cycles before cracking while the La added material averaged 412 cycles. Examination of the microstructure of the two solders demonstrated a clear refinement of the structure in the La added material. The origin of the refinement is not discussed, but I would speculate that it results from a fine dispersion of La_2O_3.

In a second article {*J. Alloys Compds.*, **334**, 224-7 (2002)}, the same authors have investigated the interface between La-free and La-containing solder and Cu. When Pb-Sn solder wets Cu, an interfacial layer of Cu_6Sn_5 is formed. The authors state that limiting the thickness of the Cu_6Sn_5 is essential to maintaining thermal fatigue life, isothermal shear fatigue life, tensile strength and fracture toughness in the solder joints. In this paper, the authors tested lap joints, which were aged for 120 h at 125°C. SEM cross sections of the joints showed that the thickness of the Cu_6Sn_5 layer for the La containing solder was slightly more than half that of the binary solder. The authors discussed this result in terms of the thermodynamics of the Cu-Sn-La ternary system and argue that the driving force for Cu_6Sn_5 is reduced by adding a small amount of La and predict that the maximum depression would be at 0.09% La. Neither paper discusses the conditions under which the solder joints were made or the O content of the solder, which I view as crucial to understanding the role of La in these materials.

Rare-Earth-Containing Lead-free Solders

A different aspect of the use of rare earths in solder was investigated by Ramirez et al. {*Appl. Phys. Lett.*, **80**, [3], 398-400 (2002)}. The lead-free solders studied were Sn-Ag and Au-Sn, and the addition used was Lu. The concentrations used were much higher at 0.5 and 2.0 wt%. The purpose of the investigation was also different as Ramirez et al. are interested in bonding optical and optoelectronic materials, which are oxides. Solders typically do not bond to oxides so metallization steps are required. These steps are expensive, and the bond of the metallization layer to the oxide is strictly physical, which raises reliability questions. The rational behind the Lu additions is that the high affinity of the Lu for

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oxygen will result in the solder wetting the oxide. With Au or Ag and Lu, these solders are clearly not inexpensive, however, a check of the binary phase diagrams shows that there is little or no solubility of rare earth elements in most solder elements. Both Au and Ag will dissolve Sc, Y and Lu but not La. I assume that magnetic moments in the solder are undesirable so other heavy rare earths are not of interest. Economically, Y is preferable, but the solubility appears to be about one third that of Sc and Lu. As expensive as Lu is, it is appreciably cheaper than Sc. In producing the solder alloys, considerable care was taken to insure that the Lu properly alloyed, since the formation of an oxide skin on the Lu, during the initial melting, would result in a refractory layer, which would prevent the Lu from dissolving in the alloy. The wetting of vitreous silica substrates was studied using high resolution TEM and EDX nanoprobe. There was a migration of the Lu to the solder–SiO_2 interface and chemical bonding due to the reduction of the SiO_2 by the Lu. The melting point of the solders was near 221°C.

CO Sensing

CO is an environmentally hazardous gas, which is both explosive and poisonous to humans. As a result, there is a demand for sensors, which will detect 50 PPM or less CO with a sensor temperature of less than 200°C. (Solid state sensors typically measure the resistivity of a solid electrolyte, which frequently requires high temperature operation for ion mobility.) Sensor manufacturing also requires an economically feasible process method. High sensitivity CO sensing films have recently been produced, using a sol-gel method to produce films of $La_{0.8}Sr_{0.2}Co_{0.5}Ni_{0.5}O_{3-d}$. In order to produce films of the desired composition, a fairly detailed process is required. Y. L. Chai et al. {*J. Alloy Compds*., 333, 147-53 (2002)} have developed a process for producing these films, which they discussed in detail. Smooth, uniform films are produced by spin coating, and the process parameters have been optimized. The process results in a low calcination-sintering temperature of ~ 200°C, compared to typical values for sol-gel films of 850°C. The result is a homogenous film of finely dispersed nanocrystals.

Short Notes:

An analysis of the potential for energy savings and the reduction of CO_2, which would result from the application of superconducting technology in several areas, is evaluated in a paper by S. Morozumi {*Physica C*, **357-360**, 20-4 (2001)}. The projections are for the year 2010 for Japan.

Superconducting Quantum Interference Devices, SQUIDs, form the basis for the most sensitive detection of magnetic fields. Using low temperature superconductors, SQUID magnetometers are common in most laboratories studying magnetic materials. The use of High Temperature Superconductor (HITC) SQUIDs should greatly expand the number of practical applications for SQUIDs. H. Itozaki {*Physica C*, **357-360**, 7-10 (2001)} has recently published an article reviewing the current status of the development and compercialization of HITC SQUIDs .

Conference Notes

"Polymer Bonded Magnets 2002 New Materials, Molding Processes and Applications for Bonded Magnetic Materials" will be held April 10-12, 2002 at the Hyatt Rosemont Hotel in Chicago (www.intertechusa.com/PBM.html). "Rare Earth Research Conference" will be held July 13-18, 2002, at the University of California, Davis (www.chem.ucdavis.edu/rerc/). "Seventeenth International Workshop on Rare-earth Magnets and Their Applications" will be held August 18-22, 2002, in Newark, Delaware (http://rem02.physics.udel.edu/). "Permanent Magnet Systems and Power Electronics for Motion Control" will be held September 9-12 at a location to be announced. (www.goradv.com).

Sincerely,

R. W. McCallum
Director of RIC