The effect of Mg content on microstructure in Al-12wt. %Zn-x Mg Alloy

M. A. Suárez*[1], B. Campillo[1-3], R. A. Rodríguez-Diaz[1], O. Alvarez-Fregoso[2], J. A. Juárez-Islas[2]

[1] Facultad de Química, Universidad Nacional Autónoma de México (UNAM),
Circuito Exterior S/N, Cd. Universitaria, CP. 04510. México D.F.
*msuarez@iim.unam.mx

[2] Instituto de Investigaciones en Materiales, (UNAM),
Circuito Exterior S/N, Cd. Universitaria, C.P. 04510, México, D.F.

[3] Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México (UNAM),
Av. Universidad s/n Col. Chamilpa, Cuernavaca, CP 62210, Morelos, México.

ABSTRACT

The effect of adding different Mg contents to an Al-12wt.%Zn master alloy was experimentally investigated. The Al-Zn-Mg alloys were unidirectionally solidified as a function of solidification parameters, temperature gradient G_L, solidification front velocity V, and composition C_0. The alloys were solidified with a constant temperature gradient (G_L=2500K/m) in the solidification front velocity range from $4X10^{-6}$m/s to $1.7X10^{-4}$m/s. The resulting microstructure was characterized to investigate the effect of solidification front velocities and composition on primary dendrite arm spacing, volume percentage of eutectic in interdendritic regions and τ intermetallic phase in α-Al matrix. Theoretical models for the dendrite arm spacing and dendrite tip radius have been compared with the experimental observations.

Keywords: aluminum alloys, dendrite arm spacing, solidification, predictions, microstructure.

RESUMEN

El efecto de la adición de diferentes contenidos de Mg a una aleación maestra Al-Zn-Mg fue investigado experimentalmente. Las aleaciones Al-Zn-Mg fueron solidificadas unidireccionalmente como una función de los parámetros de solidificación; gradiente de temperatura G_L, velocidad del frente de solidificación V, y la composición química C_0. La aleación fue solidificada con un gradiente de temperatura constante (G_L=2500K/m) en el rango de velocidades del frente de solidificación desde $4X10^{-6}$m/s hasta $1.7X10^{-4}$m/s.

La microestructura resultante fue caracterizada para investigar el efecto de la velocidad del frente de solidificación y la composición química sobre el espaciamiento dendrítico primario, el porcentaje del volumen de eutéctico en las regiones interdendriticas y la fase intermetalica τ, en la matriz α-Al. Los modelos teóricos para el espaciamiento dendrítico primario y el radio de la punta de la dendrita han sido comparados con las observaciones experimentales.

Palabras clave: aleaciones de aluminio, espaciamiento dendrítico, solidificación, predicciones, microestructura.

1. Introduction

Dendritic structures are frequently observed during the solidification of alloys in which several unidirectional studies have been carried out to predict the growth conditions for development of the instability at the solid-liquid interface and characterize the microstructural features [1-3]. It has been documented [4] that convection during solidification has a significant effect on the microstructural parameters, such as the dimension of λ_1. To minimize the convection in the alloys during solidification, it is necessary not only to have a hydrodynamic density gradient, but also a horizontal density gradient close to zero in the Bridgman method. One way to maintain this condition is having a solid-liquid interface macroscopically planar at all times. A Macroscopic planar interface can be obtained using specimens with diameters less than or equal to 4mm as has been reported by H. Jones [5]. In addition, during the solidification of a thin sample (i.e. <4mm in diameter) through a large temperature gradient, heat flow occurs radially, this may allow the

velocity of the solid-liquid interface to be equal to the withdrawal of the crucible [5].

In unidirectional solidification experiments, solidification variables such as the solidification front velocity, V, and the temperature gradient, G, can be independently controlled in order to study the dependence of the microstructural parameters (dendrite tip radius, R, primary spacing, λ_1, secondary spacing, λ_2) [6].
One of the most important quantities used to describe the solidified dendritic microstructure in unidirectional solidification is the primary dendrite arm spacing [7]. Theoretical models to characterize the cell-primary dendrite arm spacing λ_1 as a function of V, G and the composition C_0, have been proposed by Hunt [8], Kurz-Fisher [9], Trivedi [10] and Hunt-Lu [11].
Hunt [8] and Kurz-Fisher [9] have proposed theoretical models to characterize λ_1 during steady-state growth conditions. The representative equations of these two models are given respectively as

Hunt model

$$\lambda_1 = 2.83[m(k-1)D_L\Gamma]^{0.25} C_0^{0.25} V^{-0.25} G^{-0.5} \quad (1)$$

Where m, is the liquidus slope, k is the partition coefficient, D_L is the diffusion coefficient in liquid and Γ is the Gibbs-Thomson coefficient.

