

# Effect of cooling rate on structure and creep behavior of Sn-0.7Cu-0.5Zn lead-free solder alloy

E.S. Gouda<sup>a</sup>

Metal Physics Lab., Department of Solid State Physics, National Research Center, 12622 Dokki, Giza, Egypt

Received: 27 March 2009 / Accepted: 2 June 2009

Published online: 17 September 2009 – © EDP Sciences

**Abstract.** The influence of cooling rate on the structure, melting, hardness and indentation creep behavior of the Sn-0.7Cu-0.5Zn lead-free solder alloy has been studied by XRD, DSC and Vickers microhardness tester, respectively. The study was carried out for the alloy prepared at two different cooling rates of 3.5 °C/s and  $11.7 \times 10^{-3}$  °C/s. The results showed that the cooling rate significantly affects the structure, melting and mechanical properties of this alloy. Cu atoms are restricted in the formation of the intermetallic compound (IMC)  $\text{Cu}_6\text{Sn}_5$  embedded in Sn-matrix in the slow cooled sample.  $\text{Cu}_3\text{Sn}$  compound was detected in the fast cooled sample. The Zn-phase has not been detected by the X-ray diffraction analysis, which means a complete solubility of Zn in Sn-matrix has been obtained. The crystallite size of the Sn-matrix phase in the slow cooled sample was found to be 54.4 nm, while the value of the fast cooled sample was found to be 48.5 nm. This means the fast cooling condition caused grain refinement. This refinement leads to decrease the melting point from 222.7 to 221.2 °C and increase microhardness from 16.4 to 18.2 kg/mm<sup>2</sup>. Furthermore, fast cooling condition improved the creep resistance of Sn-0.7Cu-0.5Zn alloy than that of the slow cooling condition.

**PACS.** 61.66.Dk Alloys – 62.20.-x Mechanical properties of solids

## 1 Introduction

Increasing the health concerns over the toxicity of Pb in eutectic Pb-Sn solders has prompted the development of new-rich solder alloys for electronic packaging [1–3]. Many lead-free solders, such as binary alloys of Sn-3.5Ag, Sn-9Zn and Sn-58Bi have been investigated with some alloying elements [4–7]. Among many lead-free solder alloys, Sn-Cu solder, has received attention due to its comparable low price to other alloys, which is the most important factor has to be evaluated. For example, most Pb-free solders cost about 2 ~ 3 times more than Sn-Pb solders because the Pb-substitute is comparable expensive. However, the cost of eutectic Sn-0.7%Cu solder is only about 1.3 times higher than Sn-Pb solders, so Sn-0.7%Cu has been successfully transferred to practical production of consumer products [8,9] for example, National Electronics Manufacturing Initiative recommended to replace eutectic Sn-Pb alloy by the eutectic Sn-Cu alloy in wave soldering [10]. According to the phase diagram of Sn-Cu [11], there is no solid solubility of Cu in Sn; essentially all the Cu in the Sn-0.7Cu alloy resides in the  $\text{Cu}_6\text{Sn}_5$  intermetallic phase. It should be possible to improve both the mechanical creep and thermal fatigue properties of Sn-0.7Cu alloys by ternary alloying additions. This would best be achieved by introducing an element that is not soluble in solid Sn, but is soluble

in solid Cu. This type of alloying addition should assist in seeding a fine, uniform dispersion of small precipitates and combination of respective solubilities should preserve the microstructural stability of the alloy. A metallurgical examination of such potential alloying additions reveals Zn as a reasonable choice to achieve these objectives, since the Sn-Zn binary phase diagram [12] shows very little solubility of Zn in solid Sn.

The cooling rate of alloys directly affects the microstructure of the Sn-Ag solders, also significantly influences their mechanical behaviors. Hence, the effects of applied cooling rate on microstructure and mechanical behavior have been studied intensively. It was found that [13], the applied cooling rate had a significant effect on intermetallic compounds size, morphology and mechanical properties of Sn-Ag alloys. So, the present paper aims to investigate the effect of cooling rate on structure, melting and mechanical properties of Sn-0.7Cu-0.5Zn solder alloy.

