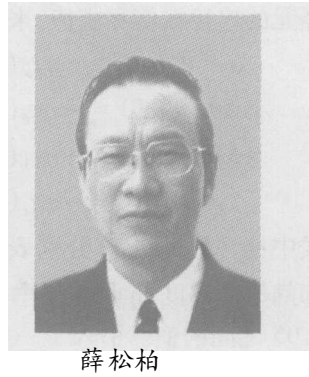
Sn-Ag-Cu-Ce无铅钎料合金体系的热力学计算及预测

薛松柏[1], 陈 燕[2], 吕晓春[2]
(1.南京航空航天大学 材料科学与工程学院, 南京 210016;
2.哈尔滨焊接研究所, 哈尔滨 150080)


薛松柏

摘 要: 利用周模型对 Sn-Ag-Cu-Ce无铅钎料合金体系进行了热力学计算预测。热力学计算结果表明, Ag Cu含量(质量分数)分别为 0.5% ~4.5%时, 当 Ce的含量(质量分数)超过 0.05%时, 体系达到化学平衡状态; 当 Ce的含量(质量分数)达到 0.6%左右时, Sn, Ag Cu分别都出现了"等活度系数"现象。这一研究结果可为无铅钎料合金的成分设计提供理论指导。

关键词: 无铅钎料; 周模型; 化学平衡; 等活度系数
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0 序 言

随着世界性的环境保护要求的不断提高, 传统的 Sn-Pb软钎料将很快被逐步淘汰。基于各国立法对软钎料无铅化的要求以及微电子元件对软钎料性能的要求, 研究开发无铅、能替代传统 Sn-Pb合金的新型软钎料已成为当前的重要和热点课题之一[1]。在众多的无铅钎料合金体系中, Sn-Ag-Cu合金体系因其具有相对较好的钎焊工艺性能、优良的焊点可靠性, 已逐渐被公认为无铅钎料中最有应用前景的合金体系[2]。

基于上述背景, 对 Sn-Ag-Cu钎料合金的改进、优化, 即通过改变合金中各成分的配比或者向合金中添加其它微量合金元素特别是稀土元素, 以期接近或超过传统的 Sn-Pb合金, 是目前国内外研究较多的课题。通过添加新元素, 然后进行冶炼、加工, 再进行大量的钎焊工艺性能及力学性能试验, 从而找到具有最佳综合性能的化学组成, 这样做势必会造成大量的人力、物力的浪费[3]。作者把合金体系热力学计算的新一代几何模型——周模型[4], 引入到 Sn-Ag-Cu-Ce合金体系的设计中, 通过计算合金体系的各种热力学性质, 如活度、过剩自由能、活度相互作用系数等, 从中发现合金体系设计时所存在的规律, 可能会达到事半功倍的效果。

1 热力学模型和计算方法

目前, 用于三元合金体系的热力学性质计算的几何模型有许多种, 但是新一代几何模型——周模型, 有效地兼容了其它几何模型的优点而又避免了其缺点, 在理论上更合理, 在实际运用中更准确、方便, 已经在黑色合金体系(特别是合金钢)的热力学计算上得到了广泛的运用。

根据周模型, $i-j-k$三元系金属熔体的过剩吉布斯自由能 G^E 可按式(1)由三个相关的二元系($i-j$系、$j-k$系和 $k-i$系)的过剩 Gibbs自由能 G^E_{ij}、G^E_{jk}、G^E_{ki}进行预测。

$$G^E=\frac{x_ix_jG^E_{ij}}{(x_i+\xi_{ji}x_k)(x_j+\xi_{ij}x_k)}+\frac{x_jx_kG^E_{jk}}{(x_j+\xi_{kj}x_i)(x_k+\xi_{jk}x_i)}+\frac{x_kx_iG^E_{ki}}{(x_k+\xi_{ik}x_j)(x_i+\xi_{ki}x_j)}。\tag{1}$$

$$RT\ln\gamma_i=\mu_i^E=G^E+\frac{\partial G^E}{\partial x_i}-\sum_{i=1}^{3}x_i\frac{\partial G^E}{\partial x_i},\tag{2}$$

