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Microstructure characterization of ceramic composites formed by controlled melt oxidation of Al-Mg-Pd alloys

M. PINKAS, N. FRAGE
Ben-Gurion University of the Negev, P.O.Box 653, Beer-Sheva, Israel
E. MANOR
Jerusalem college of engineering, P.O.Box 3566 Jerusalem, Israel
A. VENKERT
Nuclear Research Center-Negev, P.O.Box 9001, Beer-Sheva, Israel
E-mail: venkert@bgumail.bgu.ac.il

Ceramic matrix composites were produced by controlled melt oxidation of $Al_{98-x}Mg_2Pd_x$ alloys. The Pd element was chosen as an additive due to its influence on the thermodynamic conditions at the oxidation front and its effect on the surface tension of liquid aluminum. The $Al_{98-x}Mg_2Pd_x$ alloys were prepared from uniaxially cold pressed metal powders mixtures, heat-treated in an Argon atmosphere prior to the controlled oxidation process, which was conducted at a temperature of 1200°C, for 6 hours. The growth rate was evaluated according to weight gain measurements, the microstructure of the grown composites was investigated by optical microscopy and scanning electron microscopy (SEM). Micro-chemical analysis was performed using an electron microprobe analyzer (EPMA). Phase characterization was carried out using X-ray diffractometry. It was found that Pd addition increases the growth rate, the metal volume fraction and the diameter of the metal channels. Pd also promotes the formation of a uniform microstructure. The results strongly support the assumption that the wetting conditions between the melt and the Alumina grains and the thermodynamic conditions at the oxidation front have an important role in the controlled melt oxidation process.

1. Introduction

Ceramic Matrix Composites produced by direct melt oxidation of molten Al alloys can be designed to a near net shape product with high toughness, good thermal shock resistance, high stiffness, good wear resistance and high temperature stability. The high temperature oxidation of molten aluminum containing suitable alloying elements yields composite product consisting of Al_2O_3 matrix with interpenetrating three dimensional network of metal microchannels [1, 2].

During the growth process, a layered structure is formed at the upper extremity of the composite, consisting of MgO at the top surface, the Al molten alloy at the bottom and the spinel $MgAl_2O_4$ sub-layer between them [3, 4]. The bulk oxide growth mechanism involves continuous formation and dissolution of the Mg-rich oxides at the surface, diffusion of oxygen through the underlying liquid metal and epitaxial growth of Al_2O_3 on the existing composite body [5–8]. Different elements were reported to have an accelerating effect on the growth process, especially Si [1, 6, 9], which substantially reduces the activity of Mg in the liquid metal, thus increasing the driving force for dissolution of the surface oxides in the underlying metal layer [6].

The wettability between the molten alloy and the growing Alumina also has an important role in the growth process. Doping the Al-Mg alloy by suitable elements may improve the wetting of Al_2O_3 by Al and promote the impregnation of the molten metal through the matrix [1].

According to our previous thermodynamic considerations [10] Pd addition may increase the driving force for the phase transition from MgO to Al_2O_3. Pd also reduces the surface tension of liquid aluminum [11] and therefore is expected to improve the wettability in the liquid-Al/Al_2O_3 system.

In the present work the influence of palladium on the growth process and microstructural features of the composites grown from Al-Mg-Pd alloys was investigated.

2. Experimental

Metal powders mixtures of $Al_{98-x}Mg_2Pd_x$ ($x = 0.5$, 1.5, 3 at.%) were uniaxially cold pressed (40 MPa) into compacts followed by heat treatment in an Argon atmosphere at 920°C for 0.5 hour.

The purity levels (in wt.%) of the materials were: 99.95% Mg, 99.99% Pd and commercial 99.5% Aluminum powder. The main impurities in the Al were determined by spectrochemical analysis: 0.13Fe, 0.08Si, 0.012Cr, <0.02Zn, <0.02Sn, <0.02Mn, <0.02Ti.

The samples were weighted, placed in Alumina crucibles and then heated in an air atmosphere. The heating procedure was consisted of two steps: 810°C for 3 hours to ensure the spinel growth and 1200°C for 6 hours to obtain composite growth. After the growth process, the samples were cooled to room temperature and the weight gain was obtained.