## 2 Creep test

In an indentation creep test as described elsewhere, [14] the load  $F$  on the indenter is carried out by a projected indent area ( $d^2$ ), so that the indentation pressure is  $F/d^2$ . It creates a stress pitch below the indenter. For equilibrium,

<sup>a</sup> e-mail: gouda.e173@yahoo.com

each component of stress in the materials is proportional to  $(F/d^2)$ . Therefore, that, the applied stress at each point beneath the indenter is given by:

$$\sigma = K(F/d^2), \quad (1)$$

where  $\sigma$  is the applied stress and  $K$  is constant. Also, at steady state creep, the strain rate ( $\dot{\epsilon}$ ) is related to the stress,  $\sigma$  at a constant temperature by the relation:

$$\dot{\epsilon} = B\sigma^n \quad \text{or} \quad \sigma = C(\dot{\epsilon})^m, \quad (2)$$

where  $C$  and  $B$  are constants,  $n$  is stress exponent =  $1/m$ . Thus, the strain rate is related to the average diagonal length by:

$$\dot{\epsilon} = K_1(F/d^2)^{1/m}. \quad (3)$$

Using the assumption [15] that, there is a representative strain that is simply a linear function of  $d$  by:

$$\dot{\epsilon} = K_2\dot{d}, \quad (4)$$

where  $\dot{d}$  is the rate of indentation length variation with time, and  $K_2$  is constant. Substituting equation (4) into equation (3),  $\dot{d}$  can be expressed as:

$$\dot{d} = K_3(F/d^2)^{1/m}. \quad (5)$$

The integration of this equation yields to the expression:

$$d^{2/m+1}/(2/m+1) = K_3F^{1/m}t + K_4. \quad (6)$$

This equation can be simplified to the power law function:

$$d = At^b + K_5, \quad (7)$$

where  $K_5$  and  $A$  are constants and  $b$  is a time exponent which is related to  $m$  as:  $b = 1/(2/m+1)$ .

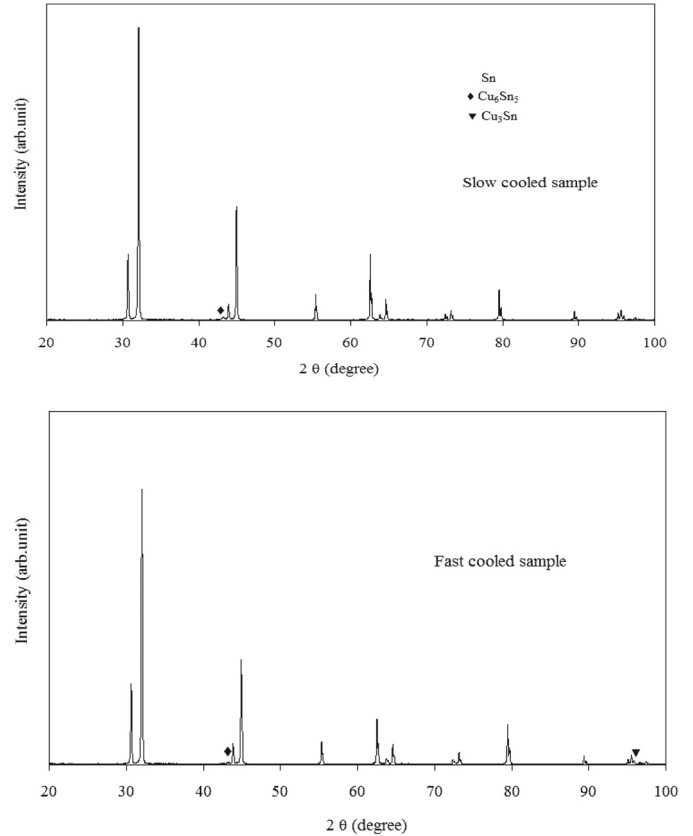
Take the ln for both sides of equation (7)

$$\ln d = \ln A + b \ln t. \quad (8)$$

Thus by plotting the  $\ln d$  against  $\ln t$ , it is possible to obtain the time exponent and thus the creep behavior of the materials.

