Laser surface alloying of aluminium-transition metal alloys

A. Almeida(*) and R. Vilar(*)

Abstract Laser surface alloying has been used as a tool to produce hard and corrosion resistant Al-transition metal (TM) alloys. Cr and Mo are particularly interesting alloying elements to produce stable high-strength alloys because they present low diffusion coefficients and solid solubility in Al. To produce Al-TM surface alloys a two-step laser process was developed: firstly, the material is alloyed using low scanning speed and secondly, the microstructure is modified by a refinement step. This process was used in the production of Al-Cr, Al-Mo and Al-Nb surface alloys by alloying Cr, Mo or Nb powder into an Al and 7175 Al alloy substrate using a CO_2 laser. This paper presents a review of the work that has been developed at Instituto Superior Tecnico on laser alloying of Al-TM alloys, over the last years.

Keywords: **Laser surface alloying. Aluminium-Transition metal alloys**

Aleación superficial mediante láser de aluminio con elementos de transición

Resumen En el presente trabajo se estudia la aleación superficial mediante laser de aluminio con metales de transición. El cromo y el molibdeno son particularmente interesantes porque producen aleaciones de alta resistencia y por el bajo coeficiente de difusión y solución sólida en aluminio. Para producir estas aleaciones se ha seguido un procedimiento desarrollado en dos partes. En primer lugar, el material se alea usando una baja velocidad de procesado y en segundo lugar la estructura se modifica mediante un refinamiento posterior. Este procedimiento se ha empleado en la producción de aleaciones Al-Cr, Al-Mo y Al-Nb mediante aleación con laser de CO_2 de polvos de Cr, Mo o Nb en aluminio y la aleación 7175. Este trabajo es una revisión del desarrollado en el Instituto Superior Técnico de Lisboa en los últimos años.

Palabras clave: **Aleación superficial mediante láser. Aluminio. Metales de transición.**

1. INTRODUCTION

High-strength aluminium alloys are widely used for structural applications in high-performance automobiles, railway cars, airplanes and spacecraft, light ships, etc., owing mainly to their excellent mechanical strength, low specific weight, good formability and relatively low cost. However, the widespread use of these materials has been limited by their low resistance to corrosion and wear. Rapid solidification processing has played a major role in recent developments of aluminium alloys, since it promotes a general refinement of the microstructure, extension of solubility of critical alloying elements in the α-aluminium solid solution and the formation of useful metastable phases, including metallic glasses and quasicrystals (1). Since these structural modifications are often responsible for an increase in the wear and corrosion resistance of aluminium alloys, rapid solidification is being seriously considered for the preparation of high performance alloys. Amongst rapid solidification techniques, laser surface alloying (LSA) is particularly efficient at producing surface layers with improved wear and corrosion resistance, since it allows to modify the chemical composition and the microstructure to adapt surface properties to service requirements (2-4).

This paper summarizes results of a study that aims to evaluate laser surface alloying as a tool to produce corrosion resistant and hard aluminium-transition metal alloys. Chromium and molybdenum were chosen because they exhibit a tendency

(*) Instituto Superior Técnico, Dep. Engenharia de Materiais. Av. Rovisco Pais, 1096 Lisboa (Portugal).

to form supersaturated solid solutions (5-8), leading to improved corrosion, and present low diffusion coefficients and solid solubility in Al, therefore, enabling the formation of AlxTMy particles dispersed in an α-Al solid solution matrix that are inherently stable. Niobium is also a very promising alloying element to aluminium, since it leads to the formation of the hard intermetallic compound Al_3Nb, even for small concentrations (9). The substrates used in this work were commercial pure aluminium and an Al-Zn-Mg alloy of the 7000 series. The latter alloy was chosen because it is widely used in the aircraft industry but is prone to localized corrosion. Furthermore, the 7000 series alloys are particularly suitable for laser treatment, owing to their reduced tendency to overage and the possibility of strengthening by natural aging (10).

2. EXPERIMENTAL METHOD

Laser processing was performed in two steps: first, laser surface alloying (LSA) of the Al-25 % (Cr, Mo or Nb) powder mixtures into pure Al and ANSI 7175 alloy substrates, and second, laser surface remelting (LSR) the alloyed surfaces in a direction normal to the alloying direction. The alloying treatments were carried out with a CO_2 laser, using a power density and an interaction time of 1.5×105 W/cm^2 and 0.26 s, respectively. Remelting was performed using the same laser power and interaction times in the range 0.03-0.26 s. To reduce moisture the Al substrates were cleaned by sand blasting and the alloying powder was dried in an oven at 70 °C for 3 hours just before the experiments.

