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PLASMA JOINING OF METAL MATRIX COMPOSITES(U) MSNW INC
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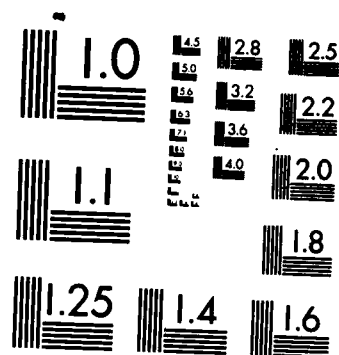
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Submitted to U.S. Army Research Office

Contract No. DAAG29-85-C-0027

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Interim Technical Report - October/November 1985

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G.H. Reynolds and L. Yang, MSNW, Inc.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Progress for the first two months of the contract period is reviewed. Aluminum-reactive metal matrix alloys for Al-SiC composite filler metals are described. Preliminary process modeling studies on constituent vaporization effects, thermochemical stability of surface oxide films, and dissolved gas evolution in-plasma are described.		

ABSTRACT

Progress for the first two months of the contract period is reviewed. Aluminum-reactive metal matrix alloys for Al-SiC composite filler metals are described. Preliminary process modeling studies on constituent vaporization effects, thermochemical stability of surface oxide films, and dissolved gas evolution in-plasma are described.

COMPOSITE POWDER PREPARATION

Rapidly solidified, inert gas atomized, aluminum-reactive metal alloy powder compositions have been ordered for use in preparation of precomposited metal matrix composite powders. The following powder compositions will be received:

1100 Al (Commercial purity)

Al - 0.5 Zr (Wt.%)

Al - 3.0 Zr

Al - 1.0 Ti

Al - 5.0 Ti

Al - 1.0 B

Following receipt of the powders, precomposited metal matrix composite powders will be prepared for initial plasma deposition studies and variation of modeling studies.



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MODELING STUDIES

Some of the physical and chemical events occurring during plasma processing of composite powders which may affect the structure and properties of the deposit have been preliminarily analyzed on the basis of thermodynamic and kinetic considerations. The initial results are described below.

1. Loss of Al Alloy Matrix by Vaporization in the Plasma.

Assuming the surface of the spherical Al droplets is clean and at a temperature of $T^{\circ}\text{K}$, the fractional loss of droplet radius $\Delta r/r$ by vaporization in a time period of t seconds, can be expressed as:

$$\frac{\Delta r}{r} = \frac{\alpha p t}{\rho r} \left(\frac{M}{2\pi R T} \right)^{1/2} \quad (1)$$

where α = vaporization coefficient ($\alpha \leq 1$)

p = vapor pressure of Al in dynes/cm² at $T^{\circ}\text{K}$

ρ = density of Al (2.7 g/cm³)

r = radius of Al droplets in cm.

R = gas constant (8.31×10^7 ergs/ $^{\circ}\text{K}$ /mole)

M = atomic weight of Al (27 g/mole)

Substituting ρ , R , and M into equation (1) we obtain:

$$\frac{\Delta r}{r} = 8.42 \times 10^{-5} \frac{\alpha p t}{(T)^{1/2} r} \quad (2)$$

Calculations of $\Delta r/r$ are performed for the following conditions:

$T = 950, 1080, 1245, 1480, 1820, 2350^{\circ}\text{K},$

$t = 10^{-2}, 10^{-3}, 10^{-4}$ seconds, and

$r = 75, 22$ microns.

These values are selected in anticipation of the ranges of the plasma deposition process parameters to be used in the experimental portion of the program. α , the evaporation coefficient, is assumed to be unity since this represents the worst case from the point of view of evaporation loss. The calculated results are shown in Table 1. It can be seen that the loss of Al alloy matrix material becomes significant only when the temperature reaches 2350°K and the residence time in plasma exceeds 10^{-3} seconds.

At 2350°K , the decrease in droplet radius is less than about 10% even for droplets of 22 microns radius if the time of residence in the plasma can be kept below 10^{-3} seconds. For a working distance of 0.3 meter and a drop velocity of Mach 1 (332 meter/second), the residence time of the droplets in the plasma should be less than 10^{-3} seconds. For droplet velocities higher than Mach 1, the residence time will be even shorter. Furthermore, since the vaporization coefficient α is usually less than unity, the actual vaporization loss should be less than shown in Table 1. The loss of Al alloy matrix material by evaporation in the plasma therefore does not appear to be a significant problem during plasma deposition processing.

