

INTERACTIONS OF Cu-SUBSTRATES WITH TITANIUM-ALLOYED Sn-Zn SOLDERS

D. Soares, J. Barbosa and C. Vilarinho

University of Minho, Mechanical Engineering Department,
Campus de Azurém, 4810-058 Guimarães, Portugal

(Received 12 June 2006, accepted 15 September 2006)

Abstract

The interactions of copper substrate with titanium-alloyed Sn-Zn eutectic solders have been studied. Two series of experiments have been performed. The first one consisted in differential thermal analyses of Sn-Zn nearly eutectic alloys containing from 1.3 to 2.2 wt. % Ti.

Diffusion couples consisted of Cu-wires and Sn-Zn-Ti liquid solders, produced at 250 and 275 °C have been prepared in the second series. The contact times were up to 3600 s. The contact zones have been characterized by optical and scanning electron microscope. Two layers have been found along the interfaces solid/liquid. The first and the second layers are identical, respectively, with γ and ϵ phases of the Cu-Zn system. No changes of the chemical compositions were detected for the tested temperatures and reaction times.

Continuous parabolic growth of the total diffusion zone thickness with the time of diffusion is observed. The growth is due mainly to one the formed layers (γ) while the thickness of the ϵ -phase layer, stays almost constant for all tested diffusion times and temperatures.

Keywords: lead-free solders, diffusion couples, Cu/(Sn-Zn-Ti) interactions

Corresponding author: dsoares@dem.uminho.pt

1. Introduction

Lead-containing solders currently used in microelectronics are under way to be replaced by lead-free alloys, due to environmental and health concerns. Various chemical, physical and mechanical properties of the candidate-solder systems, as well as economic considerations, should be taken into account in order to design the prospective materials. They are expected to be multicomponent alloys because the most common binary candidate-solders (Sn-Zn base alloys being one of them) do not satisfy some technological parameters, as the working temperature for example.

The phase equilibria in the Sn-Zn system are expressed by a simple eutectic phase diagram, so that at 198,5 °C and 8,8 at.% Zn [1], two phases (Zn and Sn) crystallize from the liquid. Thermodynamic optimizations of the system have been done by Lee [2], Ohtani et al. [3], as well as by Fries and Lukas [4]. According to Mikula [5] solders based on this system are prospective as substitutes of the lead-containing alloys, because both elements (Sn and Zn) are capable of reacting with the copper (the most used substrate) forming a sequence of intermediate phases. The beneficial influence of Zn on the microstructure of eutectic Ag-Sn alloys has been already observed, as its presence leads to the refinement of particles precipitated during the crystallization, thus improving the mechanical properties [6] that are very important for the reliability of the Ohm contacts [7-10]. Moreover, zinc is a cheap and abundant material.

Disadvantage of zinc application in solders are, firstly, its feeble corrosion resistance and, secondly, its relatively bad wettability. The chemical affinity between oxygen and zinc is large (the standard Gibbs energy of formation of ZnO is $-320 \text{ kJ}\cdot\text{mol}^{-1}$ [11]) so that, even low oxygen pollution leads to the formation of zinc oxide. Thus, Wood and Nimmo [12] recommend to work in inert atmosphere while soldering, and to alloy zinc-containing solders with other elements in order to modify the standard Gibbs energy of formation of ZnO.

Besides, there are indications that titanium alloying improves the wettability and some mechanical properties of these materials [13-16]. With such purposes, some phase diagrams constituted by low-melting elements generally taking part in lead-free solders (Sn, Bi, Zn, In), and titanium have recently been studied [17-29].

The above discussion reveals the need of further investigation of alloyed tin-zinc base solders. Thus, the main purpose of the present work is to study the interactions of copper substrate with titanium-alloyed Sn-Zn eutectic solders.

