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Effect of growth rate and lamellar spacing on microhardness in the directionally solidified Pb-Cd, Sn-Zn and Bi-Cd eutectic alloys

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Lead-cadmium, Zinc-tin and Bismuth-cadmium of (99.99%) high purity eutectic alloys were melted in a graphite crucible under vacuum atmosphere. These eutectic alloys were directionally solidified upward with a constant temperature gradient G and different growth rates V in the Bridgman type directional solidification furnace. The lamellar spacings λ and microhardness H_V were measured from both transverse section and longitudinal section of the specimen. The variations of H_V with respect to V and λ have been determined by using the linear regression analysis method. H_V values increase with the increasing values of V and decrease with the increasing λ values. The Hall-petch type relationships obtained in this work have been compared with the previous works. © *2004 Kluwer Academic Publishers*

1. Introduction

Eutectic alloys are the basis of most engineering materials [1–3]. Eutectic alloys have relatively low melting points, excellent fluidity, and good mechanical properties. Consequently, a broad spectrum of eutectic alloys have beeen developed and are available for different applications. The solidification of regular eutectic alloys generally gives rise to lamellar, fibrous, broken lamellar or complex regular spacings. The spacing of the lamellar or fibrous is typically very regular with a dispersion around an average value. The theoretical and experimental investigations are revealed for various eutectic alloys by many workers [2, 4–7].

The purpose of the present work is to investigate experimentally the dependence of the growth rate, V and lamellar spacing, λ on the microhardness, H_V. Pb-Cd (lamellar or rod), Sn-Zn (broken lamellar) and Bi-Cd (complex regular) eutectic alloy have been chosen for the study because of their lamellar eutectic structure, widely available experimental results and well defined physical properties. The detailed analysis between the lamellar spacing, λ and the solidification parameters V and G (for Pb-Cd, Sn-Zn and Bi-Cd eutectic alloys) are given in Ref. [8–10]. The Hall-Petch type relationships [11, 12] between the microhardness, the growth rate and lamellar spacing were observed on the logarithmic scales. The Hall-petch type relationships can be written as follows,

$$H_V = H_o + k_1 V^m \quad (1)$$

$$H_V = H_o + k_2 \lambda^{-n} \quad (2)$$

where H_V is microhardness, H_o is the initial hardness in the room temperature, m and n are exponent values for the growth rate, V and the lamellar spacing, λ espectively. k_1 and k_2 are experimentally determined constants.

The experimental results will be presented first and than they will be compared with current results in the literature for eutectic alloys in order to get more general information about the relationships between H_V and V and λ.

2. Experimental procedure

The eutectic samples (Pb-Cd, Sn-Zn and Bi-Cd) were prepared by using metals of 99.99% purity. Weighed amount of Pb, Sn, Zn, Cd and Bi metals were melted in a graphite crucible which was placed into the vacuum melting furnace [13]. After allowing time for melt homogenisation, molten alloy was poured into the prepared 13 graphite crucibles (250 mm in length, 4 mm

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0022–2461

ID and 6.35 mm OD) in a hot filling furnace. Then, each specimen was positioned in a Bridgman type furnace in a graphite cylinder (300 mm in length, 10 mm ID and 40 mm OD) for each eutectic alloy respectively. Accuracy of the thermocouples was checked by slowly solidifying the alloy. The measured eutectic temperature, T_E difference was less than 0.5 K with differently placed thermocouples. The temperature of the Bridgman type furnace was controlled by a Pt/Pt-13%Rh thermocouple placed between the heating element and the alumina tube. The temperature could be controlled to about ± 0.1 K during the run. The thermocouples were placed into the capillary alumina tubes (0.8 mm ID, 1.2 mm OD) which were positioned approximately 10 mm apart and parallel to the heat flow direction inside the crucible. Throughout the experiment, temperature distribution was obtained by measuring the temperature in the sample by three chromel/alumel thermocouples (type-K) which were placed within the samples. All the thermocouple leads were taken to an ice/water cold junction, then to a WPA analogy potentiometer and to a Kipp-Zonen chart recorder capable of recording to 1 μV. After stabilizing the thermal conditions in the furnace under an argon atmosphere, the specimen was grown by pulling it downwards at various constant rates by means of different speed synchronous motors. Specimens were solidified under steady state conditions with a constant temperature gradient (approximately 6.4, 6.5, and 4.7 K/mm for Pb-Cd, Sn-Zn and Bi-Cd eutectic alloys respectively) and different growth rates (8–167 μm/s) (Table I). After 100–120 mm steady state growth of the samples, they were quenched by pulling them rapidly into the water reservoir.