### 3 Experimental

The alloy of composition Sn-0.7Cu-0.5Zn was prepared by melting pure tin, copper and zinc of purity (99.98%) in a high electrical furnace. Then, the molten alloy was divided into two parts. A part of the molten alloy was fast cooled (FC) in air by casting it into a cold steel mould results a cooling rate of about  $3.5 \text{ }^\circ\text{C/s}$  and the second part was kept into a PYREX<sup>®</sup> test tube in a furnace at  $450 \text{ }^\circ\text{C}$  to cool slowly (SC) to room temperature at a cooling rate of about  $11.7 \times 10^{-3} \text{ }^\circ\text{C/s}$ . All samples were cut into small discs of about 8 mm in diameter and about 5 mm in thickness. The structure of these samples was examined by X-ray diffraction technique using a Shimadzu X-ray diffractometer with Cu-radiation. Scanning electron



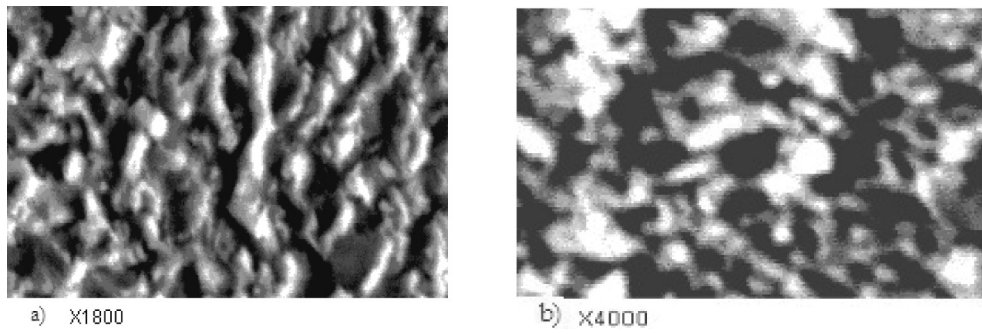
**Fig. 1.** XRD patterns of Sn-0.7Cu-0.5Zn alloy prepared at slow and fast cooling conditions.

microscopy was used to investigate the microstructure of the two samples after polishing and etching with a chemical etching solution of 5% of HCL in alcohol. DSC test with scanning rate  $10 \text{ }^\circ\text{C/min}$  was used to identify the melting properties of the two samples. The polished samples were tested in a Vickers microhardness tester where, a diamond pyramid indenter with square base is used and the Vickers hardness number is given by  $HV = 0.185F/d^2$ , where  $F$  is the applied load in gram and  $d$  is the average diagonal length in mm. Each reading was an average of at least five separate measurements taken at random places on the surface of specimens. All of the indentations were at least 5 mm away from the edges and from other indentations. Indentation creep tests were carried out using the Vickers microhardness tester by plotting the relation between the indentation diagonal lengths of the indenter with time of indentation at a fixed load of 50 gm.

## 4 Results and discussion

### 4.1 Structure

Figure 1 shows the XRD patterns of Sn-0.7Cu-0.5Zn alloy prepared at slow and fast cooling conditions. The pattern of the SC sample contains a single line due to  $\text{Cu}_6\text{Sn}_5$  compound embedded in Sn-matrix phase indicated by a single line at  $2\theta = 43.25^\circ$ . The pattern of the FC sample



**Fig. 2.** SEM of Sn-0.7Cu-0.5Zn alloy prepared at: (a) SC and (b) FC conditions.

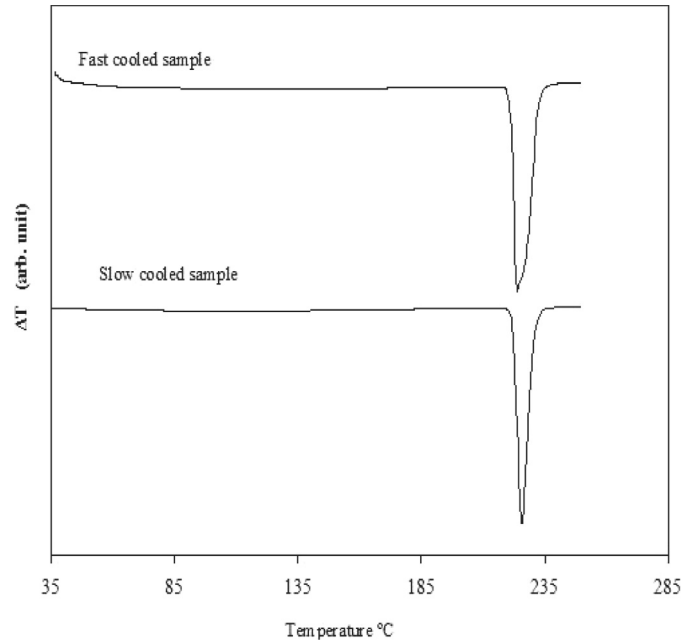
**Table 1.** Crystallite size and lattice parameters of the body center tetragonal Sn in the Sn-0.7Cu-0.5Zn alloy prepared at SC and FC conditions.