2. Experimental

Two series of experiments have been performed. The first one consisted in differential thermal analyses of Sn-Zn nearly eutectic alloys containing from 1.3 to 2.2 wt. % Ti. The alloys submitted to differential thermal analyses (Differential Scanning Calorimeter TA 2960 Instruments has been used.) have been synthesized preliminary. For this purpose, very pure (5N) titanium (purified by chemical gas-transport reaction), shots of Sn (4N) and Zn (4N) have been weighed, sealed under vacuum in quartz tubes and annealed for 70 days at 600 °C. The compositions of the alloys are situated in the vicinity of the Sn-Zn eutectic point (samples N° 1 to 4, Table 1). As one can see, they are alloyed with up to 2.2 wt. % (5 at. %) Ti.

One cycle (heating-cooling) has been performed with specimen No 1, and three consecutive cycles with heating and cooling rates of 10, 5 and 2 deg.min⁻¹ have been carried out with specimens No 2-4. Each alloy has been heated up to 430 °C in the first run, while in the second and third run the maximal heating temperature was 225 °C. Thermo-gravimetric and differential thermo-gravimetric analyses carried on simultaneously, but no meaningful mass losses have been registered.

In the second series of experiments, the reactions between the liquid solder and a pure copper substrate have been investigated. For these experiments other samples have been prepared (Table 1, nos. 5 and 6). The large difference between the melting points and volatilities of zinc, from one side, and of titanium and tin, on the other side, makes difficult the synthesis of the pertinent ternary alloys. Thus, we have manufactured a titanium crucible from bulk titanium rode with diameter of 32 mm. It was tightly closed by titanium screw, thus preventing zinc evaporation. Titanium turnings together with zinc and tin pieces have been sealed into the crucible, and thereafter heated until 1500 °C in induction furnace. In this manner two titanium-containing Sn-Zn

master-alloys have been obtained. The chemical compositions of these specimens have been determined by calibrated Philips X-Unique II X-ray spectrometer apparatus. They have been cut in pieces in order to be used as liquid end-members of the diffusion couple experiments intended for physical modeling of the interactions between copper substrate and titanium alloyed Sn-Zn solders.

Table 1. Melting ranges and chemical compositions (wt. %) of the specimens studied in this work, determined by differential scanning calorimetry and by Fluorescent X-ray analyses, respectively. n.a. - not appropriate.

Sample N ^o	Sn	Zn	Ti	Melting range (°C)
1	91.2	8.8	0	198-213
2	90.0	8.7	1.3	198-216
3	89.6	8.6	1.8	197-216
4	89.2	8.6	2.2	197-218
5 ^A	94.8	5.1	0.1	n.a.
6 ^A	88.1	11.0	0.9	n.a.

A - Specimens nos. 5 and 6 are diffusion couples. The compositions of the liquid end-members of these diffusion couples are shown in Table 1.

The soldering reaction has been simulated by immersing pieces of Cu-wire into molten solder alloys. For this purpose, freshly cleaned (mechanically and with alcohol) pieces of Cu-wire (diameter 1.5 mm) have been submerged into the respective liquid alloy for 5 different contact time periods. Two measurements have been done for each reaction time. Experiments have been done under argon flow. Temperature has been automatically controlled in such a way that its variation (due to the merging of cold Cu-wire into hot bath) was no more than 2 °C. A resistance furnace containing a specially designed graphite crucible was used for this purpose.

The experiments have been conducted at two temperatures: 250±2 and 275±2 °C (Table 2). After rapid cooling, samples are cut (normally to the length of the Cu-wire), and polished. The microstructures of the intermetallic

layers grown during these experiments have been characterized by means of optical and electronic microscopy. Energy Dispersive Spectrometry and Scanning Electron Microscopy (SEM/EDS) were used to determine the chemical compositions of the formed intermetallic compounds.