式中: γ_i为活度系数; x_i、x_j、x_k为三元系各组元的摩尔分数; ξ为相似系数, 为周模型特别引入的模型参数。三元系中任一组元的活度系数 γ_i可按式(2)求出。

鉴于周模型只能较好地应用于三元合金系的热力学性质的计算的现状, 在处理多元合金体系时, 一般都把它拆成若干个三元合金系来进行近似计算[5]。对于 Sn-Ag-Cu-Ce四元合金体系, 由于 Sn与 Ag Cu在周期表中处于比较远的位置, 它们的性质相差是比较大的, 而且其中 Ag Cu的许多热力学性质相近, 且在 760 ℃以上相互无限固溶, 在 760 ℃以下时相互固溶度均较大, 计算时可以把 Sn-Ag-Cu-Ce这个四元体系, 近似地简化为以 Sn为溶

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剂时的 Sn-Ag-Ce体系、以 Sn为溶剂时的 Sn-Cu-Ce体系、以 Ag为溶剂的 Ag-Sn-Ce体系以及以 Cu为溶剂的 Cu-Sn-Ce体系, 以这 4个三元合金体系来计算[9]、讨论, 依然具有较好的参考价值。

2　结果与讨论

图 1、2所示的是在 523 K时, 随 Ce含量 (下文中凡涉及到的元素含量均指的是质量分数)的变化, Sn、Ag、Cu各元素相应的活度系数变化情况。可以看出 Ag、Sn的活度系数在 Ce的含量约为 0. 05%左右时, 两条曲线形成交叉; Cu、Sn的活度系数在 Ce的含量约为 0. 006%左右时, 两条曲线形成交叉。此时在热力学上的含义是体系内 Ce分别与 Ag、Sn及 Ce分别与 Cu、Sn达到化学平衡。综合分析图 1、2的结果, 可以看出, 在 Sn-Ag-Cu-Ce这个四元体系中, 当 Ce的含量达到 0. 05%时, 整个体系, 即 Ce分别与 Ag、Sn、Cu都达到了化学平衡状态, 也就是, Ce加入到这个体系中的最佳含量约为 0. 05%。

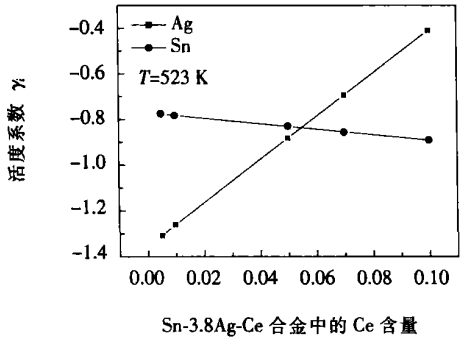

图 1　Sn、Ag活度系数与 Ce含量的关系

Fig. 1　Relationship of activity coefficient of Sn or Ag and content of Ce

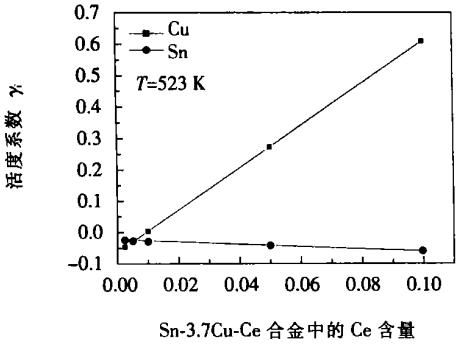

图 2　Sn、Cu活度系数与 Ce含量的关系

Fig. 2　Relationship of activity coefficient of Sn or Cu and content of Ce

图 3、4所示的是在 523 K时, 以 Sn为溶剂的 Sn-Cu-Ce系和 Sn-Ag-Ce系, 随体系中 Ce含量的变化, 体系中 Sn的活度系数变化情况。可以看到, 在 Sn含量相同时, 随着 Ce含量的增加 Sn的活度系数是显著变小的, 说明 Ce与 Sn作用明显抑制了"自由"Sn的量; 同时让 Sn的含量在 95. 5% ~99. 5%附近发生微小的变化时, 不同含量 Sn的活度系数在 Ce的某一浓度范围附近相交, 此时 Sn的活度系数与 Sn的含量无关; 在 Sn-Cu-Ce系中这个浓度在 Ce的含量处于 0. 35%左右, 在 Sn-Ag-Ce系中这个交点浓度范围为 Ce的含量为 0. 2% ~0. 25%。

