

Russian Academy of Sciences  
Israeli Academy of Sciences and Humanities  
Russian Foundation for Basic Research  
Institute of Problems of Chemical Physics of RAS  
Institute of Metallurgy of UB RAS  
Institute of Technical Chemistry of UB RAS  
Institute of High Temperature Electrochemistry of UB RAS  
Institute of Solid State Chemistry and Mechanochemistry of SB RAS  
Ariel University Center of Samaria

**THE OPTIMIZATION OF  
COMPOSITION, STRUCTURE AND  
PROPERTIES OF METALS, OXIDES,  
COMPOSITES, NANO- AND  
AMORPHOUS MATERIALS**

**ELEVENTH  
ISRAELI-RUSSIAN BI-NATIONAL  
WORKSHOP 2012  
July 9-14**

**Chernogolovka,  
2012**

is  
on  
g  
y,  
g,  
y,  
n,  
ly  
a,  
an  
ve  
ns  
ld  
se  
on  
of  
ate  
for  
so  
-  
les  
ng  
cal  
ian

intensive mechanical activation of piston vibration, than of crucible vibration. Main part of  $V_8C_7$  inclusions has also sizes  $\leq 1$  microns in such alloy. The structure of separate large  $V_8C_7$  inclusions ( $\sim 5\mu m$ ) as a result of mechanical activation is fragmented. Prolonged LFO treatment can initiate its further dispersion.

### Conclusion

Low frequency mechanical activation of melts initiates wetting in systems Cu-VC, Al-VC and Al-WC, that allows composites producing with structure of complicated layer-volumetric strengthening. However observed chemical interaction of Al melt with  $V_8C_7$  and WC carbides leads to disappearance (disintegration) of high-melting carbides and  $Al_4C_3$  aluminium carbide synthesizing. As a rule, this compound is undesirable phase in composites due to its hygroscopic property, and formed W and V aluminides have low melting temperatures. More perspective composite alloy is Cu-VC in which chemical interaction of components does not take place.

### Acknowledgment

The research is carried out with financial support OFI Presidium UrD of RAS №11-03-18-BK basing on Cooperation agreement between UrD of RAS and University centre of Samaria (Ariel, Israel) using equipment of CUC "Ural-M".

### References

1. Samsonov G. V, Panasjuk A.D., Kozina G. K. *Wetting of refractory carbides by liquid metals // Powder metallurgy. №11 (71).1968. P.42-48.*
2. Telitsin I.I. *Device for processing of melt with low-frequency oscillations. Author Certificate. № 4136144/23-02. 1987. 3p.*

## PHASE EQUILIBRIUM IN BINARY SYSTEM Cu-Ga

V.A. Bykov, T.V. Kulikova, S.A. Petrova, K.Yu. Shunyaev

*Institute of Metallurgy of UB RAS,*

*101, Amundsen st., Ekaterinburg, Russia*

*wildrobert@gmail.com*

### Introduction

Copper-gallium alloys (Cu-Ga) are applied in the industry as diffusion-hardening solders (DHS). The low melting temperature of gallium allows using it as a liquid component at mixture with solid metal. The soldering gallium solders connects structural elements joint without preliminary heating and without application of fluxes. High power benefit at production and ecological harmlessness of operation DHS is essential advantage in comparison with classical lead solders. However, creation the gallium solders meeting high technological and performance requirements is extremely difficult problem. Long time hardening DHS and many formations of phases at high temperatures of operation limits their universal application. Now the phase diagram of the gallium-copper system is not constructed definitively. The fullest phase diagram of Cu-Ga system based on researches Weibke [1], Hume-Rothery [2], Owen and Rolands [3], Kittl and Massalski [4] is offered in work Subramanian and Laughlin [5]. Solidus and liquidus curves, solubility of gallium in copper in solid state have been first established Hume-Rothery et al. [2] in 1934. Later Hume-Rothery, Raynor and Betterton [6] have carried out more detailed investigations in the field of the concentration of gallium from 18 to 100 at.% and also have essentially changed the first variant of Cu-Ga phase diagram developed Weibke [1]. By SEM, XRD and thermal analyses in Cu-Ga system detect of eight phases:  $\beta$ ,  $\gamma_0$ ,  $\gamma_1$ ,  $\gamma_2$ ,  $\gamma_3$ ,  $\zeta'$ ,  $\zeta$ ,  $\theta$  with wide solubility range. In the same works, for the first time it has been established, that high-temperature phase  $\gamma_0$  in the concentration region of 29-42.6 at. % Ga is available low-temperature modifications ( $\gamma_1$ ,  $\gamma_2$ ,  $\gamma_3$ ) with  $\gamma$ -brass-like type structure and a line of transition from disorder in the order state. Kittl and Massalski [4] have added phase diagram of Cu-Ga, in the region related to the phase  $\zeta$ . Zang, Liu, Liang, etc [7] in 2007 have carried out detailed research of the phase relations and the crystal structure of the