Polished cross sections were characterized using optical and scanning electron microscopy (SEM). The metal volume fraction and the average diameter of the metal channels were determined by quantitative image analysis techniques. Micro chemical analysis and element distribution in the composites were performed with an electron probe microanalyzer (EPMA) using energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS) techniques. Phase characterization was carried out using X-ray diffractometry.

3. Results and discussion

A representative back scattered electrons (BSE) image of the product grown from an $Al_{98-x}Mg_2Pd_x$ alloy is presented in Fig. 1a. In this image, taken from an $Al_{96.5}Mg_2Pd_{1.5}$ alloy, three regions are revealed: the metal reservoir at the bottom, the composite bulk at the upper part and the spinel layer, about 70 μm wide, between the metal reservoir and the composite bulk. The spinel layer is very obvious at the Mg X-ray mapping shown at Fig. 1b and was found to track the metal reservoir contour. Pd X-ray mapping (Fig. 1c) reveal the Al_3Pd_2 precipitates (identified by XRD and EDS analysis) in the metal reservoir and along the metal-reservoir/spinel interface. In the microanalysis line scans (Fig. 2) taken across the metal reservoir/composite interface the spinel layer is characterized by a sharp increase in the Mg content and a decrease in the Al content. The scattered nature of the line scan within the spinel layer and the composite bulk is due to the discontinuity of the composite (e.g.: metal channels which produce high Al signal, Al_2O_3 produces Al and O signals, the spinal layer produces Mg, O and Al signals and the pores produce no signal).

Optical micrographs of polished cross sections of the composites grown from the Al-Mg-Pd alloys are shown in Fig. 3. The dark matrix is the grown Alumina and the bright areas are the metal channels. The optical micrographs at low magnification show that the microstructure of the composites grown from the Al-Mg-Pd alloys is homogenous. In each composite the ratio between the metal to Al_2O_3 volume fraction was uniform. It