2.1. Metallographic examination

The unidirectionally grown and quenched specimen were removed from the graphite crucible and 3 cm lengths from the top and bottom were cropped off and discarded, then ground to observe the solid-liquid interface and the longitudinal section, which included the quenched interface was separated from the specimen. This part was ground, polished and etched to reveal the quenched interface. Furthermore, the longitudinal and the transverse sections of the ground specimen were mounted in a cold-setting epoxy resin. The microstructural of the specimens were determined by metallographic analysis. Mechanical and electropolishing techniques were used to prepare the transverse and the longitudinal sections for both optical microscopy (OM) and scanning electron microscopy (SEM) (Fig. 1).

2.2. The measurement of growth rates, V and temperature gradient G

The thermocouples were recorded simultaneously for measurement of the growth rates and the temperature gradients on the solid/liquid interface in the liquid. The values for the growth rates, V were calculated from the measurements of the time taken for the solid/liquid interface to pass the thermocouples separated by a known distance. When the second thermocouple was at the solid-liquid interface and the third thermocouple in the liquid, their temperatures were used to obtain the temperature gradient, G. The positions of the thermocouples were measured after the quench. The values of V and G are given in Table I. The experimental details are given in Ref. [13].

2.3. The measurement of lamellar spacing λ and microhardness H_V

The samples were prepared for microstructural examination, including the solid-liquid interface on the longitudinal section. The transverse section was taken near the solid-liquid interface (2–3 mm) to measure λ. The lamellar spacings, λ^* values were measured on the longitudinal section at least in 4–6 different regions on the longitudinal section and λ values on the transverse section at least 10–30 different regions of the samples (Fig. 1). Lamellar spacing was measured with a linear intercept method [14]. The average values of λ^* and λ, were obtained from the detailed measures and given in Table I. In order to make accurate λ measurement from the longitudinal polished plane, the normal of the α and β planes must be parallel to the polished surface, however this is not always possible [15].

Microhardness values (H_V) of the specimens for Pb-Cd, Sn-Zn and Bi-Cd eutectic alloys were also measured at the same places where λ was measured using a Vickers type Highwood model hardness measuring test device equipped with a square-based pyramidal indenter which an angle of 136°. Ten indentations obtained from each specimen using the test loads of 10–25 gf were used at these microhardness analysis. The microhardness values were the average of at least 10 measurements on transverse section (H_V) and longitudinal section (H_V^*). The minimum impression spacing (centre to edge of adjacent impression) was about 3 times the diagonal and at least 0.5 mm from the edge of the specimen. λ, V and H_V values are given in Table I. H_V^* values are also given in Appendix A, with the purpose of comparing the transverse section values with the longitudinal section values.

3. Result and discussion

Pb-Cd, Sn-Zn and Bi-Cd eutectic alloys were unidirectionally solidified with a constant G but five different V in order to see the effect of the growth rate on the lamellar spacings (λ, λ^*). As can be seen from Fig. 1, during eutectic growth, a large number of eutectic grains can be formed. All grains seem to be oriented parallel to growth direction but usually differed in rotation about the growth axis. The normal of the α and β planes must be parallel to the polished longitudinal plane, however this is not always possible. When the normal of the α and β planes are not parallel to the longitudinal plane, the lamellar spacings λ^* observed on the longitudinal plane give larger value than the lamellar spacings λ observed the transverse polished plane (see Table I and Appendix A). So λ and H_V values measured on the transverse section of the sample are more reliable. Also λ and H_V measurements were taken near to the solid-liquid interface (1–3 mm) of the *in-situ* annealing effect on λ and H_V. Since the microhardness values are more subject to local material variations, a considerable