Table 1

Fractional Decrease Of Al Droplet Radius As A Function
Of Temperature And Time Of Residence In Plasma

(A) Droplet Radius = 75×10^4 cm.

<u>Temperature (°K)*</u>	<u>Residence Time in Plasma</u>		
	10^{-2} sec.	10^{-3} sec.	10^{-4} sec.
950	4.85×10^{-11}	4.85×10^{-12}	4.85×10^{-13}
1080	4.55×10^{-9}	4.55×10^{-10}	4.55×10^{-11}
1245	4.24×10^{-7}	4.24×10^{-8}	4.24×10^{-9}
1480	3.89×10^{-5}	3.89×10^{-6}	3.89×10^{-7}
1820	3.51×10^{-3}	3.51×10^{-4}	3.51×10^{-5}
2350	3.08×10^{-1}	3.08×10^{-2}	3.08×10^{-3}

(B) Droplet Radius = 22×10^4 cm.

<u>Temperature (°K)*</u>	<u>Residence Time in Plasma</u>		
	10^{-2} sec.	10^{-3} sec.	10^{-4} sec.
950	1.65×10^{-10}	1.65×10^{-11}	1.65×10^{-12}
1080	1.55×10^{-8}	1.55×10^{-9}	1.55×10^{-10}
1245	1.45×10^{-6}	1.45×10^{-7}	1.45×10^{-8}
1480	1.33×10^{-4}	1.33×10^{-5}	1.33×10^{-6}
1820	1.20×10^{-2}	1.20×10^{-3}	1.20×10^{-2}
2350	1.05	1.05×10^{-1}	1.05×10^{-2}

* Vapor pressure of Al at these temperatures obtained from Reference (1).

2. Loss Of Alloying Elements By Vaporization In Plasma

Alloying elements in the Al matrix, such as Zr, Ti, or B, can be lost by selective vaporization in the plasma. Assuming the concentration of the alloying element is low (less than a few mole percent) and that the alloying element forms an ideal solution with Al, the number of atoms of the alloying element lost by vaporization $-dn_x$, in time dt from the Al alloy droplet can be expressed as

$$-dn_x = \frac{\alpha p_x x}{(2\pi m_x kT)^{1/2}} 4\pi r^2 \cdot dt \quad (3)$$

where:

α = vaporization coefficient for the alloying element,

p_x = vapor pressure of the alloying element at temperature T ,

x = mole fraction of the alloying element in Al,

r = radius of the Al droplet,

m_x = weight of the atom of the alloying element, and

k = Boltzmann constant

For dilute solutions:

$$x = \frac{n_x}{n_{Al}} \quad (4)$$

and

$$n_{Al} = \frac{4}{3} \pi r^3 c_{Al} \frac{N_o}{M_{Al}} \quad (5)$$

where:

n_x = number of atoms of the alloying element in the Al alloy droplet,

n_{Al} = number of atoms of Al in the Al alloy droplet

ρ_{Al} = density of Al (2.7 g/cc)

M_{Al} = atomic weight of Al (27 g/mole)

N_o = Avogadro's Number (6.1×10^{23} /mole)

Substituting Equations (4) and (5) into Equation (3), we obtain:

$$-\frac{dn_x}{n_x} = 1.31 \times 10^{-3} \frac{\alpha p_x}{r(M_x T)^{1/2}} \cdot dt \quad (6)$$

where M_x = atomic weight of the alloying element.

If α is taken as unity, Equation (6) can be integrated to give

$$n_x = {}^o n_x \exp \left(- \frac{1.31 \times 10^{-3} p_x t}{r(M_x T)^{1/2}} \right) \quad (7)$$

where n_x = number of atoms of the alloying element in the Al droplet after time t in the plasma, and ${}^o n_x$ = number of atoms of the alloying element in the Al droplet at $t = 0$.