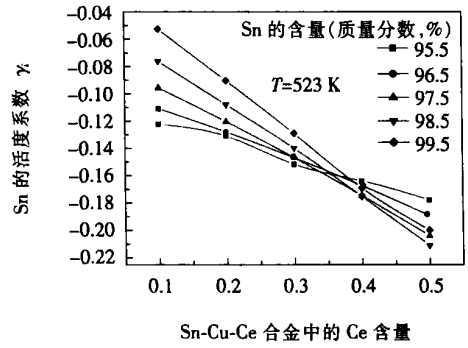

图 3　Sn-Cu-Ce系 Sn活度系数与 Ce含量的关系

Fig. 3　Relationship of activity coefficient of Sn and content of Ce in Sn-Cu-Ce system

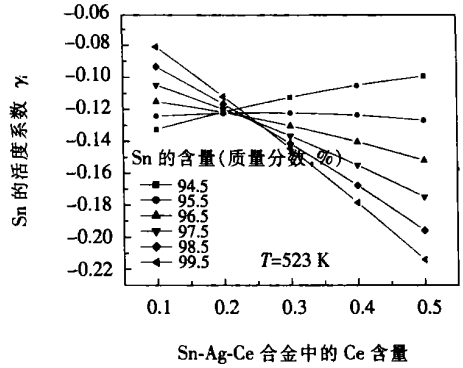

图 4　Sn-Ag-Ce系 Sn活度系数与 Ce含量的关系

Fig. 4　Relationship of activity coefficient of Sn and content of Ce in Sn-Ag-Ce system

图 5所示的是在 1 100 K(因为 Ag95-Sn5合金的熔点为 1 073 K左右)时以 Ag为溶剂的 Ag-Sn-Ce系随体系中 Ce含量变化, 体系中 Ag的活度系数变化情况。图 6所示的是在 1 000K时以 Cu为溶剂的 Cu-Sn-Ce系随体系中 Ce含量变化, 体系中 Cu的活度系数变化情况。由图也可以看到, 在 Ag、Cu含量

分别不变时，Ag、Cu的活度系数也是显著变小的，在Ag、Cu含量分别在 95.5% ~98.5%变化时，不同含量 Ag、Cu的活度系数也在 Ce的某一浓度范围附近相交，Ag-Sn-Ce系中相交点为 Ce的含量为 0.6%左右，Cu-Sn-Ce 系中相交点为 Ce 的含量为 0.5%左右。

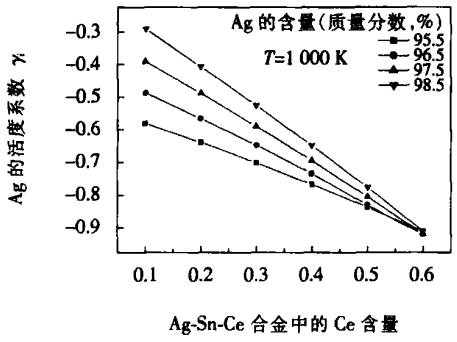

图 5 Ag-Sn-Ce系 Ag活度系数与 Ce含量的关系

Fig. 5 Relationship of activity coefficient of Ag and content of Ce in Ag-Sn-Ce system