phases in the Cu-Ga system and founded that the phase  $\zeta$  has  $A3$  ( $P6_3/mmc$ ) structure, and the  $CuGa_2$  was an intermetallic compound without solubility range as suggested Betterton and Hume-Rothery [6]. According to works [7,8] in low-temperature region single-phase intermetallic compounds of Cu-Ga cannot be easily synthesized under equilibrium conditions due to the occurrence of a series of peritectic reactions. Single-phases copper-gallium alloys can be obtained by methods of powder metallurgy and an arc melting, but thus the time costs connected with annealing of samples extremely increase. So for reception of a homogeneous phase  $\gamma_1$  (66 wt. % Cu) a duration annealing Cu-Ga powders at 400 °C makes 100 hours [8].

The aim of this work is to study the formation and decomposition phases in the Cu-Ga in an inert atmosphere at a heating and cooling.

### Experimental procedure

For the study we prepared samples containing 20.5, 26, 32, 34, 38, 68% of gallium (here and hereinafter referred to article alloy composition is given in weight percent). The Cu-Ga alloys were prepared from pure gallium (99.999 %) and copper (99.95 %) induced by double arc melting in a high-purity helium atmosphere.

Thermal analysis techniques were used to investigate the behaviors of Cu-Ga alloys during the heating and cooling under the argon atmosphere in the range from room temperature up to 1300 K at a heating (cooling) rate of 10 K·min<sup>-1</sup>. The experiments were carried out on the NETZSCH STA 409 Luxx system. For calibration the temperature and the enthalpy of reaction were used Sn (99.999 %), Bi (99.999 %), Al (99.99 %), Ag (99.999 %) and Au (99.999 %) under same experimental conditions. The onset temperature of heat peaks was taken as the transformation temperature. The liquidus was determined from the onset temperature of cool peaks.

The XRD patterns were obtained using a D8 ADVANCE X-ray diffractometer with  $CuK\alpha$  radiation,  $\beta$ -filter and super speed VANTEC-1 detector. Analysis of phase composition and crystallographic characteristics calculations were performed using software DIFFRAC<sup>plus</sup> [9,10] and database of the International Centre for Diffraction Data PDF4+[11].

### Result and Discussion

Results of the XRD characterization of selected samples are presented in Table 1.

Table 1 The qualitative and semiquantitative phase composition of the samples and unit cell parameters of the coexisting phases

Sample	Phase composition	Amount, wt. %	Unit cell parameters, nm	
Cu-34%Ga	$\gamma_2(Cu_9Ga_4)$	100	0.87320	
Cu-38%Ga	$\gamma_2(Cu_9Ga_4)$	80	0.87218	
	$\gamma_3(Cu_9Ga_4)$	20	0.86731	
Cu-32%Ga	$\gamma_2(Cu_9Ga_4)$	82	0.87324	
	$\gamma_1(Cu_9Ga_4)$	18	0.87466	
Cu-66.7%Ga	$CuGa_2$	98	0.28289	0.58275
	X	2	-	
Cu-26%Ga	$\gamma_1(Cu_9Ga_4)$	29	0.87582	
	$Cu_{0.76}Ga_{0.24}$	65	0.26191	0.42689
	$Cu_{0.85}Ga_{0.15}$	6	3.6950	
Cu-20.5%Ga	$Cu_{0.76}Ga_{0.24}$	6	0.26124	0.42536
	$Cu_{0.85}Ga_{0.15}$	94	0.36718	

According to the calorimetric studies most of the alloys have the temperature of phase transitions in good agreement with the phase diagram, except for the sample Cu-26%Ga. During heating in the alloy Cu-26%Ga occurs seven endothermic transitions (see Fig.1). Six endothermic reactions are in good agreement with these transformations on the equilibrium phase diagram of Cu-Ga with the exception of the thermal effect at 588.7 K.