Sample condition	Crystallite size nm	$a$ Å	$c$ Å	Volume of unit cell Å <sup>3</sup>
SC	54.4	5.819	3.175	107.5
FC	48.5	5.831	3.179	108.1

indicates the same phases in addition to the precipitation of Cu<sub>3</sub>Sn compound, which indicated by a single line at  $2\theta = 96.68^\circ$ . There are no others peak due to Zn phase, which means a complete solubility of Zn in the Sn-matrix has been obtained. Also, FC condition causes shift of the X-ray diffraction lines to the lower angular positions and consequently the body center tetragonal Sn had higher lattice parameters than that of the SC sample (Tab. 1). Another important point emerges from this figure that, the (200) Sn reflection had a much higher intensity than that of the (101) Sn reflection in the two samples but the ratio in the FC sample is higher than that of the SC sample, which means that, the FC condition tend to cause preferred orientation. On the other hand, the crystallite size was also calculated from the (200) and (101) reflections as illustrated in Table 1 using Scherer's equation [16]. The results showed that the crystallite size is equal to 54.4 and 48.5 nm for the slow and fast cooled samples, respectively which means that the FC condition causes crystal refinement than the SC condition. Figure 2 shows the SEM photograph of the two samples. It shows the matrix of gray color of Sn-rich phase with some precipitations of black color indicating the presence of the intermetallic compounds Cu<sub>6</sub>Sn<sub>5</sub> and Cu<sub>3</sub>Sn.

## 4.2 Thermal analysis

Melting temperature is one of the most important considerations for the development of solder alloys because the high melting temperature of the solder alloy increases the reflowing temperature in the electronic packaging process and causes thermal damage to the polymer substrate. Figure 3 shows the DSC endothermic peaks of the prepared samples during heating with heating rate 10 K/min. It

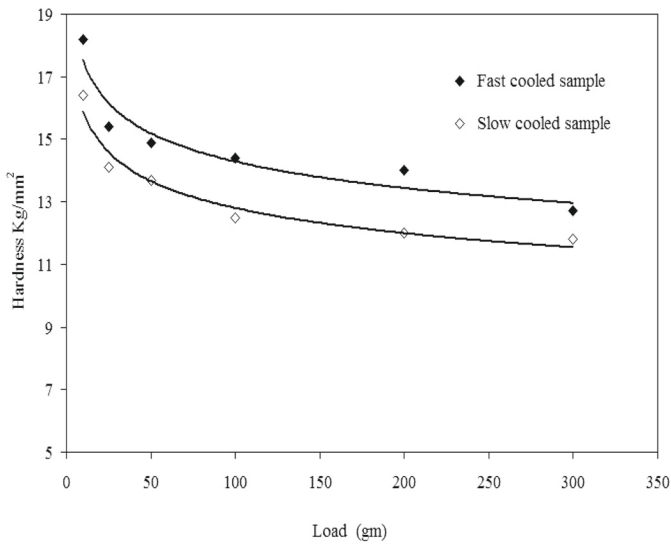


**Fig. 3.** DSC endothermic peaks of Sn-0.7Cu-0.5Zn alloy prepared at slow and fast cooling conditions.

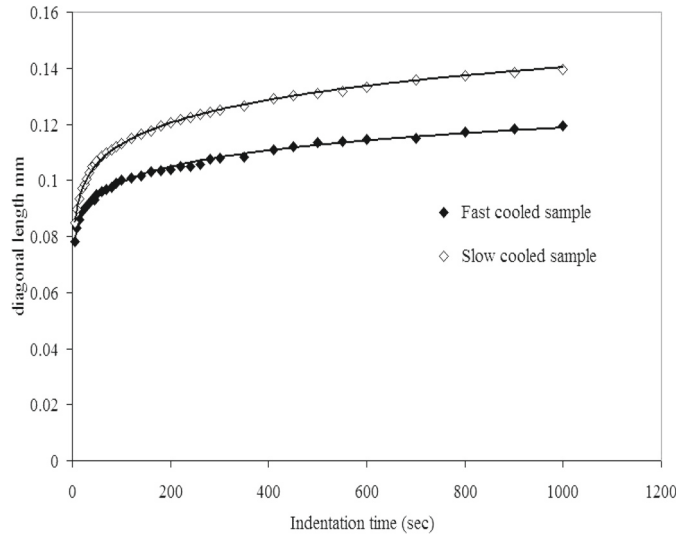
shows only one endothermic peak due to the melting reaction for each sample indicating that the Sn-0.7Cu-0.5Zn alloy has a near-eutectic composition. The melting point of the SC and FC samples has been determined as 222.7 and 221.2 °C, respectively. This means that, the FC condition slightly decreases the melting point than that of the SC condition due to grain refinement which agrees with other work [6,17]. Furthermore, the heat of fusion for SC and FC samples has been determined as 57.6 and 63.02 J/g, respectively. These values are much lower than the values of the eutectic lead-tin solder, 104.2 J/g, [18] which indicates that the Sn-0.7Cu-0.5Zn is a more beneficial material for saving energy than lead-tin solders.