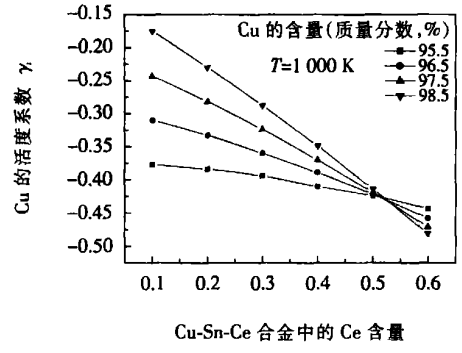

图 6 Cu-Sn-Ce系 Cu活度系数与 Ce含量的关系

Fig. 6 Relationship of activity coefficient of Cu and content of Ce in Cu-Sn-Ce system

综合分析图 3~图 6的结果可以看出，在 Sn-Ag-Ce、Sn-Cu-Ce中，当 Ce的含量处于 0.2% ~0.35%时，Sn的活度系数已经与 Sn的含量无关；在 Ag-Sn-Ce中当 Ce的含量约为 0.6%时，Ag的活度系数已经与 Ag的含量无关；在 Cu-Sn-Ce中当 Ce的含量约为 0.5%时，Cu的活度系数已经与 Cu的含量无关。

在此可以做一个这样的假设，在 Sn-Ag-Cu-Ce的体系中存在着不均匀现象，某些地方 Sn偏析，某些地方 Ag偏析、还有某些地方 Cu偏析，依次对应于以 Sn为溶剂、以 Ag为溶剂、以 Cu为溶剂的情况，这些情况在实际的钎料生产中也是可能存在的。根据文献[6]中“等活度系数”的概念可知，当 Ce的含量达到 0.6%左右时 Sn、Ag、Cu都已出现了各自的等活度系数现象，也就是说，在 Sn-Ag-Cu-Ce合金体系中，Ce的最大加入量(最大存在量)约为 0.6%左右。

在实际的 Sn-Ag-Cu-Ce钎料成分设计时，应当把 Ce的有效含量控制在 0.05%左右，生产时，Ce的加入量不要超过 0.6%，以减少不必要的浪费，节省人力和物力。

3 结 论

利用周模型对无铅钎料 Sn-Ag-Cu-Ce四元合金体系进行了热力学计算预测，发现当 Ce的含量达到 0.05%时，体系达到化学平衡状态。说明在 Sn-Ag-Cu合金体系中，Ce的最佳含量为 0.05%左右；当 Ce的含量达到 0.6%左右时，Sn、Ag、Cu分别都已出现等活度系数现象，说明在 Sn-Ag-Cu合金体系中，Ce的最大加入量不应超过 0.6%。

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作者简介：薛松柏，男，1956年 4月出生，工学博士，教授，博士生导师。主要研究方向为新型焊接材料与工艺、微电子焊接，发表论文 60余篇。

Email：xuesb@nuaa.edu.cn

MAIN TOPICS, ABSTRACTS & KEY WORDS

Study on drawing force of flux cored wire LI Zhuo xin, JIANG Jian-min, HUANG Fu-ping, TANG Chun-tian (Welding Insititute, Beijing University of Technology, Beijing 100022, China). p1-4

Abstract: By analyzing the drawing stress of flux-cored wire (FCW), a new model for the calculation of the drawing force for FCW was formed. The factors that influence drawing force were also discussed. Mechanical properties of the steel strip, deformation of flux-cored wire, the hole size of dies, drawing speed, friction and lubrication conditions had obvious effects on the drawing stress. The drawing stress increased with the speed rise at low speed. At moderate speed the drawing stress decreased. The drawing stress did not change when the speed increase further.

Key words: flux-cored wire; drawing force; math model

Research on shape from shading in welding pool topsile height acquisition LI Lai-ping, LIN Tao, CHEN Shan-ben (Welding Engineering Institute, Shanghai Jiaotong University, Shanghai 200030, China). p5-8

Abstract: The general reflectance map equation proposed by Lee and Kuo was introduced and the resolution method was improved. The surface height was calculated from its synthetic image under real imaging characteristics and compared with Lee-Kuo. Based on the imaging characteristics of welding process, reflectance model of welding pool was set up. The surface height of welding pool was calculated from its image.