For determining the sequence of phase transitions in the sample Cu-26%Ga in the range 475-720 K was carried out high X-ray studies

(Diffractometer D8 ADVANCE, equipped with a camera Anton Paar XRK900). Heating of the samples was performed at 0.2 K·s<sup>-1</sup>.

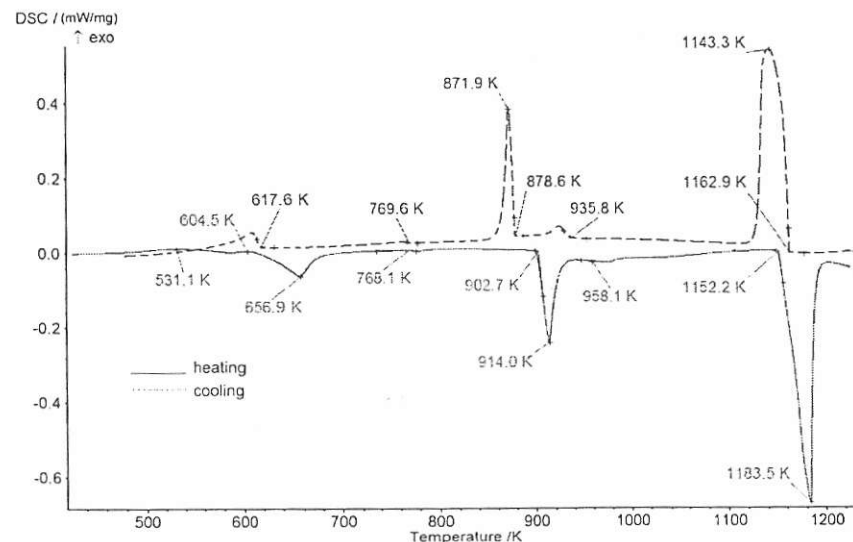


Fig.1. DSC curves of Cu-26%Ga alloy

The isothermal delay time on imagery of the diffraction pattern in the range of 475-720 K was 250 s with a step of 5 K (exposure at the point 20 s). Measurements were carried out in normal atmosphere at  $\lg PO_2 = -15$ , which was achieved by using a system of "oxygen pump-probe" based on yttrium-zircon ceramic [5]. Traces of oxidation of the sample, as well as the formation of new phases during heating and after the experiment were not found. In all phase transitions take part phase I -  $Cu_9Ga_4$ , II -  $Cu_{0.85}Ga_{0.15}$  and III -  $Cu_{0.76}Ga_{0.24}$ . Below 530 K, the amount of phase II is unchanged while the amount of phases I and III slightly are increased and decreased respectively. Growth of the amount of phases I and II due to phase III is observed in the range 530 - 640 K. The amount of phase III above 640 K begins to increase due to phase II. The amount of phase I while slowly decreasing.

## Conclusion

The transformation temperatures and enthalpy of transition of the solid solution phases of  $Cu_{0.85}Ga_{0.15}$ ,  $\beta$  and  $\zeta$ , the solution compounds of  $Cu_9Ga_4$  ( $\gamma_1$ ,  $\gamma_2$ ,  $\gamma_3$ ), stoichiometric compounds  $Cu_{0.76}Ga_{0.24}$  ( $\zeta'$ ) and  $CuGa_2$  were determined for samples containing 20.5, 26, 32, 34, 38, 68 wt. % of gallium by differential scanning calorimetry.

According to the calorimetric studies most of the alloys have the temperature of phase transitions in good agreement with the phase diagram, except for the sample Cu-26%Ga at 531.1 K. Thermal effect at a temperature 531.1 K can be attributed to the cooperative process of transformation of the three phases  $\gamma_1(Cu_9Ga_4)$ ,  $Cu_{0.85}Ga_{0.15}$  and  $Cu_{0.76}Ga_{0.24}$ , where the quantity and intensity of change is determined by the solid solution based on copper.