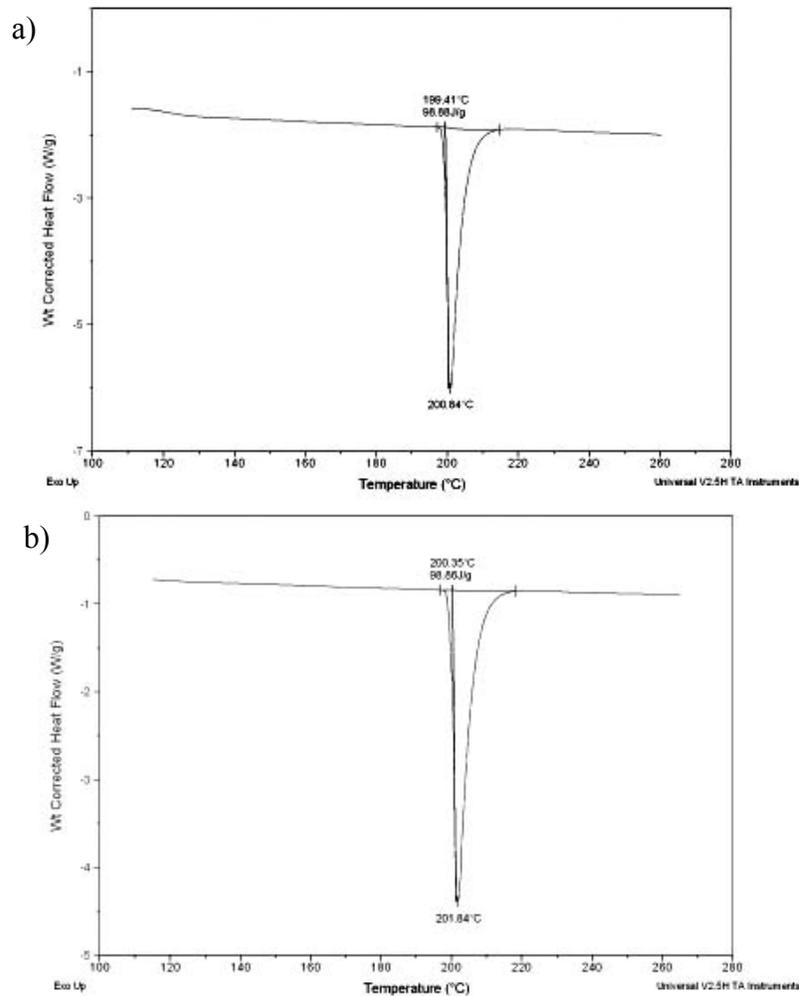


Fig. 1. Differential scanning calorimetry curves, near to the melting ranges, for specimens with the lower and higher Ti contents, sample N°1 a) and sample N° 4 b), with the heating rate of 10 deg.min⁻¹.

Table 2. Chemical compositions (wt. %) of the phases obtained in the diffusion zones of specimens N° 5 and N° 6 by SEM/EDS analyses. Phase - identified by SEM/EDS

Sample N°	T, °C	Layer	Sn wt. %	Zn wt. %	Cu wt. %	Ti wt. %	Phase
5	250	II*	-	-	-	-	-
		I	0.0	69,2	30,8	0.0	γ -(Cu-Zn)
6	250	II	0.0	80,7	19,3	0.0	ϵ -(Cu-Zn)
		I	0.0	65,6	34,4	0.0	γ -(Cu-Zn)
6	275	II	1,9	79,9	18,1	0.0	ϵ -(Cu-Zn)
		I	0.0	69,9	30,2	0.0	γ -(Cu-Zn)

* - the layer has not been analyzed

3.Results and Discussion

In the discussion below the notion of "melting range" is used. The latter is defined as the approximate temperature intervals between the beginning and the end of the corresponding melting peaks. Generally, this interval depends on the heating rate. In the present study it is referred to measurements done with a heating rate of 10 deg.min⁻¹. The melting ranges of the samples, obtained by differential scanning calorimetry, are shown in Table 1. One can see that all melting ranges are approximately equal.

As mentioned above, rates of 10, 5 and 2 deg.min⁻¹ have been applied. The use of various heating rates allowed the extrapolation to a hypothetical zero-velocity heating rate (Fig. 2). Numbers in italic show the melting point of the corresponding alloys obtained by extrapolation of the linear fit of the experimental data for every specimen separately. As one can see there is not a clear trend towards lowering the binary eutectic melting point by titanium additions for the analyzed samples (when compared with sample N°1). This is in agreement with the result reported by Vassilev et al. [28] for similar conditions.