The laser treated samples were cross-sectioned and cut longitudinally for observation. Metallographic samples were prepared using standard techniques and etched with Keller's reagent. The microstructure was characterized by optical, scanning and transmission electron microscopy. The distribution and morphology of the intermetallic compounds were studied by SEM, using backscattered electron images of unetched samples. The phases present were identified by X-ray diffraction and electron diffraction and chemical analysis was performed using electron probe microanalysis (EPMA). Microhardness measurements were made with a Vickers indenter, under a 100 g load. Each hardness value reported is the average of ten measurements.

The corrosion resistance of the samples laser alloyed with Cr and Mo and the substrates was evaluated by anodic polarization tests, using a 3 % NaCl deaerated solution. The polarization tests were performed in a three-electrode cell. The work electrode was the specimen under study, the reference electrode was a saturated calomel electrode and the auxiliary electrode was platinum foil.

3. RESULTS AND DISCUSSION

3.1. General features of alloys

After LSA many Cr, Mo and Nb particles remain undissolved (partially or totally) (fig. 1). This behavior is explained by the difference in melting point between these TM and aluminium and by their low solubility in molten aluminium. The partially dissolved particles are surrounded by a TM-rich layer of intermetallic compounds. Cracks often nucleate in this layer and propagate across the material. These cracks result from the difference between the thermal expansion coefficients of α-aluminium solid solution and of the intermetallic compounds. The laser alloyed layers are chemically and structurally heterogeneous, showing zones enriched in TM and zones depleted in these elements. Moreover, they present considerable porosity (fig. 1) that is due to the release of hydrogen during solidification. To eliminate porosity and homogenize the surface layers the samples were laser remelted.

After remelting the structure of the alloyed layers is homogenized and the pores and undissolved particles are eliminated. In fig. 2 a cross-section of an Al-Cr alloy typical of the alloys produced in this work is depicted. The alloyed layer (A) and the remelted layer (R) can be observed. The depth of the remelted layers increases with increasing laser power and decreasing scanning speed (fig. 3). When the remelted layer is thinner than the alloyed one, some pores remain in the non-remelted material.

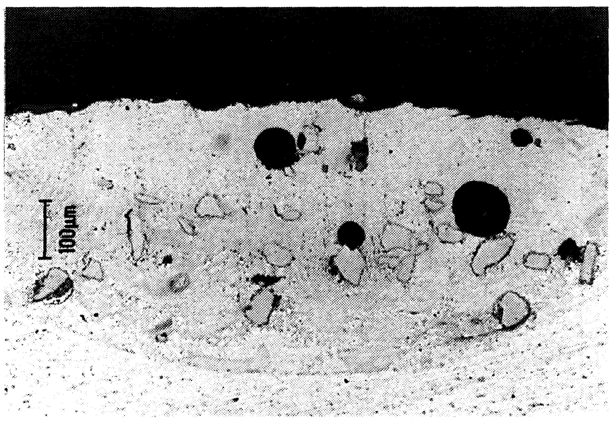

FIG. 1.— Cross-section of Al-Cr alloy produced by LSA.

FIG. 1.— Sección transversal de la aleación Al-Cr producida por aleación superficial por láser.

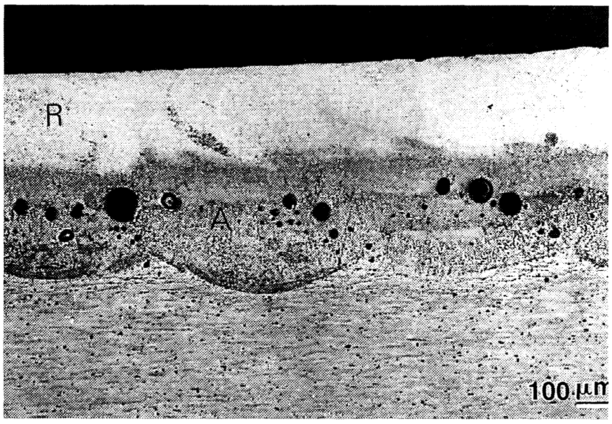

FIG. 2.— Cross-section of Al-Cr alloy after remelting.

FIG. 2.— Sección transversal de la aleación Al-Cr tras el proceso de refusión superficial por láser.