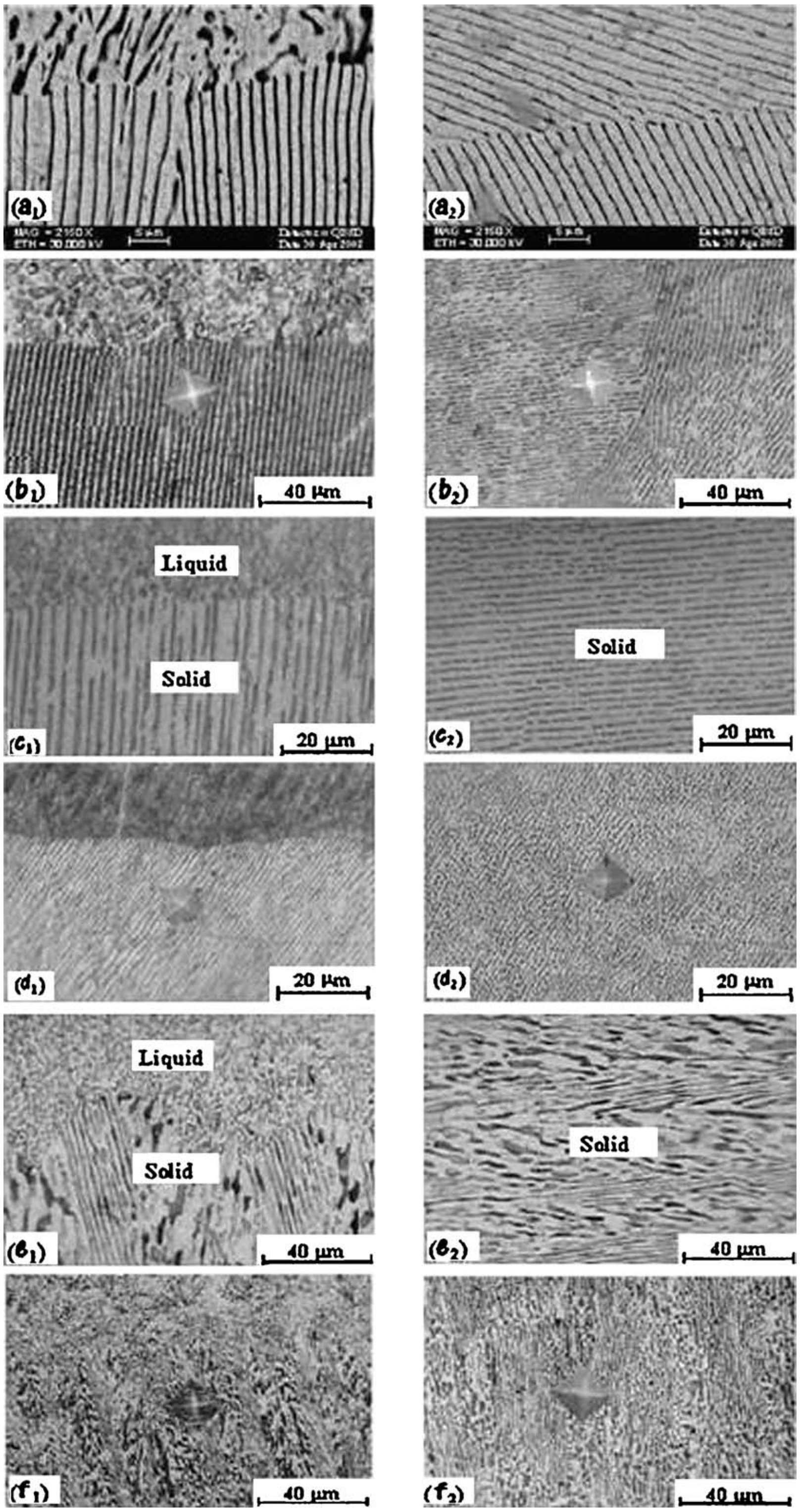

Figure 1 Optical and SEM micrographs of the directional solidified eutectic alloys showing: the microstructure, [(a_1) longitudinal section, (a_2) transverse section (SEM, $G = 6.41$ K/mm, $V = 16.55 \times 10^{-3}$ mm/s)], and microhardness measurements [(b_1) longitudinal section, (b_2) transverse section ($G = 6.41$ K/mm, $V = 40.18 \times 10^{-3}$ mm/s)] for Pb-Cd eutectic alloy, the microstructure, [(c_1) longitudinal section, (c_2) transverse section ($G = 6.52$ K/mm, $V = 8.33 \times 10^{-3}$ mm/s)], and microhardness measurements, [(d_1) longitudinal section, (d_2) transverse section ($G = 6.52$ K/mm, $V = 165.13 \times 10^{-3}$ mm/s)] for Sn-Zn eutectic alloy, the microstructure [(e_1) longitudinal section (e_2) transverse section ($G = 4.73$ K/mm, $V = 8.30 \times 10^{-3}$ mm/s)], and microhardness measurements [(f_1) longitudinal section, (f_2) transverse section ($G = 4.73$ K/mm, $V = 167.32 \times 10^{-3}$ mm/s)] for Bi-Cd eutectic alloy.

scatter was experienced, in spite of all. The precautions taken in determining the microhardness.

3.1. The effect of the growth rate on the microhardness

It is seen that the microhardness, H_V, of the Pb-Cd, Sn-Zn and Bi-Cd directionally solidified eutectic alloys increases with the increasing growth rate, V. Variation of H_V as a function V at constant G is given in Table I, Appendix A and Fig. 2 for the eutectic alloys. The values of V have increased approximately 20 times but H_V values have increased about 1.4 times for the Pb-Cd alloy and 1.3 times for Sn-Zn and Bi-Cd alloys. These increases are associated with the structural refinement