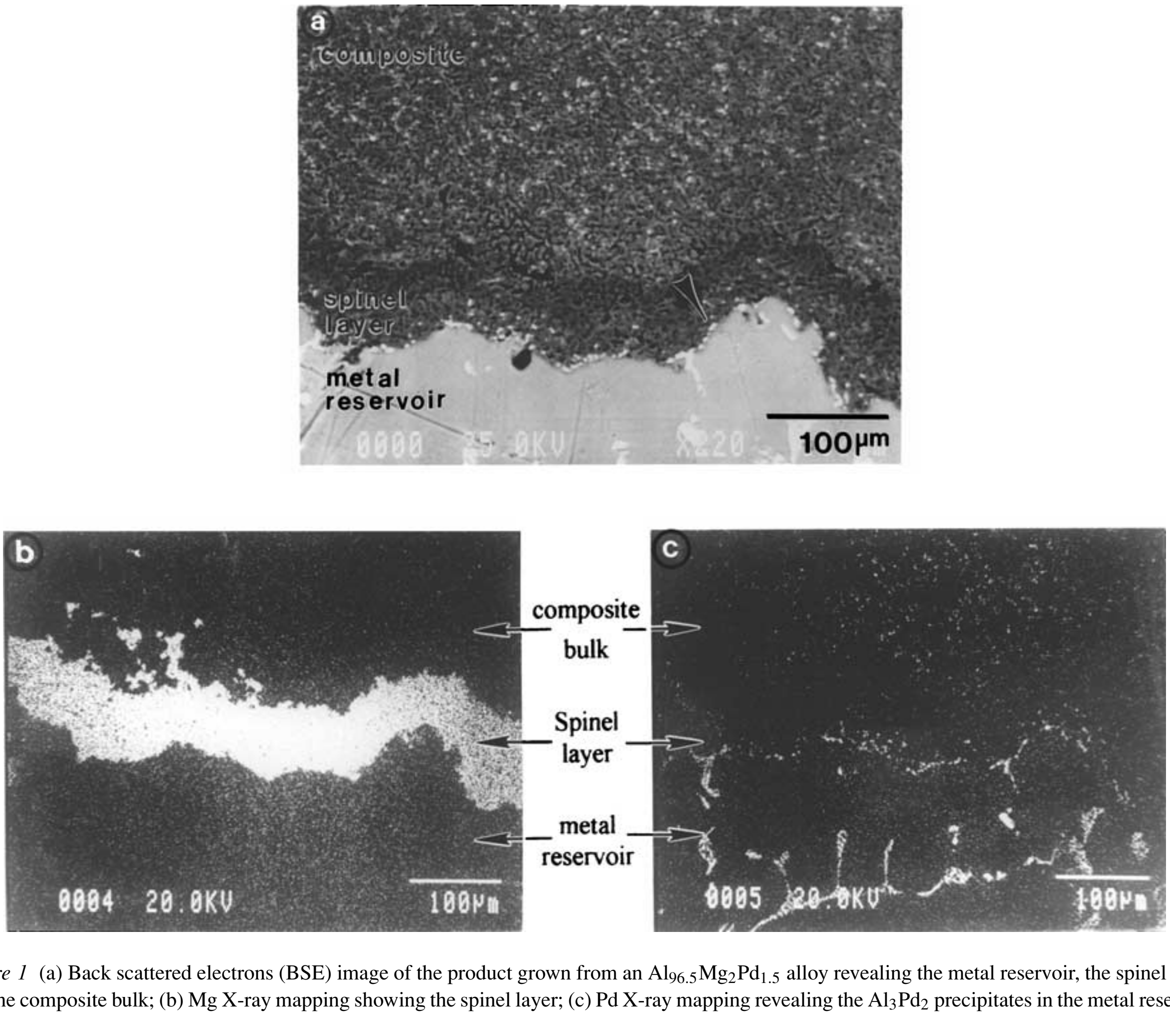


Figure 1 (a) Back scattered electrons (BSE) image of the product grown from an $Al_{96.5}Mg_2Pd_{1.5}$ alloy revealing the metal reservoir, the spinel layer and the composite bulk; (b) Mg X-ray mapping showing the spinel layer; (c) Pd X-ray mapping revealing the Al_3Pd_2 precipitates in the metal reservoir and along the metal-reservoir/spinel interface.

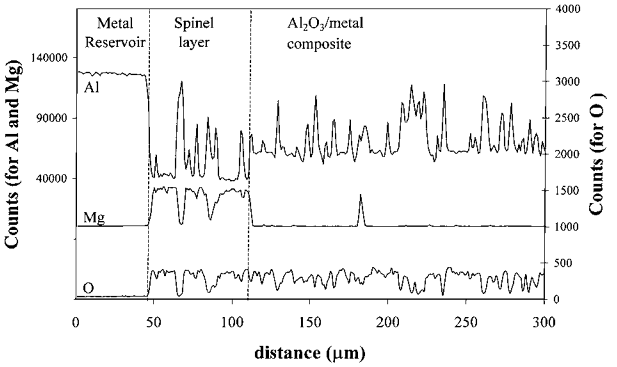


Figure 2 Microanalysis line scans of Al, Mg and O taken across the metal reservoir/composite interface layer. The Spinel layer is characterized by the sharp increase in the Mg content.

must be noted that in the composites grown from Al-Mg alloys a variation in the ceramic-to-metal ratio, along the growth direction, was observed [12, 13]. This behavior was explained by the alteration in the Mg concentration at the oxidation front, which causes oscillations in phase equilibrium from liquid/Al_2O_3/$MgAl_2O_4$ (at low Mg contents) to liquid/Al_2O_3/MgO (at high Mg contents) and vice versa. A higher ratio between Al_2O_3 and metal volume fraction is obtained when the oxygen needed to the formation of Al_2O_3 is supplied by the dissolution of $MgAl_2O_4$ rather then by the dissolution of MgO [13]. The formation of a uniform microstructure in the composites grown from the Al-Mg-Pd alloys indicates that the addition of Pd affects the thermodynamic conditions at the oxidation front in such a way that the alterations in the Mg concentration do not change the equilibrium conditions at the growth front. This assumption is supported by our thermodynamic calculations [10], which show that the addition of Pd shifts the equilibrium point between $MgAl_2O_4$ and Al_2O_3 to the higher Mg concentration range, thus enlarging the liquid/Al_2O_3/$MgAl_2O_4$ stability region in the ternary Al-Mg-O phase diagram. This enlargement of the stability region eliminates the oscillations from the liquid/Al_2O_3/$MgAl_2O_4$ equilibrium to the liquid/Al_2O_3/MgO equilibrium and the variations in the Al_2O_3/metal ratio are avoided.