## 4.3 Hardness

Figure 4 shows the variation of the hardness values with the applied load in the range of 10 to 300 g measured at a fixed indentation time of 10 s. It shows a non linear



**Fig. 4.** Hardness versus applied loads of Sn-0.7Cu-0.5Zn alloy prepared at the two cooling conditions.

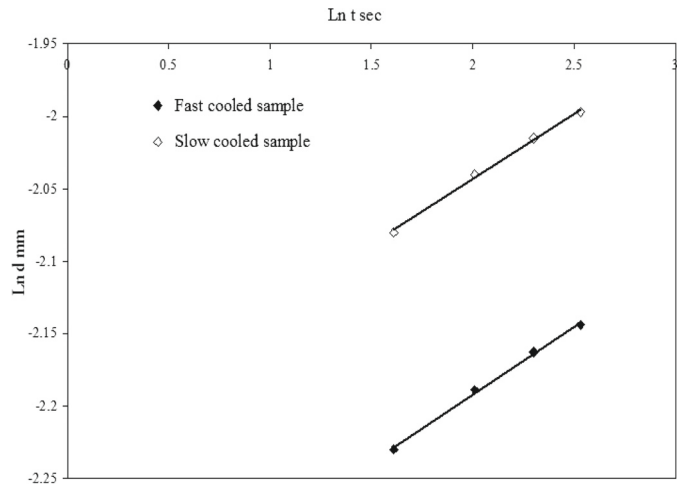


**Fig. 5.** Indentation creep behavior of Sn-0.7Cu-0.5Zn alloy prepared at slow and fast cooling conditions.

variation in which there are two regions i.e. the first region starts at the beginning load up to 50 g, in which there is a fast decrease of hardness with the applied load for the two samples followed by the second region starts from 50 up to 300 g. The second region is called the steady state region in which, hardness decreases linearly with the applied load. This behavior of hardness is agreed with the results observed elsewhere [19–21] and known as indentation size effect (ISE). On the other hand, the hardness values of the FC sample have higher values than that the SC sample. This behavior can be attributed to two reasons; grain refinement of the FC sample and more precipitations of Cu-Sn compounds which may act as hard inclusions in soft matrix.

#### 4.4 Indentation creep behavior

The indentation creep data are measured at room temperature under constant load of 50 g during the time interval 5–1000 s. The results shown in Figure 5 show the variation of the indentation diagonal length with time of the indentation. It shows that, the indentation diagonal length of the two samples increases with the indentation time through two stages. The first stage records a rapid increase of diagonal length with time with a decreasing rate followed by the second stage which is the steady-state region where indentation length increases linearly with time. As the hardness test is actually a compression test, fracture of the samples dose not occurs and hence, it is obviously impossible to record a third stage of the curve contrary to what happens in an ordinary creep test. It can be depicted from this figure that, the level of indentation curves and their slopes in the steady-state region are higher for SC sample than that of FC sample. The differences in the indentation creep behavior of the



**Fig. 6.** Ln of the indentation diagonal length versus Ln time of indentation for Sn-0.7Cu-0.5Zn alloy prepared at slow and fast cooling conditions.