TABLE I The experimental relationships among microhardness, the growth rate and lamellar spacing in the directionally solidified

Solidification parameters		Lamellar spacings	Microhardness	
G (K/mm)	$V \times 10^{-3}$ (mm/s)	$\lambda \times 10^{-3}$ (mm)	H_V (kg/mm^2)	The relationships
(a) Pb-Cd eutectic alloy				
6.41	8.27	2.35 ± 0.15	14.28 ± 0.58	$H_V = k_1 V^{0.11}$
	16.55	1.56 ± 0.12	14.95 ± 0.90	$H_V = k_2 \lambda^{-0.20}$
	40.18	1.13 ± 0.06	16.18 ± 0.60	$k_1 = 22.91$ (kg · mm$^{-2.10}$ · s$^{0.10}$)
	83.33	0.79 ± 0.06	17.85 ± 0.78	$k_2 = 2.78$ (kg · mm$^{-1.80}$)
	163.55	0.56 ± 0.02	19.55 ± 0.36	$r_1 = 0.993, r_2 = -0.995$
(b) Sn-Zn eutectic alloy				
6.52	8.33	2.16 ± 0.20	15.42 ± 0.28	$H_V = k_3 V^{0.08}$
	16.32	1.57 ± 0.11	16.28 ± 0.30	$H_V = k_4 \lambda^{-0.21}$
	41.48	0.98 ± 0.10	17.40 ± 0.25	$k_3 = 22.80$ (kg · mm$^{-2.08}$ · s$^{0.08}$)
	81.96	0.70 ± 0.09	18.20 ± 0.32	$k_4 = 4.36$ (kg · mm$^{-1.79}$)
	165.13	0.53 ± 0.22	20.01 ± 0.23	$r_3 = 0.994, r_4 = -0.999$
(c) Bi-Cd eutectic alloy				
4.73	8.27	1.79 ± 0.09	16.66 ± 0.36	$H_V = k_5 V^{0.10}$
	16.52	1.38 ± 0.11	17.28 ± 0.53	$H_V = k_6 \lambda^{-0.22}$
	40.99	1.02 ± 0.16	18.35 ± 0.45	$k_5 = 23.51$ (kg · mm$^{-2.10}$ · s$^{0.10}$)
	81.66	0.72 ± 0.07	20.10 ± 0.36	$k_6 = 4.35$ (kg · mm$^{-1.78}$)
	167.32	0.46 ± 0.02	22.05 ± 0.33	$r_5 = 0.988, r_6 = -0.997$