Higher magnification optical micrographs (Fig. 3) combined with image analysis techniques were used to determine the porosity, metal volume fraction and the average diameter of the channels. The porosity of all the composites was estimated to be <1%. Increasing the Pd content resulted in an increased length and diameter of the metal channels and a formation of more tortuous channels. The average diameter of the metal channels in the composites grown from the alloy containing 0.5 at.% Pd was about 1 μm. In the composites grown from the alloys containing 1.5 and 3 at.% Pd the average diameter was about 3 μm (the difference in the composition had no affect the average diameter of the metal channels). The influence of the Pd content on the growth rate and on the metal volume fraction is shown in Fig 4. These results indicate that an addition of up to 1.5 at.% Pd to Al-Mg alloy sharply increases the growth rate and enlarge the metal volume fraction. A further increase of the Pd content to 3 at. % only slightly increases the growth rate and did not affect the metal volume fraction.

The wetting condition on the Alumina-liquid metal interface has an important role in the composite growth process. The increase in the driving force for wettability accelerates the transport of the metal via the channels to the reaction interface and consequently, the growth rate could be accelerated. An increase in the driving force will also enlarge the energy gain by the formation of interfaces between Al_2O_3 and metal on the expense of Al_2O_3/Al_2O_3 interfaces. The preferred formation of Al_2O_3/metal interfaces will promote the melt penetration between the Al_2O_3 grains. As a result, longer and more tortuous channels will be generated and the metal volume fraction will increase.

The driving force for the capillary penetration is the pressure difference (ΔP) across the curved surface of the meniscus. The relevant equation, when the contact angle between a ceramic and metal phases is not zero, may be written as [14]:

$$\Delta P = \frac{2(\gamma_{\mathrm{lg}} - \gamma_{\mathrm{sl}})}{r} \tag{1}$$

where γ_{lg} is the surface tension of the liquid, γ_{sl} is the interfacial tension of the liquid/solid interface and r-denotes the radius (or equivalent radius) of the capillary. The principle requirement for a large ΔP is that γ_{lg} be made as small as possible.

In order to understand the experimental results one should examine the actual wetting conditions between the melt and the Alumina grains during the controlled oxidation of the Al-Mg-Pd alloys and to try correlate these conditions to the characteristics of the oxidation product.

Since Pd does not participate in the oxidation process, its concentration in the metal channels increases during the growth process. The actual Pd concentration within the metal channels were calculated for each alloy according to Equation 2 and are presented in Table I.