SC and FC samples can be attributed to their crystal refinement. Also, the indentation curves can be well represented by equation (8). The validity of this equation is shown in Figure 6. As can be seen, the measured points lie along the straight lines for the two samples. From this figure, the time exponent and the corresponding values of  $n$  and  $m$  are calculated. The value of  $b$  is found to be 0.092 and 0.076 for the SC and FC samples, respectively. Moreover, the corresponding values of stress exponent are found to be 5 and 6.1 for the SC and FC samples, respectively. These values are much higher than the values obtained in other work for Sn-Pb-Sb alloy measured by the same technique [14]. Other results obtained in impression creep tests on cast and homogenized Sn-9Zn

in the temperature range of 303–418 K are indicative of  $n$  value of 5.1 [22]. According to the power law creep, the higher value of stress exponent of the FC sample would result in a decrease in creep rate due to the increase in the yield strength as evident elsewhere [23]. Lower value of stress exponent indicates that indentation creep takes place more readily in the SC samples. This also can be noticed from Figure 5 where, both the level of indentation curve and the slope in the steady state region are slightly higher for the SC sample than that of the FC sample.

## 5 Conclusion

The influence of the cooling rate on the structure, melting, hardness and indentation creep behavior of cast Sn-0.7Cu-0.5Zn lead-free solder alloy has been studied by XRD, DSC and Vickers microhardness tester, respectively. This alloy has been prepared at two different cooling rates of 3.5 °C/s and  $11.7 \times 10^{-3}$  °C/s. The results showed that the cooling rate significantly affect on structure, melting and mechanical properties of this alloy. Cu atoms were restricted in the formation of the intermetallic compound (IMC) Cu<sub>6</sub>Sn<sub>5</sub> embedded in Sn-matrix in the two samples and the compound Cu<sub>3</sub>Sn was detected in the fast cooled sample. The Zn-phase has not been detected by the X-ray diffraction analysis, which means complete solubility of Zn in Sn-matrix in the two samples. The fast cooling condition decreased the crystallite size of the Sn-matrix from 54.4 to 48.5 nm. This refinement leads to decrease the melting point from 222.7 to 221.2 °C and increase the microhardness from 16.4 to 18.2 kg/mm<sup>2</sup>. Furthermore, the fast cooling condition improved the creep resistance than that of the slow cooling condition.

## References

1. M.M. Cormack, S. Jin, G.W. Kammlott, H.S. Chen, Appl. Phys. Lett. **63**, 15 (1993)
2. M.M. Cormack, S. Jin, Electron. Mater. **23**, 635 (1994)
3. J. Glazer, Electron. Mater. **23**, 693 (1994)
4. A. Guédon, E. Woïrgard, C. Zardini, Microelectron. Reliab. **42**, 555 (2002)
5. M. Kamal, M.S. Meikhail, E.S. Gouda, A.B. El-Bediwi, Rad. Eff. Def. Sol. **160**, 45 (2005)
6. M. Kamal, E.S. Gouda, Mater. Manuf. Proc. **21**, 736 (2006)
7. M. Kamal, E.S. Gouda, Cryst. Res. Technol. **12**, 1210 (2006)
8. K.S. Bae, S.J. Kim, Mater. Res. **17**, 743 (2002)
9. K. Sugauma, Curr. Opin. Solid State Mater. Sci. **5**, 55 (2001)
10. <http://www.nemi.org/projects/ese/ifassembly.html>
11. C.E. Homer, H. Plummer, Inst. Metal. **64**, 169 (1939)
12. E. Jenckel, L. Roth, Z. Metallkde. **30**, 135 (1938)
13. F. Ochoa, J. Williams, N. Chawla. J. Electron. Mater. **32**, 1414 (2003)
14. R. Mahmudi, A.R. Bazzaz, Mater. Lett. **59**, 1705 (2005)
15. T.O. Mulhearn, D. Tabor, J. Inst. Met. **89**, 7 (1960-1961)
16. B.E. Warren, *X-Ray diffraction* (Addison Wesley, Reading, MA, 1969)
17. K.F. Peters, Y.W. Chung, J.B. Cohen, Appl. Phys. Lett. **71**, 20 (1997)
18. W. Wendlandt, *Thermal Analysis* (Wiley, New York, 1986), p. 271
19. J. Gong, Mater. Sci. Lett. **19**, 515 (2000)
20. A. Leenders, M. Ullrich, H.C. Freyhardt, Physica C **279**, 173 (1997)
21. J. Suwanprateeb, Polym. Test. **17**, 495 (1998)
22. S.D. Rani, G.S. Murthy, Mater. Sci. Technol. **20**, 403 (2004)
23. B. Walser, O.D. Sherby, Scr. Metal. **16**, 213 (1982)