Equation (7) is used to calculate n_x for Zr ($M_x = 91.22$) in an Al alloy droplet of radius equal to 22×10^{-4} cm after 10^{-2} second at 2275 °K. At 2275 °K, $p_{Zr} = 0.133$ dynes/cm²; therefore

$$n_x = {}^o n_x \exp \left(- \frac{1.31 \times 10^{-3} \times 0.133 \times 10^{-2}}{22 \times 10^{-4} (91.22 \times 2275)^{1/2}} \right) \approx {}^o n_x$$

Thus the loss of Zr from the Al alloy droplet is negligible. Similar conclusions are reached for Ti and B alloying additions in the Al alloy droplet under these conditions. Therefore the loss of these alloying elements from Al alloy droplets during their residence time in plasma does not seem to be a significant problem even at high temperatures and for relatively long residence times (10^{-2} seconds) in the plasma. The above calculations assume that the alloying element forms an ideal solution with Al. Zr, Ti, and B, however, all form intermetallic compounds with Al, indicating strong affinity between these elements and Al. Vaporization losses should therefore be even lower than those calculated on the basis of an ideal solution.

3. Loss Of The Dispersed Reinforcing Phases (SiC, ZrC or TiC) In Plasma.

SiC, ZrC and TiC dissociate at high temperatures according to the equations:



and the dissociation products may be lost by condensation in the cooler part of the system. To assess the magnitude of such loss, calculations can be made for the loss of these materials at 2300°K for a residence time of 10^{-2} seconds in the plasma.

On the basis of thermodynamic data available [Reference (2)], the equilibrium vapor pressures of Si, Zr, and Ti for reactions (8), (9), and (10) at 2300°K are calculated by using the equation:

$$\Delta F^{\circ} = -RT \ln p^2 \quad (11)$$

where ΔF° is the standard free energy change for the reaction at temperature T, R is the gas constant, and p is the equilibrium vapor pressure of Si, Zr, or Ti over the respective carbide. At 2300°K, $p_{\text{Si}} = 1.07 \times 10^{-6}$ atm, $p_{\text{Zr}} = 3.81 \times 10^{-10}$ atm., and $p_{\text{Ti}} = 1.47 \times 10^{-8}$ atm. Assuming a vaporization coefficient of unity, the loss of the thickness of carbide in time t can be calculated from these vapor pressure values by the equation:

$$\Delta l = \frac{p_x}{c_{\text{MC}}} \left(\frac{M_x}{2\pi RT} \right)^{1/2} \frac{M_{\text{MC}}}{M_x} \cdot t \quad (12)$$

where:

- l = loss of thickness of carbide in cm,
- p_x = vapor pressure of Si, Zr, or Ti in dynes/cm²,
- c_{MC} = density of carbide ($c_{\text{SiC}} = 3.20 \text{ g/cm}^3$, $c_{\text{ZrC}} = 6.70 \text{ g/cm}^3$,
 $c_{\text{TiC}} = 4.25 \text{ g/cm}^3$)
- R = gas constant ($8.31 \times 10^7 \text{ erg/}^{\circ}\text{K/mole}$),
- T = temperature in °K,
- M_{MC} = molecular weight of carbide,
- M_x = atomic weight of Si, Zr, or Ti,
- t = time in seconds

Using Equation (12) and the vapor pressures of Si, Zr, and Ti calculated from Equation (11), Δl values for $T = 2300^\circ\text{K}$, and $t = 10^{-2}$ seconds are found to be:

$$\Delta l_{\text{SiC}} = 2.34 \times 10^{-8} \text{ cm}, \quad \Delta l_{\text{ZrC}} = 2.39 \times 10^{-12} \text{ cm}, \text{ and}$$

$$\Delta l_{\text{TiC}} = 2.77 \times 10^{-10} \text{ cm}.$$

Thus the loss of these carbide dispersions is negligible even at high temperatures (2300°K) and relatively long residence time (10^{-2} seconds). Therefore the loss of the reinforcing carbide dispersion during plasma processing of precomposited powders does not appear to be a significant problem.