Kurz-Fisher model

$$\lambda_1 = 4.3[m(k-1) D_L\Gamma/k^2]^{0.25} C_0^{0.25} V^{-0.25} G^{-0.5} \quad (2)$$

The other model to predict λ_1 as a function of G, V and C_0 was proposed by Trivedi [10] as a modification of the Hunt model, given by

$$\lambda_1 = 2.83[m(k-1) D_L\Gamma L]^{0.25} C_0^{0.25} V^{-0.25} G^{-0.5} \quad (3)$$

Where L is a constant that depends on the harmonic perturbations [12].

The purpose of the present work is to experimentally study the effect of the solidification front velocity, V, and the Mg content on microstructural parameters, mainly on primary dendrite arm spacing, λ_1, in unidirectionally solidified Al-5.3at.%-xMg alloy and to compare the results with the theoretical models.

2. Experimental procedure

Alloys of Al-12% Zn-4.5% Mg, Al-12% Zn- 6% Mg and Al-12% Zn-7.6% Mg (in wt.%), are identified in the phase diagram of Figure 1[13], as A, B and C, respectively. The alloys were prepared from high purity (99.99%) aluminum, zinc (99.9%) and magnesium (99.9%) by melting them into a vacuum induction furnace under a constant flux of argon and casting them into a copper mould of cavity dimension of $2.5X10^{-2}$m thick, $5X10^{-2}$m wide and 0.12m high. In order to produce material suitable for the unidirectional solidification experiments, rods of $3X10^{-3}$m in diameter and 0.12 m of length were fabricated directly from the ingots, which were poured into cylindrical graphite crucibles. The samples were unidirectionally solidified by using a modification of the Bridgman technique for crystal growth.

During the unidirectional solidification experiments, a period of 25 minutes at 373 K above the liquidus temperature of the alloy was allowed for the apparatus to reach thermal equilibrium; the liquid alloy was unidirectionally solidified at a selected withdrawal velocity in the

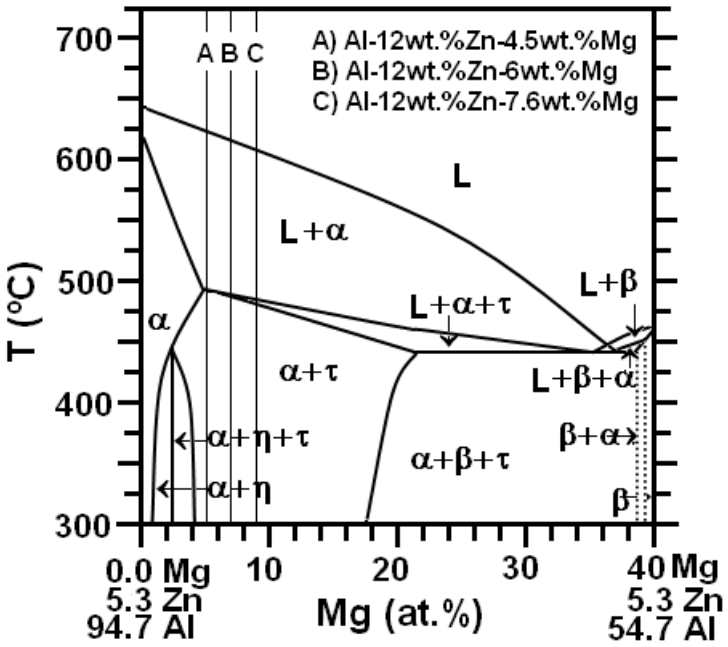


Figure 1. Vertical section of ternary Al-Zn-Mg phase diagram [13]. The vertical lines show the magnesium content added to the Al-12wt.% Zn master alloy.

range of $4X10^{-6}$ to $1.7X10^{-4}$m/s with a temperature gradient of 2500 K/m, which was measured experimentally using two thermocouples type K inserted directly into the sample separated by a distance of 1cm from tip to tip. The longitudinal and the traverse sections of the specimens were grounded from 600 to 1200 mesh grit, polished with alumina 1 μm and etched in Keller´s reagent (1ml HF, 1.5ml HCl, 2.5ml HNO_3 and 95ml H_2O) for 0.5 minutes and examined in optical microscope (OM), scanning electron microscope (SEM) and transmission electron microscope (TEM).