Generally, when the peak temperatures have to be determined, they are recorded at the point, where the projection of a peak crosses with the projection of the pertinent baseline. However, for practical assessment of the

candidate-solders the so-called "temperature of total melting" is useful as well. This notion was introduced by Kuck [29]. The measurements are done by recording the liquidus temperature at the point where the DSC signal returns to the baseline (i.e. the upper limit of a peak). Recently, Korhonen and Kivilahti [30] and Vassilev et al. [31] have used such an approach in their studies of the candidate-solder Ag-Sn-In system. The total melting temperatures of the analyzed specimens coincide, in reality, with the upper limits of the melting ranges shown in Table 1.

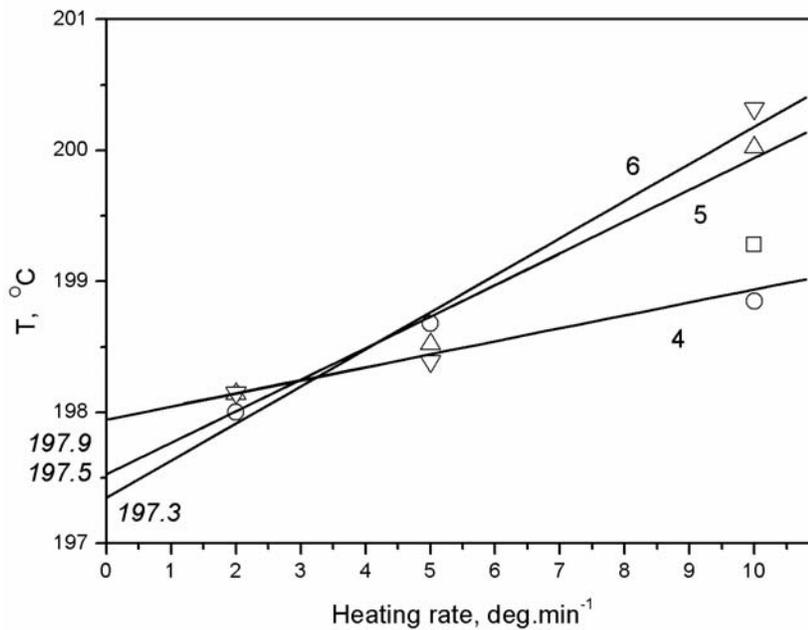


Fig. 2. Dependence of the melting temperature on the heating rate for specimens with various titanium content. The curves 4, 5 and 6 (for samples N° 2 (Δ), 3 (O) and 4 (∇), respectively) represent linear regressions of the data for the corresponding specimens.

The diffusion zones formed along the interface between the Cu-wires and the titanium-alloyed liquid solders have been studied by scanning electron microscopy. The microstructure and chemical compositions of the phases grown are presented in Fig. 3 and Table 2, respectively.

For both tested alloys, with different Ti contents (No. 5 and 6, Tables 1 and 2), the diffusion zones are constituted by two phases. The first layer (I), on the copper side, can be associated with the γ -(Cu-Zn) phase and the second layer (II) with the ϵ -(Cu-Zn) phase. Similar sequence of the phases has been detected in previous works with Sn-Zn based solder alloys [32].