Key words: shape from shading; general reflectance map equation; imaging characteristics of welding process; reflectance model of welding pool; surface height of welding pool

Effect of ball milling condition on formation of Sn-0.7Cu alloy LIU Xia, XIA Zhi-dong, LEI Yong-ping, SHI Yao-wu (The Key Laboratory of Advanced Functional Material, Ministry of Education, China, Beijing University of Technology, Beijing 100022, China). p9-12

Abstract: The mixed Sn and Cu powder was milled by mechanical ball milling. The milled powders were analyzed by X-ray diffraction, differential thermal analyzer and scanning electron microscope. The effect of ball milling conditions on the formation of Sn-0.7Cu alloy was investigated. The results showed that voltage, ball-to-powder mass ratio and milling time affect the formation of Sn-0.7Cu alloy significantly. The mechanism of mechanical alloying Sn-Cu was that the mechanically-induced atom diffusion drives substitutional solid solution and interface dissolution as a result of which Cu_6Sn_5 was formed.

Key words: mechanical alloying; Sn-0.7Cu alloy; ball milling condition; reactive mechanism

Prediction of tensile properties of welded joint with mechanical heterogeneity ZHU Liang, CHEN Jian-hong (State Key Lab of Gansu New Non-ferrous Metal Materials, Lanzhou University of Technology, Lanzhou 730050, China). p13-16, 26

Abstract: An approach to evaluate the strength of welded joints with mechanical heterogeneity was proposed. The hardness measurement and tensile testing were performed on the specimens, which were cut from the undermatching joints of pipeline steel. According to the relation between hardness and strength for metals, methods were developed to determine the yield stress, true stress at maximum load and work hardening component from the hardness measurement. Thereby the local material properties across welded joints could be obtained from the hardness distribution on them. Finite element model of welded joints was constructed to calculate their yield strengths and tensile strengths. In this model, weld and heat affected zone were divided into small partitions to be given the special material properties. Comparison between the results from finite element analysis and tensile test showed that with this model, the strength of welded joints with mechanical heterogeneity could be predicted with an accuracy of ±40 MPa.

Key words: strength of welded joint; mechanical heterogeneity; finite element analysis; hardness

Weld width prediction based on artificial neural network YU Xiu-ping[1], SUN Hua[2], ZHAO Xi-ren[1], Alexandre Gavrilov[3] (1. School of Automation, Harbin Engineering University, Harbin 150001, China; 2. Harbin University of Science and Technology, Harbin 150080, China; 3. Bauman Moscow State Technical University, Moscow 107005, Russia). p17-19, 45

Abstract: The method of weld width prediction based on artificial neural network (ANN) was studied, and the weld quality could be estimated by it. Problems and questions relating to the welding process monitoring system were considered, such as picking up the characteristics of arc welding, welding quality prediction and the application of ANN. The welding quality monitor system based on ANN was designed and its composing structure was given. The weld quality prediction model based artificial neural network is build up, and simulation is given. The results of simulation showed that the ANN model could predict the weld width, and the welding quality monitor system based on ANN was efficient.

Key words: artificial neural networks; weld quality prediction system; weld width prediction

Thermodynamic calculation and evaluation for Sn-Ag-Cu-Ce lead-free solder alloy system XUE Song-bai[1], CHEN Yan[2], LÜ Xiao-

chun[2] (1. Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China; 2. Harbin Welding Institute, Harbin 150080, China). p20-22

Abstract: Thermodynamic calculation and evaluation for Sn-Ag-Cu-Ce lead-free solder alloy system were carried out by means of Chou model. The results showed that chemical balance attained in the system of Sn(rest)-Ag(0.5wt%-4.5wt%)-Cu(0.5wt%-4.5wt%) when the content of Ce was over 0.05wt%. The equivalent activity coefficient phenomenon of Sn, Ag and Cu emerged in the system when the content of Ce increased to about 0.6wt%. The results will provide theoretical guidance for designing chemical constitutions of new lead-free solders.