4. Stability of Oxide Film On The Surface Of Al Alloy Droplets In Plasma.

The precomposited Al alloy powders, like any Al powders used for the fabrication of Al matrix composites, are expected to have a surface film of Al_2O_3 . Whether this surface oxide film is stable in the plasma during plasma deposition is of great interest since this oxide film may impede the adhesion between particles in the deposited composite microstructure. It may have to be broken up by mechanical working of the deposit in order to achieve optimum mechanical properties.

The removal of the oxide surface film by vaporization has been evaluated according to the following two mechanisms



or,



The standard free energy of reaction is deduced from free energy data given in Reference (3).

For Equation (13) $\Delta F^{\circ} = 357,410 - 92.16 T$ calories per mole

For Equation (14) $\Delta F^{\circ} = 411,700 - 106.15 T$ calories per mole

The equilibrium pressures of Al_2O_3 and AlO are calculated for various temperatures by using these ΔF° values assuming no oxygen contamination in the carrier gas. The results are shown in Table 2.

It can be seen that Equation (14) yields a higher dissociation pressure than Equation (13). However, the rate of removal of the Al_2O_3 surface film according to Equation (14) is still not high enough to lead to appreciable cleaning of the droplet surface. At $2300^{\circ}K$ and for a residence time as long as 10^{-2} seconds in the plasma, the loss of thickness of the Al_2O_3 surface film, calculated by using $p_{AlO} = 5.55 \times 10^{-7}$ atm. and an equation similar to Equation (12), is only 1.02×10^{-8} cm. Since the carrier gas usually contains some oxygen impurities, the loss of the surface Al_2O_3 film should therefore be even lower than this value.

5. Removal Of Hydrogen From The Al Matrix During Heating In Plasma

It would be extremely useful if the hydrogen present in the Al alloy matrix could be removed during heating in the plasma. The Al matrix alloy powder can contain as much as several ppm of hydrogen which can cause porosity in the consolidated products. The loss of hydrogen from the molten Al alloy droplet

Table 2

Equilibrium Pressures of Al_2O and AlO over Al_2O_3 At Various Temperatures

$T (^{\circ}\text{K})$	$p_{\text{Al}_2\text{O}}(\text{atm.})$	$p_{\text{AlO}}(\text{atm.})$
1000	9.68×10^{-30}	2.41×10^{-27}
1500	1.04×10^{-16}	2.46×10^{-15}
2000	3.41×10^{-10}	2.48×10^{-9}
2300	1.21×10^{-7}	5.55×10^{-7}

during residence in the plasma is calculated by using the following equation [Reference (4)] assuming zero concentration of hydrogen at the surface of the droplet because of the rapid removal of the surface hydrogen atoms by the carrier gas.

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(- \frac{n^2 \pi^2 D t}{r^2} \right) \quad (15)$$

where:

F = fractional loss of hydrogen from the Al alloy droplet,

D = diffusivity of hydrogen in aluminum in cm^2/sec ,

t = time of diffusion in seconds,

r = radius of the Al alloy droplet in cm.

F values have been calculated for an Al droplet at its melting point ($D = 7.6 \times 10^{-4} \text{ cm}^2/\text{sec}$., Reference [5]), with $r = 75 \times 10^{-4} \text{ cm}$ (upper particle size limit for the precomposited powder) and $22 \times 10^{-4} \text{ cm}$ (lower size limit), and for $t = 10^{-2}$, 10^{-3} , and 10^{-4} . The results are shown in Table 3.

It can be seen that the fractional removal of hydrogen from the smaller droplets is complete at $t = 10^{-2}$ seconds and approximately 90% complete at $t = 10^{-3}$ seconds. For the larger droplets, 10^{-2} seconds is required for removing 84% of the hydrogen. To remove all the hydrogen from the larger droplets at $t = 10^{-3}$ seconds or less, the droplets have to be heated to temperatures higher than the melting point of Al.

Table 3

Removal Of Hydrogen From Molten Al Alloy Droplets In Plasma

Droplet Radius (cm)	Residence Time In Plasma (Sec.)	Fractional Removal of Hydrogen From Al Droplets
75×10^{-4}	10^{-2}	0.84
	10^{-3}	0.35
	10^{-4}	0.12
22×10^{-4}	10^{-2}	1.00
	10^{-3}	0.87
	10^{-4}	0.38

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