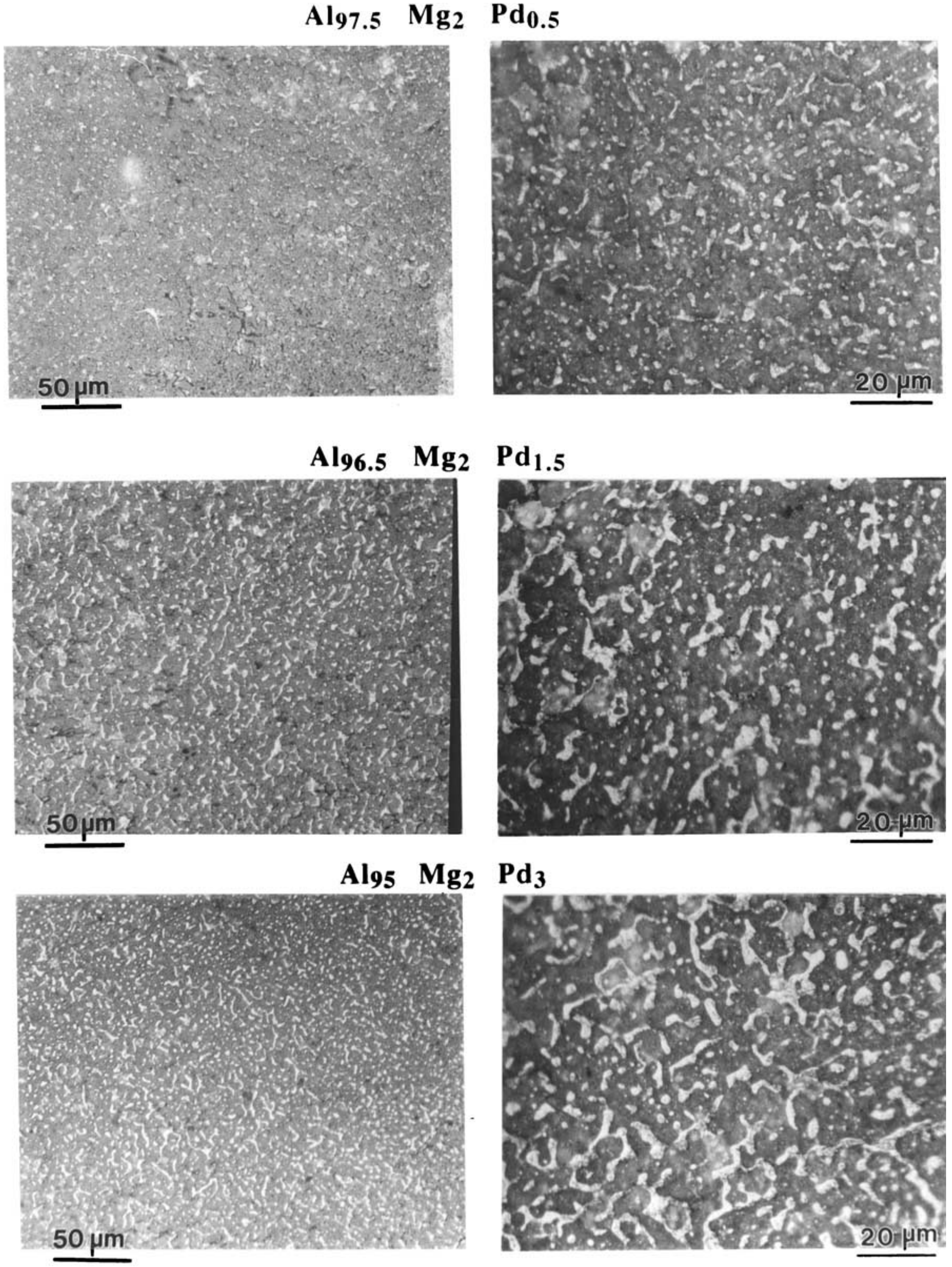
$$X_{\mathrm{a}} = \frac{X_{\mathrm{i}}}{X_{\nu\mathrm{f}} \cdot X_{\mathrm{Al_i}} + X_{\mathrm{i}}} \tag{2}$$

where X_{a} is the actual Pd content, X_{i} is the initial Pd content, $X_{\mathrm{Al_i}}$ is the initial Al content and $M_{\nu\mathrm{f}}$ is the measured metal volume fraction.

Nizhenko and Floka [11] have measured the surface tension of liquid Al-Pd alloys (γlg), as a function of the Pd content (Fig. 5). According to the reported data, Pd addition up to 8 at.% strongly decreases the surface tension of the alloys. Thus an addition of 0.5 at.% and 1.5 at.% Pd to the Al-Mg alloys (corresponding to an actual concentration of ~4.5% and ~6.5% in the metal

TABLE I Actual Pd content within the metal channels

Alloy	Metal volume (%)	Actual Pd concentration (calculated), [at.%]
$Al_{97.5}Mg_2Pd_{0.5}$	10 ± 3	4.35 ± 0.55
$Al_{96.5}Mg_2Pd_{1.5}$	20 ± 5	6.55 ± 0.65
$Al_{95}Mg_2Pd_3$	20 ± 5	12.4 ± 1.20


$Al_{97.5}$ Mg_2 $Pd_{0.5}$

$Al_{96.5}$ Mg_2 $Pd_{1.5}$

Al_{95} Mg_2 Pd_3

Figure 3 Optical micrographs of polished cross sections of the composites grown from the $Al_{98-x}Mg_2Pd_x$ alloys.

channels, respectively) are expected to improve the wetting conditions and affect the growth characteristics, as was observed in our study. The minimum value of γ_{lg} was obtained at a Pd concentration of 10%. Thus an addition of 3 at.% Pd to the Al-Mg alloy (corresponding to an actual concentration of $\sim$12%) will result in similar wetting conditions as for the alloy containing 1.5 at.% Pd. Hence, as expected, the microstructural characteristics and the growth rate of the composites grown from the alloys containing 1.5 at.% and 3 at.% Pd were very similar. The correlation between the actual wetting conditions and the growth parameters supports the assumption that the wetting conditions strongly affect the controlled melt oxidation process.