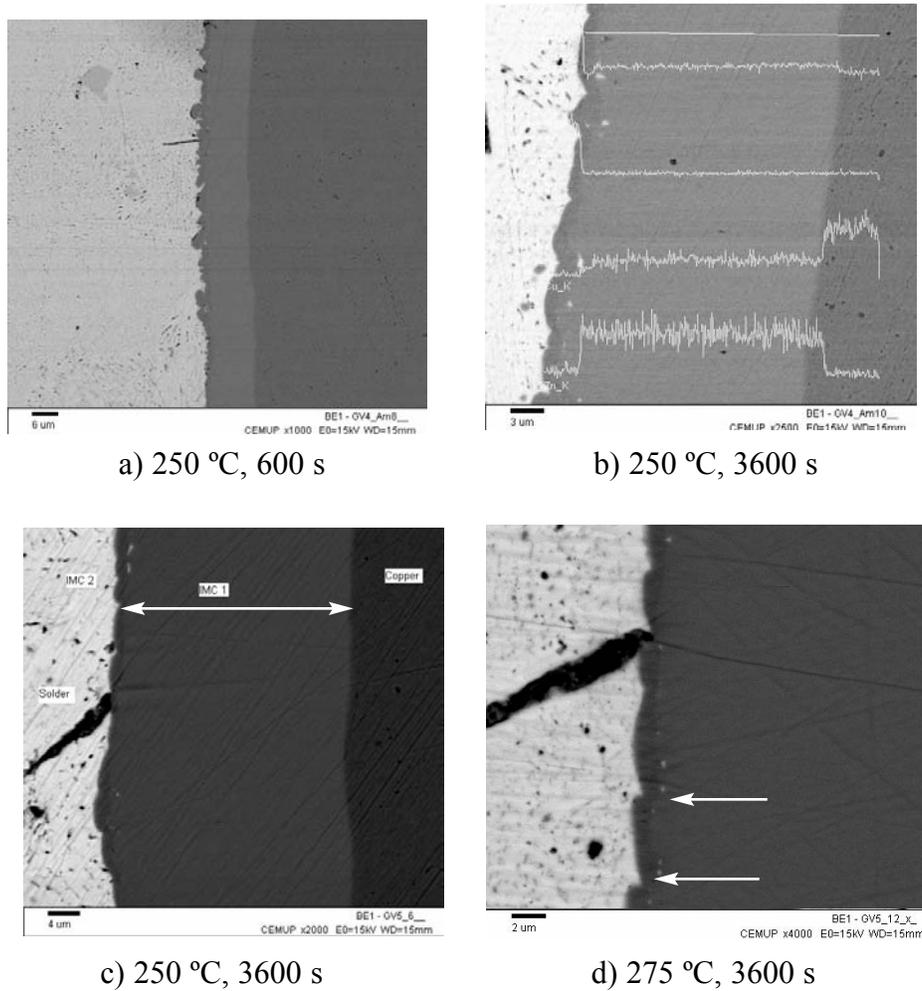


Fig. 3. Microstructure of the solder/substrate interface obtained for samples N°4 a-b) and N°5 c-d)

The layer I is planar in both cases. The second layer (II) develops as an irregular layer (scallop shape) in the interconnection with the liquid phase. This behaviour can be associated with the laterally growth of the initial grains, at the solid/liquid interface, with disappearing grooves. The morphology of the layers II changes with the reaction time, from a rounded scallop shape to an almost continuous layer (Fig. 3 a) and 3d)).

Some small volumes of the solder alloy are distinguished between the first and second layers. Fig. 3d shows a detail of the zone between the IML with the non-contact zones (white zones pointed by the arrows) between the two IMCs.

No titanium was detected in these two phases for the tested temperatures and times of contact. This might mean that the presence of titanium in the solder does not change the local chemical equilibrium, at the solder/substrate interface. A similar result was obtained with tin. It seems that only copper and zinc are relevant for the interface definition.

The second layer (II) has not been found up in all the samples of the experiments conducted at 250 °C with the alloy N° 5. This might be due to the small size of the layer, making the detection difficult by SEM analysis. However, as seen in Fig. 3b, for longer contact times the presence of the second layer can be distinguished by the differences in the chemical composition profile through the contact zone.

The presence of tin at the interface was only detected in one sample (N° 6) annealed at 275 °C. Because of the method used for chemical analysis (SEM/EDS) there might be some lateral effects, leading to difficulties for the revealing of tin in the layers II. In any case, the tin contents should be very feeble. No changes were detected in the layers' chemical compositions for the tested temperatures and reaction times.

The interface thicknesses, obtained with alloys N° 5 and 6 for the tested times and temperatures of diffusion, are presented in Fig. 4a) and 4b). No major differences were detected for both diffusion couples, with different titanium contents of the liquid end-members. As expected, there is a small increase in the total thickness of the diffusion layers (Fig. 4b) for higher temperatures of diffusion.