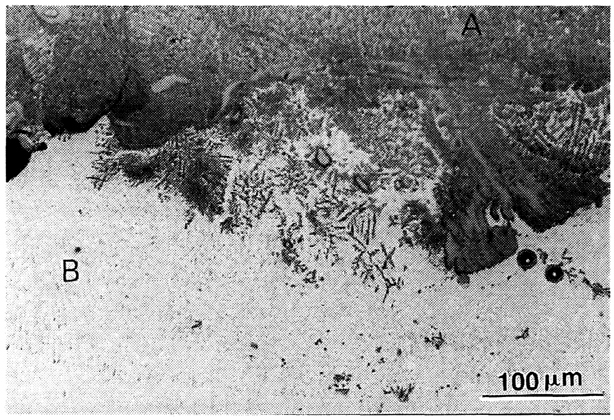

FIG. 4.— Cross-section of Al-Nb alloy showing deep segregation of Al at the bottom.

FIG. 4.— Sección transversal de la aleación Al-Nb producida por aleación superficial por láser, mostrando segregación de aluminio.

The pores can be completely eliminated if an appropriate choice of processing parameters is made.

The examination of the cross-section of Al-Nb alloys (fig. 4) reveals a strong segregation of niobium leading to the formation of two different zones: a top layer, about 700 μm thick, where the niobium concentrated forming a niobium-rich alloy (A), and a bottom layer that is formed essentially by resolidified aluminium solid solution (B).

The average chemical composition of the alloyed and remelted layers determined by electron probe microanalysis is depicted in table I. In 7175 alloy there are significant losses of Mg and Zn by vaporization (about 50 %), which increase with decreasing scanning speed and with increasing laser power (2). The losses of alloying elements are more significant in the alloyed and remelted layers than in the layers that were only alloyed, due to the fact that the material was melted twice.

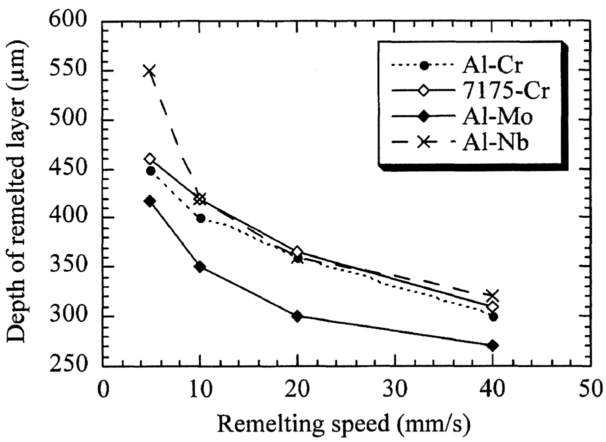

FIG. 3.— Remelted layer depth variation with scanning speed.

FIG. 3.— Variación de la profundidad de capa (tras refusión) con la velocidad de procesado.

3.2. Microstructure

The structure of the Cr and Mo-alloyed layers (A) consists of intermetallic compounds in a matrix of α-aluminium solid solution. In Al-Cr and 7175-Cr alloys these intermetallic compounds appear with two different morphologies: isolated blocky particles and long faceted needles, a microstructure similar to that reported by Luft et al. (11) for an Al-Cr alloy submitted to laser surface melting. In the remelted layer (R), if the solidification rate during remelting is similar to that used for alloying there is no significant change in the morphology of the intermetallics; they form a dense network of needles, but finer than in the alloyed layer. However, for higher solidification rates during remelting the microstructure becomes very fine and its morphology changes drastically. The structure presents a cellular equiaxed morphology, with θ-Al7Cr, η-$Al_{11}Cr_2$ and ε-Al_4C intermetallics organized radially around

TABLE I.– Composition of alloys produced by LSA and remelting

TABLA I.– Composición de las aleaciones producidas por LSA y refusión.

Alloy	Al-Cr	7175-Cr	Al-Mo	Al-Nb
Composition (wt.%)	8 ± 1.8 Cr	5 ± 1.4 Cr 12 ± 1.8 Cr	5 ± 1.6 Mo 8 ± 1.5 Mo	52 ± 4 Nb

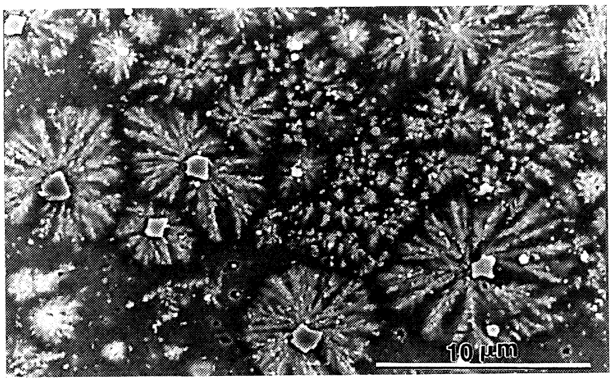

FIG. 5.— Microstructure of remelted layer (R) of Al-Cr alloy

FIG. 5.— Microestructura de la aleación Al-Cr tras la refusión superficial por láser.