The primary dendrite arm spacing, λ_1, in solidified microstructures were measured by averaging the distances between the nearest two dendrite tips. In this method at least 50-200 λ_1 values were measured in both sections for each specimen.

3 Results and discussion

Figure 1 shows the vertical section at constant 12wt.% (5.3at.%) Zn of the Al-Zn-Mg phase diagram [13], where the vertical lines indicate the Mg content added to the Al-12wt. %Zn master alloy. The microstructures are constituted mainly by columnar dendrites of α-Al with small τ ($Al_2Mg_3Zn_3$) precipitates and eutectic (α+τ) in interdendritic regions, as is shown in Figure 2 and in agreement with the work of Alvarez et al. [14].

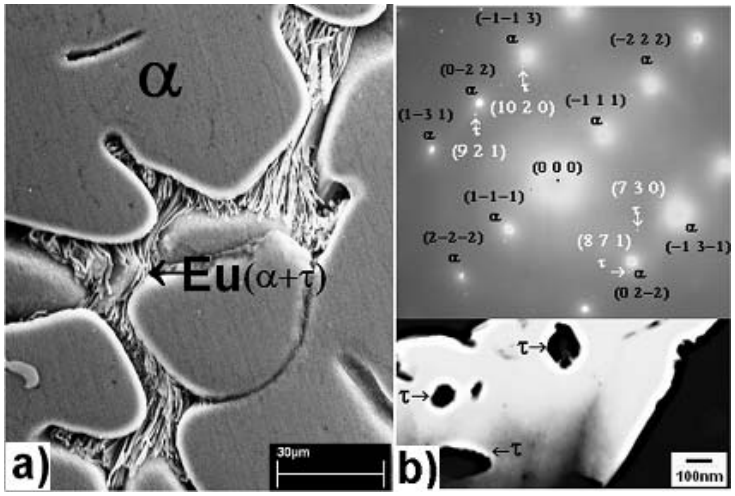


Figure 2. A representative microstructure observed in Al-Zn-Mg alloys. Bottom right hand side shows τ precipitating in α- Al matrix and left hand side shows the eutectic observed in interdendritic regions.

Figure 3 shows a series of representative micrographs of alloy A unidirectionally solidified in the solidification front velocity range of $4X10^{-6}$ to $1.7X10^{-4}$m/s, where a refinement on the microstructure as the front velocity increases is observed. Regarding primary dendrite arm spacing, it is observed that it decreases from $2.5X10^{-4}$m to $1.23X10^{-4}$m, as the solidification front velocity is increased.

The effect of Mg content produced a decrease of λ_1 obtaining values of $2.05X10^{-4}$ to $1.05X10^{-4}$ m and of $1.95X10^{-4}$ to $9.3X10^{-5}$ m for the alloys with contents of 6 and 7.6wt.%Mg, respectively, in the solidification front velocity range under study.

On the other hand, the individual effect of V and V plus Mg content produced an increase in the amount of eutectic in interdendritic regions obtaining a minimum value of 8.4 Vol% in alloy A at $V=4X10^{-6}$ m/s, and a maximum value of 25 Vol% in alloy C at $V= 1.7X10^{-4}$ m/s. In the same way, an increment was obtained regarding the amount of τ intermetallic phase in α-Al, presenting a value of 0.25Vol% in alloy A at $V=4X10^{-6}$m/s and a maximum value of 1.95Vol% in alloy C at $V=1.7X10^{-4}$m/s.

In order to compare the experimental results of λ_1 with the prediction of theoretical model, the Kurz-Fisher model for dendrite tip radius [9] was applied to evaluate the primary dendrite arm spacing as a function of V and C_0.