Key words: lead-free solders; Chou model; chemical balance; equivalent activity coefficient

Realization of slow stud plunge in arc stud welding CHI Qiang[1], ZHANG Jian-xun[1], FU Ji-fei[2], ZHANG You-quan[2] (1. School of Material Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China; 2. Central Research Institute of Building and Construction, MCC Group, Beijing 100088, China). p23-26

Abstract: Stud plunge speed is one of the important parameters in arc stud welding. Through the analysis of operating principle of electromagnetic welding gun which was widely employed in engineering, it was proposed that stud welding procedure could be realized even with a slower plunge speed, however an adequate extrusion force was needed simultaneously. An arc stud welding gun based on stepping motor and its control system were developed to accomplish the slow plunge arc stud welding. A stepping motor was taken as actuating unit and screw-driven device as moving unit to furnish the adequate extrusion force for melted metal during the course of the slow plunge. It was indicated from test results that the stepping arc stud welding gun could realize the welding process of slow stud plunge. Furthermore, the result of bend test proved that the joint was fit for service.

Key words: arc stud welding; stud welding gun; stepping motor

Distortion research on projection welding of car door hinge – Part Ⅱ: residual stresses and distortions analysis of projection welding LUO Ai-hui, CHENG Guan-long, LAI Xin-min, ZHU Wen-feng (BMTC, Mechanical and Power Engineering School, Shanghai Jiaotong University, Shanghai 200030, China). p27-30

Abstract: According to the actual condition, a 2D finite element model had been built for the car door hinge and reinforced plate. Based on the result of temperature distribution by the process analysis of projection welding, the heat distortions and the distribution of residual stresses were gained by the analysis of heat stresses in the free constrain condition. Then the distortion tendency of car door hinge was analyzed in the end and coincident conclusions were gained.

Key words: projection welding; finite element analysis; welding distortion; residual stresses

Image processing and tracing data collection for welding groove laser detection LI Ming-li, LIU Zhan-min (Beijing Institute of Petrochemical Technology, Beijing 102617, China). p31-35

Abstract: Laser line reflection images of welding groove in various lighting conditions were taken. These lighting conditions were darkness and fluorescent light in the night, natural light in room and under the sun light during daytime. Experiment results show that more light disturbances existed in images taken under lighting condition than that in darkness at night. But these disturbances could be cleared off by fitting up monochromatic filter and by using suitable distubance removing methods. Information such as width and center location of the groove and the groove clearance could be obtained by optimization method of complex polygon. The accuracy of data collected could reach 0.125mm and met the needs of welding tracing.

Key words: laser detection; image processing; complex polygon optimization method; welding tracing

Development of welding computing aided process planning system for Intranet KONG Jian-shou, WU Ling-long, ZHANG Yong (Department of Material Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China). p36-40

Abstract: Through analyzing welding process planning, the system of computer welding aided process planning for Intranet was present. The system was composed of C/S and B/S mixed distributed computer architecture, in which welding process planning could be dealt with among all relating departments for enterprise. The OLE, ActiveX, ASP, Word macro and AutoCAD redevelopment technologies etc were utilized in the system developing, and the functions of welding process documents computer aided management, welded joint parameter design, welding computer process aided planning and Word documents customizing for welding process were implemented in the system. In addition, remote authorized users could share the system information by Web technology.

Key words: welding process planning; computing aided design; Intranet; architecture

Application of artificial neural network method in prediction of bend strength of welded joint XU Pei-quan[1], YANG De-xin[2], ZHAO Xiu-juan[2], LU Feng-gui[1], YAO Shun[1] (1. Welding Engineering Institute, Shanghai Jiaotong University, Shanghai 200030, China; 2. College of Material Science and Engineering, Dalian Jiaotong University, Liaoning Dalian 116028, China). p41-45

Abstract: Good WC-30Co/45 steel TIG (tungsten inert gas) welded joint could be obtained using Ni-Fe-C alloy as filler metal. However