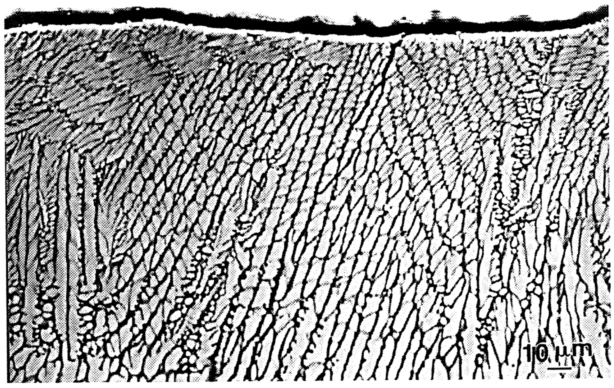

FIG. 7.— Microstructure of Al-Nb alloy after remelting.

FIG. 7.— Microestructura de la aleación Al-Nb tras la refusión superficial por láser.

primary cubic particles (fig. 5). The solidification path of these alloys was discussed in detail in previous papers (2, 12). The solubility of Cr in aluminium is increased to 0.6 at. % after the laser treatment.

In the Al-Mo alloys the intermetallic compounds appear with different morphologies: isolated blocky particles and long faceted needles (or plates). After remelting, the intermetallic compounds are very homogeneously distributed and present a dendritic morphology (fig. 6). The average size of their particles decreases with increasing scanning speed. The only intermetallic compound found by X-ray diffraction was Al_5Mo. However, this intermetallic is observed in different allotropic forms, depending on its temperature of formation (13), and all these forms seem to be present in the samples studied here. The Mo content in the matrix is 0.9 at. %.

In the Nb alloys the structure of the top niobium-rich zone (A) consists of dendrites of an intermetallic compound and α-Al solid solution in the interdendritic regions. The intermetallic compound was identified as Al_3Nb by X-ray diffraction. The constitution of this Nb-rich layer is not modified by remelting but its structure is refined (fig. 7). A comparison of the relative intensity of the aluminium and Al_3Nb peaks in X-ray diffractograms obtained for alloyed and alloyed and remelted samples shows that remelting produces a decrease in the volume fraction of α-Al solid solution. This effect is probably due to the complete melting of niobium particles that were only partially dissolved during alloying and subsequent incorporation of niobium in the surface layer resulting from the remelting treatment. The microstructures observed are compatible with the Al-Nb phase diagram but it is not clear that a peritectic reaction has occurred, as predicted by that phase diagram.

FIG. 6.— Microstructure of remelted layer (R) of Al-Mo alloy.

FIG. 6.— Microestructura de la aleación Al-Mo tras la refusión superficial por láser.

3.3. Hardness

The hardness of the alloys is higher in the remelted layers than in the alloyed ones and it varies in the ranges: 110-220 HV for Al-Cr, 170-320 HV for 7175-Cr, 65-350 HV Al-Mo and 500 to 650 HV for Al-Nb alloys. The increase of hardness depends on the content of alloying element in the alloy and also on the remelting speed (fig. 8). Alloys with higher content of alloying element present a higher fraction of intermetallic compounds and therefore a higher hardness. For alloys of similar composition the hardness increases with the remelting speed. Higher scanning speeds lead to finer particles/dendrites and, consequently, to harder structures. The hardnesses obtained for the Cr and Mo-alloys are higher than those reported by previous authors (14), a discrepancy that is explained by the fine dispersion of intermetallics formed during remelting,

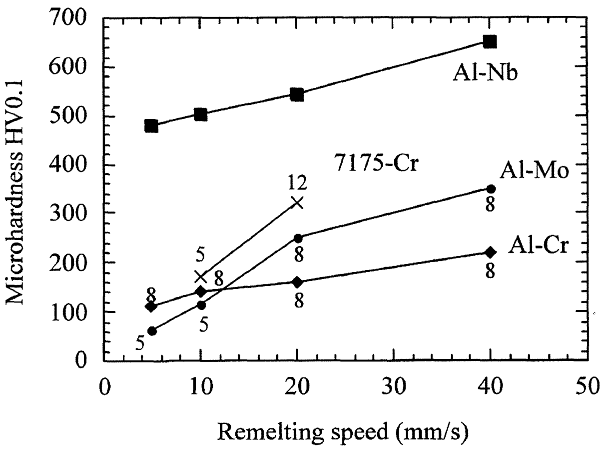

FIG. 8.— Hardness variation with remelting scanning speed. The numbers indicate the mean TM content in the alloy.