To predict λ_1, the liquidus slope (m_L= -1.45K/at.%) and the partition coefficient (k=0.687) were obtained from the equilibrium phase diagram in the L+α+τ region, that is the last region to solidify. Values for $D_{L,\ Zn}=8.8x10^{-8}m^2/s$ and $D_{L,\ Mg}=9.45x10^{-9}m^2/s$ were taken from references [16, 17], $\Gamma_{Zn}=1.52x10^{-7}$Km and $\Gamma_{Mg}= 9.87x10^{-7}$Km were derived from the thermodynamic data for the Al-Zn-Mg system reported in reference [18].

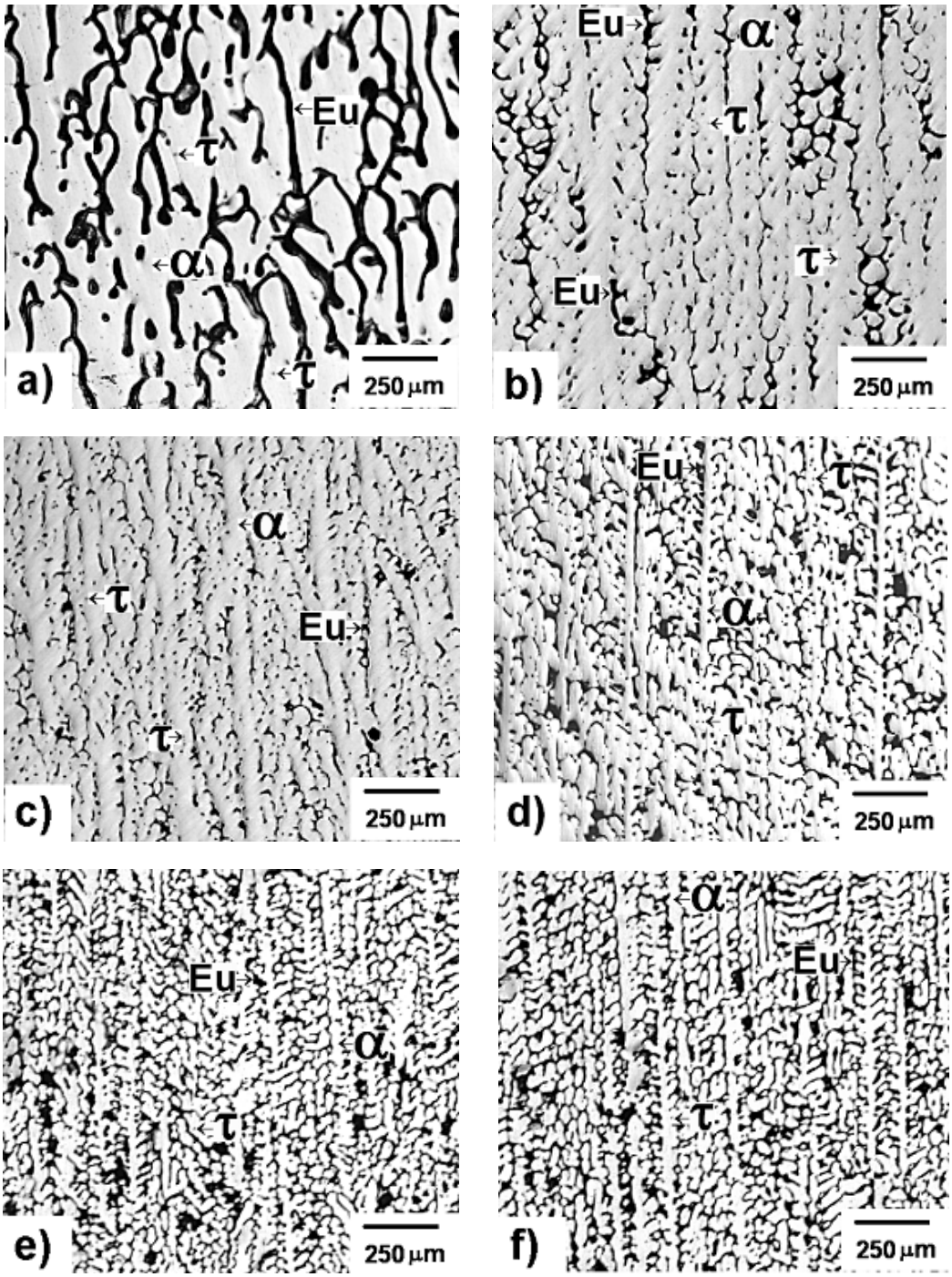


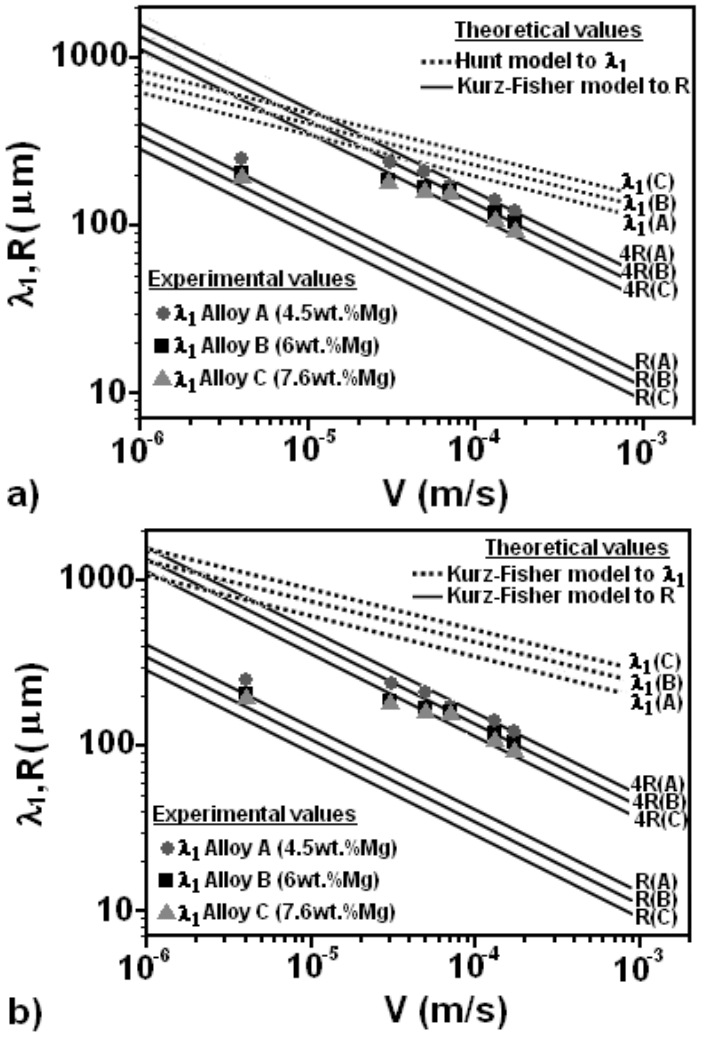
Figure 3. Dendritic structures of unidirectionally solidified Al-12wt.%Zn-4.5wt.%Mg alloy with constant G_L (2500K/m) for solidification front velocities of a) $4X10^{-6}$m/s, b)$3X10^{-5}$m/s, c) $5X10^{-5}$m/s d) 7X10-5 m/s, e) $1.3X10^{-4}$m/s, f)$1.7X10^{-4}$m/s.

These data, together with an experimental value of G_L= 2500K/m, were fed into equations 1 to 4. Fig. 4a to 4c show, for the three different Mg contents in Al-12wt.%Zn master alloy, measurements of λ_1 as a function of V and are compared with predictions of R (see Equation 4), 2R and 4R as a function of V according to Eq.(4).

Measurements of the primary dendrite arm spacing fall within the range $R<\lambda_1<4R$ and show the same dependences on Mg content and V as are predicted for R. The experimental results for λ_1 show good agreement with the dependence on V and C_0 predicted by Equation (4), whereas Equations 1-3 predict an increase in λ_1 with an increase in C_0.

$$R = 2\pi [D_L\Gamma/m(k-1)]^{0.5} C_0^{-0.5} V^{-0.5} \qquad (4)$$

Equation for tip radius predicts that it will decrease parabolically with an increase in both V and C_0 [15], in contrast, with the models previously mentioned (Equations 1-3), it predicts a decrease in λ_1 as V increases, and it predicts an increase of λ_1 as content Mg increases.