## Acknowledgment

Authors are grateful for support to the Russian Foundation for Basic Research (RFBR grant 10-03-96037-r-ural-a), Presidium of RAS (research program 12-P-3-1032), Grant of the President of the Russian Federation (MK-6581.2012.3) and Ministry of Education and Science Russian Federation (Federal Program GK 16.552.11.7017). This work was carried out on the scientific instruments granted by Collective Equipment Center "Ural-M".

## References

1. F. Weibke // *Z. Anorg. Chem.* 1934, V.220, p.293
2. W. Hume-Rothery, G.W. Mabbott, K.M.C. Evans // *Philos. Trans. R. Soc. A* 1934, V.233, p.1
3. E.A. Owen, V.W. Rowlands // *J. Inst. Met.* 1940, V.66, p.361
4. J.E. Kittl, T.B. Massalski // *J. Inst. Met.* 1964-65, V.93, p.182
5. P.R. Subramanian, D.E. Laughlin // *Binary Alloy Phase Diagrams* (2nd ed.), V. 2 ASM International. 1990, p. 1410
6. J.O. Betterton, W. Hume-Rothery // *J. Inst. Met.* 1951-52, V.80, p.459
7. Y. Zhang, J.-B. Li, J.K. Liang, Q. Zhang, B.J. Sun, Y.G. Xiao, G.H. Rao // *J. Alloys Compounds* 2007, V.438, p.158
8. O.I. Tikhomirova, M.V. Pikunov, I.D. Tochenova, I.P. Izotova, *Mater. Sci.* 1974, V.12, p.355

9. *DIFFRACPlus: Eva Bruker AXS GmbH, Ostliche. Rheinbruckenstraße 50, D-76187 (Karlsruhe, Germany, 2008)*
10. *DIFFRACPlus: TOPAS Bruker AXS GmbH, Ostliche. Rheinbruckenstraße 50, D-76187 (Karlsruhe, Germany, 2008)*
11. *Powder Diffraction File PDF4+ ICDD (Release 2009)*

## FLUORESCENCE QUENCHING OF N-ARYL-3-AMINOPROPIONIC ACIDS BY COPPER IONS(II)

**E. Dedyukhina, N. Pechishcheva, K. Shunyaev, A. Belozero**  
*Institute of Metallurgy of UB RAS, Ekaterinburg, Russian Federation*  
*dedyukhina@gmail.com*

### Introduction

N-aryl-3-aminopropionic acids (AAPA) are water-soluble compounds, which absorb ultraviolet light and have fluorescent properties [1].

N,N-di(2-carboxyethyl)aniline (**I**), N,N-di(2-carboxyethyl)-p-anisidine (**II**) and N-(2-carboxyethyl)-o-aminobenzoic acid (**III**) are representatives of the classes of AAPA (fig. 1).

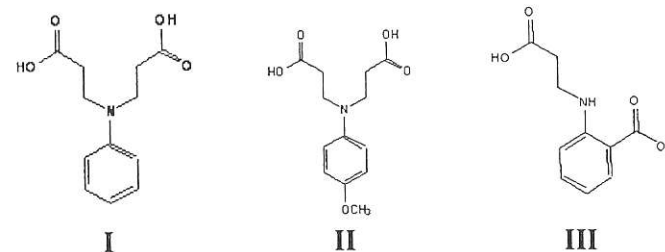


Fig. 1. Compounds of the class of AAPA

The high selectivity AAPA towards Cu(II) ions has been shown earlier [2]. Fluorescence of AAPA was found to be quenched by these ions. So AAPA can be used as analytical reagents for the fluorometric determination of Cu(II) ions in drinking and waste water [1]. But mechanism of the quenching has not been studied.

Fluorescence quenching refers to any process that decreases the fluorescence intensity of a sample [3]. A variety of molecular interactions can result in quenching, including excited-state reactions, molecular rearrangements, energy transfer, ground-state complex formation and collisional quenching. Quenching resulting from collisional encounters between the fluorophor and quencher is called collisional or dynamic quenching. In static quenching a complex is