FIG. 8.— Variación de la dureza con la velocidad de refusión. Los números indican la media de los elementos de transición presentes en la aleación.

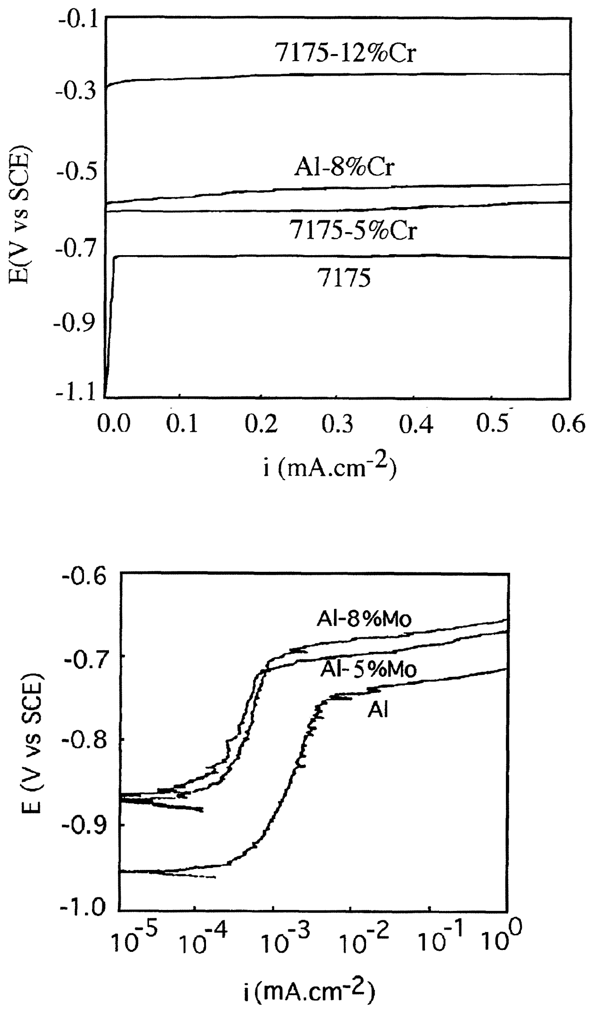

FIG. 9.— Anodic polarization curves for Al-Cr, 7175-Cr and Al-Mo alloys.

FIG. 9.— Curvas de polarización anódicas para las aleaciones de Al-Cr, 7175-Cr y Al-Mo.

since the hardness values obtained in the alloyed layers are similar to the ones reported by these authors.

In the Nb alloys, the high hardness values result from the large volume fraction of Al_3Nb present in the structure and also from the refinement of the microstructure resulting from the remelting treatment and are similar to those found in alloys produced by laser cladding (15). Despite the brittleness of Al_3Nb intermetallic compound (16), no cracks were observed in Al-Nb alloys and this is probably due to the existence of the thin interdendritic film of α-Al solid solution. The aluminium solid solution is soft and ductile and contributes to a better accommodation of stresses.

3.4. Corrosion resistance

Anodic polarization curves for aluminium and 7175 alloy before and after laser alloying are presented in fig. 9. The pitting potential of untreated 7175 alloy is –730 mV while in the Cr-alloyed layers it increases up to –270 mV for 12 wt. % Cr in the alloyed layer. These results show that laser surface alloying improves the pitting resistance of the Cr-alloyed layers. This improvement depends on the chromium content in the laser alloyed layer and is more significant for 7175 alloy than for Al. The higher the amount of chromium in the alloyed layer, the higher the pitting potential is, since the formation of CrOOH and/or Cr_2O_3 enhances the passive film formed. This film is less soluble in acid solutions than the film containing only aluminium oxide and thus a higher potential is needed to propagate the pits.