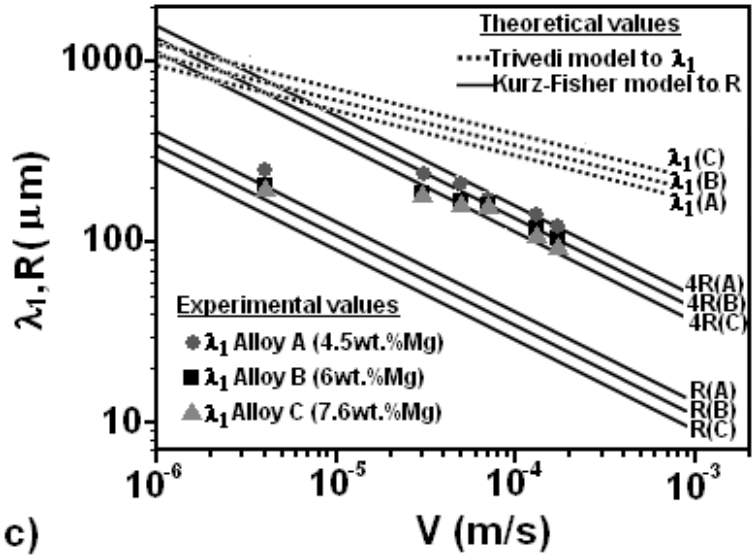


Figure 4. Experimental primary dendrite arm spacing λ_1 as a function of solidification front velocity V for (●)A (Al-12wt.%Zn-4.5wt.%Mg), (■)B (Al-12wt.%Zn-6wt.%Mg) and (▲)C (Al-12wt.%Zn-7.6wt.%Mg) alloys and comparison with theoretical models. The dotted lines show the predictions based on the following models: a) Hunt; b) Kurz-Fisher and c) Trivedi, while the full lines indicate the predicted dendrite tip radius R, with 2R, 4R according to Eq. (4).

4. Conclusion

The primary dendrite spacing of Al-12wt.%-xMg alloys decreases gradually as the solidification front velocity, V, and the Mg content increasing. Increasing the amount of magnesium in the alloy causes an increase in both eutectics (α+τ) in interdendritic regions and τ intermetallic phase on α-Al matrix. The experimental results of λ_1 were in good agreement with the theoretical values predicted by the dendrite tip radius model of Kurz-Fisher as a function of solidification front velocity V; however, it did not predict a decrease λ_1 as a function of alloy composition. In addition, equation for tip radius predicts that λ_1 will decrease parabolically with increasing both V and C_0 [14], in agreement with our experimental results.

References

[1] Y.C. Liu, Y. Han, G.C. Yang, Y.H. Zhou, Materials Letters 59 (2005) 2915-2919.

[2] J.E. Spinelli, A. Garcia, Materials Letters 59 (2005) 1691-1695.

[3] D.M. Rosa, J.E. Spinelli, A. Garcia, Materials Letters 60 (2006) 1871-1874.

[4] M.H. Burden, D.J. Hebditch, J. D. Hunt, J. Crystal Growth 20 (1973) pp.121.

[5] H. Jones, Rapid solidification of Metals and alloys, Published by the Institution of Metallurgists Northway House, London (1982) pp. 4, 5.

[6] M. Gündüz, E. Cadirli, Materials Science and Engineering A327 (2002) 167-185.
[7] H. Kaya, E. Çadirli, K. Keşlioğlu, N. Maraşli, Journal of Cristal Growth 276 (2005) 583-593.

[8] J.D. Hunt, Solidification and Casting of Metals, The Metal Society, London, 1979, p.3.

[9] W. Kurz, D.J. Fisher, Acta Metall. 29 (1981) 11.

[10] R. Trivedi, Metall. Trans. 15A (1984) 977 .

[11] S.Z. Lu, J.D. Hunt, Metall. Trans. 27A (1996) 611

[12] S-C Huang, M.E Glicksman: Acta Metall. 29 (1981)701.

[13] D.A. Petrov, in: G. Petzow, G.E. Effemberg (Eds.) Ternary Alloys, vol.3, VCH Weinheim, Germany, 1986, p. 57.

[14] O. Alvarez, C. Gonzalez, G. Aramburu, R. Herrera, J.A. Juarez-Islas, Materials Science and Engineering A 402 (2005) 320-324.