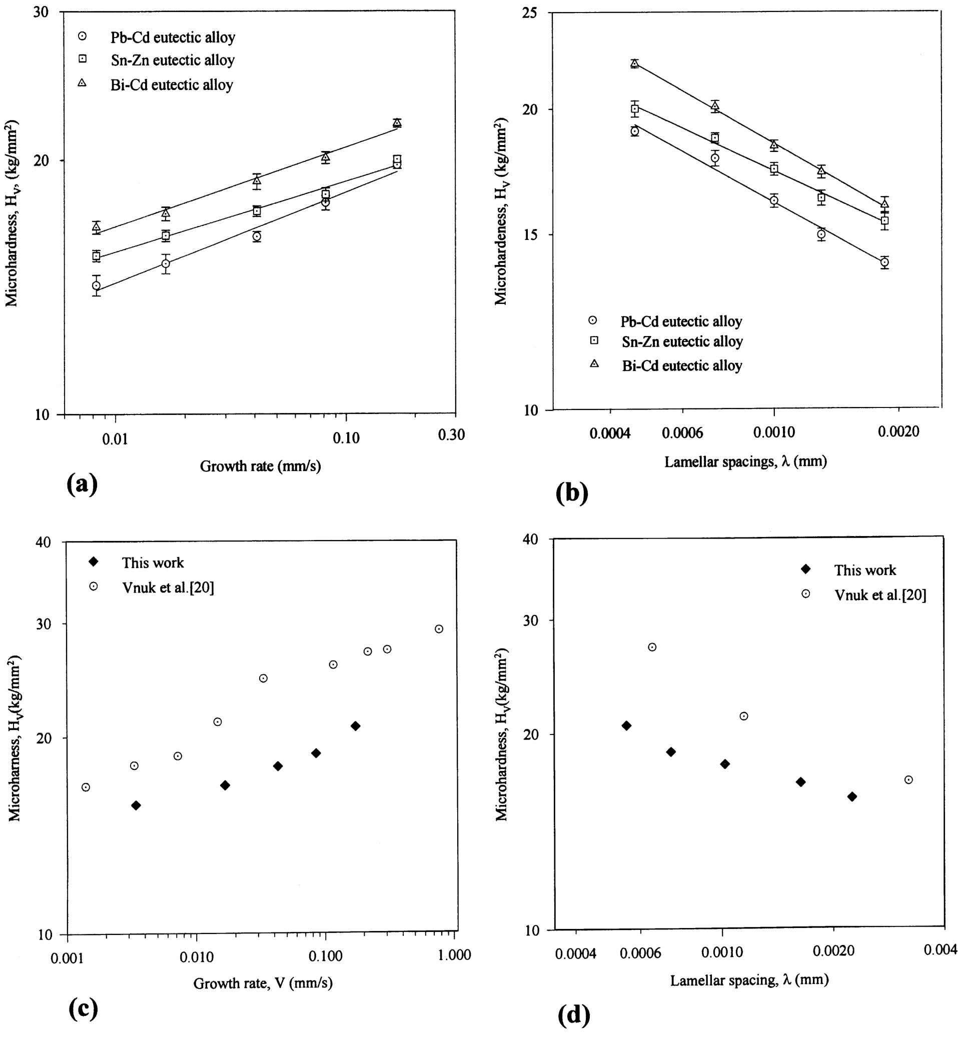

Figure 2 (a) Variation of microhardness H_V as a function growth rate V, at a constant G [(6.41 K/mm for Pb-Cd, 6.52 K/mm for Sn-Zn, 4.73 K/mm for Bi-Cd eutectic alloys, respectively)], (b) variation of microhardness H_V as a function lamellar spacing, λ at a constant G [(6.41 K/mm for Pb-Cd, 6.52 K/mm for Sn-Zn, 4.73 K/mm for Bi-Cd eutectic alloys, respectively)], comparison of H_V values for Sn-Zn eutectic alloy (c) variation microharness, H_V with growth rate V, (d) variation of microhardness H_V, with lamellar spacing, λ (the λ values obtained from graphics of Vnuk *et al.* [20]).