The pitting potential of the molybdenum-alloyed layers is only slightly enhanced (about 35-40 mV). This improvement is due to the formation of a passive film containing MoO_2 that is less soluble in acid solutions than the film containing only aluminium oxide. However, this enhancement is less significant than the one observed for samples alloyed with chromium.

The results obtained suggest that alloying with chromium is interesting for corrosion applications, while all three alloying elements tested may find application to increase the wear resistance of aluminium alloys. On the basis of the higher hardness values obtained and the absence of cracks, niobium is probably the most promising alloying element for applications where wear resistance is critical.

Furthermore, since the increase in hardness observed in these alloys is due to the formation of stable intermetallic compounds that contain an element with a low diffusion coefficient in aluminium, they should not be seriously affected by heating to moderately high temperatures. To investigate its potential, abrasive wear tests are being carried out.

4. CONCLUSIONS

1. Laser alloying with Cr, Mo or Nb powder produces very hard surface layers on aluminium and 7175 high strength alloy substrates. However, the distribution of alloying element is not homogeneous and the alloyed layers present defects like undissolved particles and pores.
2. The structural integrity of the surface layers is largely improved by laser remelting: most defects are eliminated, the material is homogenized and a fine and dense dispersion of intermetallic compound particles forms.
3. The structure consists of idiomorphic particles of intermetallics in a matrix of α-aluminium solid solution for Al-Cr and Al-Mo alloys and dendrites of Al_3Nb intermetallic compound with interdendritic α-aluminium solid solution in Al-Nb alloys.
4. The laser alloyed layers present very high hardness as compared to bulk materials produced by other techniques due to the formation of fine and dense distribution of intermetallic compounds.
5. The corrosion resistance of 7175 alloy and aluminium is significantly enhanced by LSA with Cr while there is only a slight improvement in the Al-Mo layers.

REFERENCES

(1) LAVERNIA, E.J., AYERS, J.D. and SRIVATSAN, T.S. Intern. Mater. Rev., 37 (1), 1992: 1.

(2) ALMEIDA, A., ANJOS, M.A., VILAR, R., LI, R., FERREIRA, M.G.S., WATKINS, K.G. and STEEN, W.M. Surf. Coat. Techn, 70 (2-3), 1995: 221.

(3) ALMEIDA, A. and VILAR, R. Proc. Euromat'97-5th European Conf. Adv. Materials, Processes and Applications, Vol. 3, Sarton, L.A.J.L. and Zeedijk, H.B. eds., Netherlands Society for Materials Science on behalf of The Federation of European Materials Societies, Zwijndrecht, Holanda, 1997: 95.

(4) PETROV, P., VILAR, R. and ALMEIDA, A. NATO ASI Series Vol. 307, Laser Processing: Surface Treatment and Film Deposition, Mazumder, J., Conde, O., Vilar, R. and Steen, W. eds., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1996: 565. Materials Societies, Zwijndrecht, Holanda, 1997: 95.

(5) WARLIMONT, H., ZINGG, W. and FURRER, P. Mater. Sci. Eng., 23, 1976: 101.

(6) ADKINS, N.J.E. and TSAKIROPOULOS, P. Mater. Sci. Eng., A134, 1991: 1158.

(7) BI, Y.J. and LORETTO, M.H. Mater. Sci. Eng., A134, 1991: 1188.

(8) MILLER, D.J. and FRASER, H.L. Acta Metall. Mater., 41 (1), 1993: 73.

(9) KUMAR, K. Intern. Mater. Rev., 35 (6), 1990: 293.

(10) POLMEAR, I.J. Light Alloys-Metallurgy of the Light Metals, 3rd ed., Arnold, London, 1995: 115.

(11) LUFT, U., BERGMAN, H.W. and MORDIKE, B.L. Laser Treatment of Materials, Mordike, B.L. ed., DGM Informationsgesellschaft mbH, Oberursel, Germany, 1987: 147.

(12) ALMEIDA, A., QUE, Y.Y. and VILAR, R. Scripta Met. et Mater., 33 (6), 1995: 863.

(13) SCHUSTER, J.C. and IPSER, H. Metall. Trans., 22A, 1991: 1729.

(14) LIU, P. and DUNLOP, G.L. Mater. Sci. Eng., A134, 1991: 1238.

(15) HAASCH, R., TEWARI, S., SIRCAR, S., LOXTON, C. and MAZUMDER, J. Metall. Trans., 23A, 1992: 2631.

(16) SHECHTMAN, D. and JACOBSON, L.A. Metall. Trans., 6A, 1975: 1325.