The growth kinetics of the diffusion layers observed in alloy N° 6, at 250 and 275 °C, for 600 to 3600 s reaction time, is presented in Fig. 4c) and 4d).

The thickness of the layers II is almost constant with the contact time. In opposite, the first layer exhibits a continuous growth with the solder/substrate reaction time.

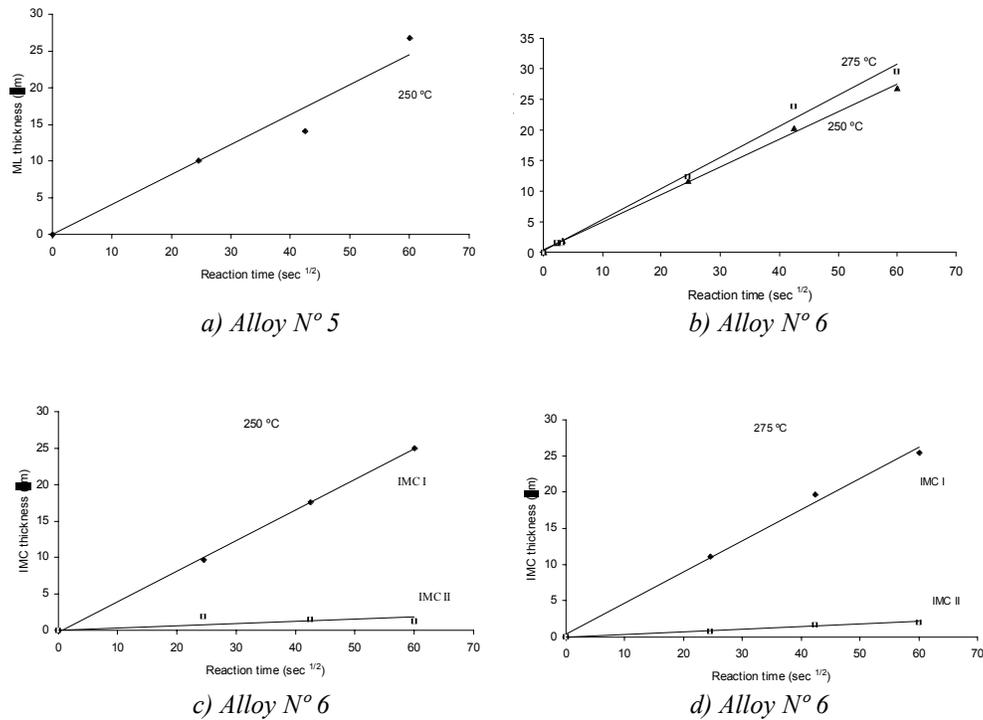


Fig. 4 - Solder/substrate IML total thickness (figures a and b), and partial IMCs thickness for the 250 and 275 °C diffusion temperatures (figures c and d).

4. Conclusions

Interfaces solder/substrate formed between Cu-wires and Sn-Zn-Ti liquid solders have been produced and characterized. It has been found that two layers constitute these interfaces. The first and the second layers are identical, respectively, with γ and ϵ phases of the Cu-Zn system. No changes were

detected in their chemical compositions for the tested temperatures and reaction times.

Consequently, a small addition of Ti, in the solder, does not change the interface local equilibrium established by the copper/zinc interaction.

Continuous parabolic growth of the total diffusion zone thickness with the time of diffusion is observed. The growth is due to one the formed layers (γ) while the thickness of the ϵ -phase layer, stays almost constant for all tested diffusion times and temperatures.

Acknowledgments

This work is related to the European action for development of lead-free solders COST 531. Thanks are due to Prof. G.P. Vassilev (University of Sofia, Bulgaria) for precious advices and discussions.