of the eutectic specimens (Fig. 1). As can be seen from Table I and Fig. 2a, the dependence of H_V on V can be represented by an equation:

$$H_V = kV^{m} \tag{3}$$

The value of the exponent m is equal to 0.11, 0.08 and 0.10 for the transverse sections of the Pb-Cd, Sn-Zn and Bi-Cd eutectic alloys respectively. Similarly, the value of the exponent m is equal to 0.10, 0.08 and 0.09 for the longitudinal section of the same eutectic alloys. (see Appendix A). These exponent values have been compared with the previous results [16–22] for the similar solidification conditions in different eutectic alloys. The exponent values obtained in this study are fairly close to 0.12, 0.07, 0.08 and 0.11 values obtained by Khan *et al.* [16], Vnuk *et al.* [17], Telli and Kısakürek [18] and Kaya *et al.* [19] for different eutectic alloys, respectively. 0.10 obtained by Vnuk *et al.* [20] for the Sn-Zn eutectic alloy for the similar solidification conditions. Our exponent values are quite higher than the values, 0.04, and 0.034, obtained by Yılmaz and Elliot [21] and Yılmaz [22] for the Al-Si eutectic alloys, respectively.

Although differences exist in the values because of the possible differences in purity, solidification conditions, and the surface preparation of the test pieces, all have a linear $H_V - V$ and $H_V - \lambda$ relations on a logarithmic scale.

3.2. The effect of the lamellar spacing on the microhardness

The variation of the microhardness, H_V as a function of the lamellar spacing λ, is given in Table I, and Fig. 2b for the Pb-CD, Sn-Zn and Bi-Cd eutectic alloys. It can be observed that a decrease in the lamellar spacing leads to increase in the microhardness. The values of λ have decreased approximately 3 times, H_V values have increased 1.4 times for the Pb-Cd eutectic alloy and λ values decreased 4 times, H_V values increased 1.3 times for the Sn-Zn and Bi-Cd eutectic alloys, (see Table I). A linear regression analysis gives the proportionality the Hall-Petch [9, 10] type equation as

$$H_V = k\lambda^{-n} \tag{4}$$

The value of the exponent n is equal to 0.25, 0.21 and 0.22 for the transverse sections of the Pb-Cd, Sn-Zn and Bi-Cd eutectic alloys in respectively. The value of n is equal to 0.24, 0.18 and 0.21 for the longitudinal sections of the same eutectics alloys. These values of n for the transverse section are in good agreement with the values of 0.22 and 0.18 obtained by Khan *et al.* [16] and Kaya *et al.* [19], but quite higher than the value of 0.08 obtained by Yılmaz and Eliot [21], and does not confirm the value of 0.5 suggested by Telli and Kısakürek [18] for Al-Si eutectic alloys. The exponent value, 0.21 for Sn-Zn eutectic alloy in this work is close to the experimental values 0.27 obtained by Vnuk *et al.* [20] for the same eutectic alloy. As can be seen from Fig. 2c and d, variations of H_V vs. V and H_V vs. λ for the Sn-Zn eutectic alloy are in accord with the values obtained for the same eutectic alloy under the similar solidification conditions by Vnuk *et al.* [20].

Fig. 2c shows the variation of microhardness, H_V as function of the growth rate V. H_V increases with the increasing V. And also Fig. 2d shows the variation of microhardness, H_V, as function of lamellar spacing, λ. H_V decreases with the increasing λ. Further more, since $\lambda \, \alpha \, V^{0.5}$ [5, 6, 23, 24], then it is to be expected that (from Equations 1 and 2)

$$H_V \, \alpha \, V^{m} \tag{5}$$

As can be seen from Table I and Fig. 2a and b for the variation of H_V vs. V and H_V vs. λ, the exponent values, m of V are half of the exponent values n of λ for the Pb-Cd and Bi-Cd eutectic alloys but the value of m is smaller than half of the value of n for the Sn-Zn alloy. It is worth noting that the hardness of the transverse and the longitudinal sections of the Pb-Cd specimens are almost the same but the microharnesses of the transverse sections of the Sn-Zn and Bi-Cd specimens are slightly higher than equivalent measurements made on the longitudinal sections of the same specimens. This suggests that the principal deformation around an indentation occurs perpendicular to the plane of the specimen surface for the Sn-Zn and Bi-Cd eutectic alloys.