[15] J.A. Juarez-Islas, H. Jones, Materials Letters, V19, number 9,10 (1989)322-324.

[16] N.L. Peterson, S.J. Rothman, Phys. Rev. B: Solid State 1 (1970) 3264.
[17] B.V. Deryagin, R.M. Friedland, Zh. Teca. Fiz. 18 (1984) 1443.

[18] H. Liang, Y.A. Chang, Metall. Mater. Trans. 28A (1997) 172.

Acknowledgments

The authors acknowledge the financial support from Consejo Nacional de Ciencia y Tecnología (CONACYT). We also want to thank G. Aramburo, O. Novelo, Cain Gonzalez and A.G. Lara for the technical support.

Authors Biography

Julio Alberto JUÁREZ- ISLAS

He obtained his degree in chemical metallurgical engineering in 1980 from Universidad Nacional Autónoma de México. In 1982, he obtained the graduate degree in metallurgy in the Department of Metallurgy of the University of Sheffield, England and in 1986, his doctorate degree in metallurgy in the School of Materials of the University of Sheffield, England. In April 1989, he joined the Institute of Physics in Cuernavaca as a level C associate researcher and in 1994 he was transferred to the Instituto de Investigación en Materiales of the UNAM. At the moment, he is a regular level C full-time senior research, a level 3 researcher of the National System of Researchers and a level D researcher in the academic personnel acting. Because of his involvement with the industrial sector, in 2001 he was named Coordinator of the University Program for Science and Engineering of Materials.

Octavio ÁLVAREZ- FREGOSO

Octavio Álvarez Fregoso is a senior researcher on nanostructured materials at the Universidad Nacional Autónoma de México-Instituto de Investigación en Materiales. He has a doctorate degree in science and engineering and a master´s degree in physics. His research interests include the study of properties of semiconductors, ceramics and alloys nanostructured materials, involving the use of different microscopical characterization techniques. He has authored more than 120 scientific papers and is an international referee for 14 indexed journals. He has more than 500 paper citations indexed on an international level. At present, he is a level C senior researcher, a level 2 member of the National System of Researchers and a science faculty professor.

Bernardo CAMPILLO- ILLANES

He is a graduate in chemical metallurgical engineering from the Faculty of Chemistry-UNAM, 1975. He has a specialization in foundry, and took the Pan-American Course on Metallurgy (UNAM-IPN-OAS) from 1975 until 1976. Dr. Campillo obtained a master´s degree in engineering from the University of Liverpool, England, 1982 and a doctorate degree in engineering from the Faculty of Chemistry-UNAM, 2002. He has been a full-time professor in the Faculty of Chemistry from 1982 to the date and has taught diverse classes such as physical metallurgy, thermal treatments, mechanical metallurgy, analysis of flaws, superficial treatments, etc. Also, he carries out research on diverse areas of applied physical metallurgy such as special steels, steels microalloys, alloys of Mg and Al, hard coatings, mechanical properties and processes, etc. He is a level 2 national researcher of the National System of Researchers. Dr. Campillo has published more than 45 works in journals on an international level and 25 in international conferences and national symposia. He has taught at different degree levels such as master´s and doctoral courses.

Miguel Angel SUÁREZ- ROSALES

He obtained his bachelor´s degree in metallurgical engineering from Universidad Autónoma Metropolitana (Azcapotzalco) and his master´s degree in science and engineering of materials from the Instituto de Investigación de Materiales. Recently, he completed his PhD studies in engineering at the Faculty of Chemistry (UNAM) in March 2009. His main research area is the solidification of ferrous and non ferrous alloys.

Roberto Ademar RODRÍGUEZ-DÍAZ

Dr. Roberto A. Rodríguez Díaz obtained his bachelor´s degree in mechanical engineering from the Universidad del Estado de Michoacán with the support of a scholarship provided by the university to outstanding students. He then earned his master´s degree from the Instituto Tecnológico de Morelia with the thesis entitled “Kinetic and Thermodynamic Study of the Reduction of Hematite with H2, Co and H2/Co Mixtures at Low Temperatures”. Finally, Dr. Rodríguez obtained his PhD degree from the UNAM (Universidad Nacional Autónoma de México) with the thesis entitled “Rapid Solidification Processing of FeAl Intermetallic Compounds - Microstructure and Mechanical Properties”.