References

1. T. Massalski, CD ROM: Binary Alloy Phase Diagrams, *ASM International*, OH, USA, 1996.
2. B.J. Lee, *Calphad.*, 29 (4) (1996) 471.
3. Ohtani, H., M. Miyashita, K. Ishida, J. *Japan Inst. Metals*, 63/6 (1999) 685.
4. COST 507, Definition of thermochemical and thermophysical properties to provide a database for the development of new light alloys, Vol. 2, 1998, European Commission, Belgium.
5. A. Mikula, in: Yazawa International Symposium, Metallurgical and Materials Processing: Principles and Technologies. Vol. 1: Materials Processing Fundamentals and New Technologies. Edited by F. Kongoli, K. Itagaki, C. Yamauchi and H.Y. Sohn, TMS The Minerals, Metals & Materials Society) 2003.
6. M. McCormack, S. Jin, *J. Electron. Mater.*, 23(7) (1994) 635.
7. H. Mavoori, J. Chin, S. Vaynman, B. Moran, L. Keep, M. Fine, *J. Electron. Mater.*, 26(7) (1997) 783.
8. V. Igoshev, J. Kleiman, D. Shanguan, C. Lock, S. Wong, M. Wiseman, *J. Electron. Mater.*, 27(12) (1998) 1367.

9. Y. Kariya, M. Otsuka, *J. Electron. Mater.*, 27(7) (1998) 866.
10. T. Reinikainen and J.K.Kivilahti, *Metallurgical and Mater. Transactions*, 30A(1)(1999) 123.
11. I. Barin, *Thermochemical Data of Pure Substances*, VCH Verlags, Weinheim, 1993.
12. E. Wood, K. Nimmo, *J. Electron. Mater.*, 23 (1994) 709.
13. G.L. Leone, P. Niessen, and H.W. Kerr, *Metall. Trans. B* 6 (1975) 503.
14. G.L. Leone and H.W. Kerr, *J. Crystal Growth*, 32 (1976) 111.
15. D. Karpinos, L. Tuchinskii, A. Sapozhnikova, A. Panasyuk, V. Enevich, *Poroshk. Metall.*, (Kiev) 3 (1983) 54.
16. N. Koblyuk, L. Akselrud, R. Skolozdra, *Pol. J. Chem.*, 73 (9) (1999) 1465.
17. G. P. Vassilev, E. Dobrev, J.-C. Tedenac, T. Czeppe, in: *Proceedings of the VIII-th Seminar "Diffusion and Thermodynamics of Solids"*, 2002, pp. 119-122, September 4-6, Brno, Czech Republic.
18. G.P. Vassilev, *J. Alloys and Comp.*, 365 (1-2) (2004) 164.
19. G.P. Vassilev, X.J. Liu, K. Ishida, *J. Alloys and Comp.*, 375(1-2)(2004)162.
20. G.P. Vassilev, *Cryst. Res. Technol.*, 39 (9) (2004) 763.
21. G.P. Vassilev, K. Ishida, *J. Alloys and Comp.*, 376 (1-2) (2004) 125.
22. G.P. Vassilev, K. Ishida, *J. Alloys and Comp.*, 385 (1-2) (2004) 181.
23. G.P. Vassilev, *Z. Metallkunde*, 95 (9) (2004) 813.
24. G.P. Vassilev, *Archives of Metallurgy and Materials*, 49 (3) (2004) 519.
25. G. P. Vassilev, *Cryst. Res. Technol.*, 40 (7) (2005) 713.
26. G. P. Vassilev, *Cryst. Res. Technol.*, 41(4) (2006) 349.
27. G. P. Vassilev, *J. Mining and Metallurgy*, 41 B (2005) 79.
28. G.P. Vassilev, E. Dobrev, J.-C. Tedenac, *J. Alloys and Comp.*, 407 (2005) 170.
29. V. Kuck, *Thermochimica Acta*, 99 (1986) 223.
30. T.-M. Korhonen, J.K. Kivilahti, *J. Electronic Mater.*, 27 (3) (1998) 149.
31. G. P. Vassilev, E. Dobrev, J.-C. Tedenac, *J. Alloys and Comp.*, 399 (2005) 118.
32. B.-J. Lee, N. M. Hwang and H. M. Lee, *Acta Mater.*, 45 (5) (1997) 1867.