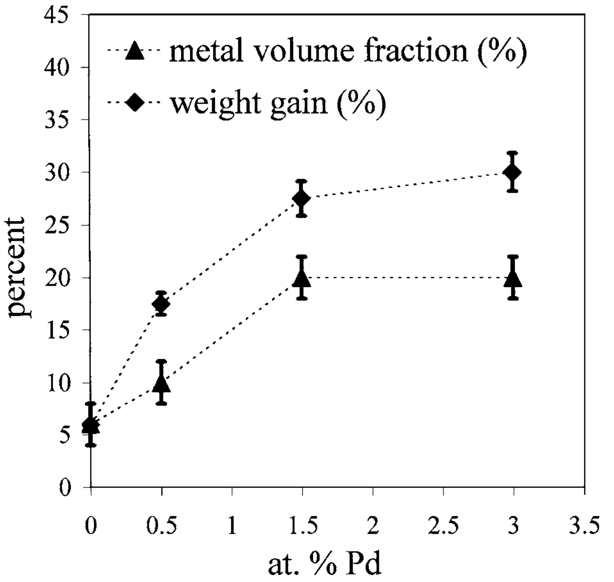


Figure 4 The influence of the Pd content on the composite growth and on the metal volume fraction.

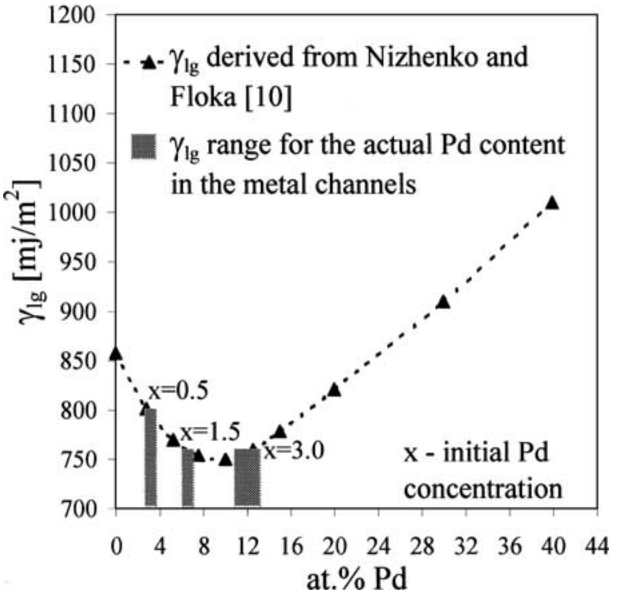


Figure 5 Surface tension of the Al-Pd alloys derived from Nizhenko and Floka [11]. The bars denote the relation between the actual Pd concentration in the metal channels to the surface tension of an Al melt with the same Pd content.

4. Summary

The effect of Pd addition to an Al-Mg alloy on the growth characteristics of composites produced by the controlled melt oxidation process was evaluated. Pd addition was found to increase the growth rate, the metal volume fraction, the diameter of the metal channels and promoted the formation of a uniform microstructure.

The uniform microstructure and the absence of variations in the ceramic-to-metal ratio within the composites was attributed the effect of Pd on the thermodynamic conditions at the oxidation front.

The results strongly support the assumption that the wetting conditions between the melt and the Alumina grains have an important role in the controlled melt oxidation process. The composites grown from the alloys having similar wetting conditions have shown similar characteristics regarding the growth rate, the metal volume fraction and the morphology of the metal channels.

The results of the present study indicate that the directed melt oxidation process can be controlled by an appropriate choice of the elements added to the basic Al-Mg alloy.

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