4. Conclusion

1. The microhardness values of the specimens, H_V's were measured in at least 10 regions on the transverse and the longitudinal sections. It was found that the hardness values, H_V of the specimens increased as V values were increased. The relationships between H_V and V can be given as $H_V = kV^{m}$. The exponent value, m, is 0.11, 0.08, and 0.10 for the transverse sections of the Pb-Cd, Sn-Zn and Bi-Cd uetectic alloys respectively and fairly close to the values obtained by Vnuk *et al.* [17], Telli and Kısakürek [18] and Khan *et al.* [16] but quite higher than the values obtained by Yılmaz and Elliott [21] and Yılmaz [22].

2. The relationships between the microhardness and the lamellar spacing were obtained by linear regression analysis. It shows that the value of H_V increases as the values λ decrease. The establishment of the Hall-Petch type relationships given as $H_V = k\lambda^{-n}$ relating to these parameters. The exponent value, n, is equal to 0.25, 0.21 and 0.22 for the transverse sections of the Pb-Cd, Sn-Zn and Bi-Cd eutectic alloys respectively. The values, n, show good agreement with the value of 0.22 obtained by Khan *et al.* [16] but quite higher than value of 0.08 obtained by Yılmaz and Elliott [21] and does not confirm the value of 0.5 suggested by Telli and Kısakürek [18].

3. Although differences exist in the values because of differences in purity, solidification conditions and the surface preparation of the specimens all have a linear $H_V - V$ and $H_V - \lambda$ relations on a logarithmic scale. Dependence of H_V on V and λ found in this study for the eutectic alloys is in agreement with the previous results [16–24] for similar solidification conditions in different eutectic alloys.

APPENDIX A

Solidification parameters		Lamellar spacings	Microhardness	
G (K/mm)	$V \times 10^{-3}$ (mm/s)	$\lambda^* \times 10^{-3}$ (mm)	$H_V{}^*$ (kg/mm^2)	The relationships
(a) Pb-Cd eutectic alloy				
6.41	8.27	1.45 ± 0.09	14.22 ± 0.48	$H_V^* = k_1 V^{0.11}$
	16.55	1.12 ± 0.08	15.05 ± 0.45	$H_V^* = k_2(\lambda^*)^{-0.24}$
	40.18	0.85 ± 0.11	16.23 ± 0.12	$k_1 = 23.4$ (kg · mm$^{-2.11}$ · s$^{0.11}$)
	83.33	0.59 ± 0.08	17.80 ± 0.44	$k_2 = 2.82$ (kg · mm$^{-1.76}$)
	163.55	0.37 ± 0.13	19.70 ± 0.52	$r_1 = -0.991, r_2 = -0.993$
(b) Sn-Zn eutectic alloy				
6.52	8.33	2.23 ± 0.21	15.38 ± 0.28	$H_V^* = k_3 \mathrm{V}^{0.08}$
	16.32	1.84 ± 0.14	15.89 ± 0.60	$H_V^* = k_4\ (\lambda^*)\ ^{-0.18}$
	41.48	1.30 ± 0.23	16.35 ± 0.31	$k_3 = 21.73$ (kg · mm$^{-2.08}$ · s$^{0.08}$)
	81.96	0.96 ± 0.12	17.60 ± 0.29	$k_4 = 5.01$ (kg · mm$^{-1.82}$)
	165.13	0.63 ± 0.08	19.78 ± 0.20	$r_3 = -0.944, r_4 = -0.987$
(c) Bi-Cd eutectic alloy				
4.73	8.27	1.81 ± 0.09	16.70 ± 0.61	$H_V^* = k_5 V^{0.09}$
	16.52	1.49 ± 0.12	17.15 ± 0.35	$H_V^* = k_6\ (\lambda^*)^{-0.21}$
	40.99	1.08 ± 0.09	18.26 ± 0.73	$k_5 = 24.84$ (kg · mm$^{-2.09}$ ·s$^{0.09}$)
	81.66	0.76 ± 0.18	19.90 ± 0.29	$k_6 = 4.29$ (kg · mm$^{-1.79}$)
	167.32	0.51 ± 0.12	21.70 ± 0.18	$r_5 = -0.979, r_6 = -0.996$

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