Modeling of Oxide Dispersions in Reactively Processed Al

YAOJUN LIN, YIZHANG ZHOU, and ENRIQUE J. LAVERNIA

The present article reports on the formulation of an analytical model to predict the size scale of oxide dispersoids in Al alloys processed by a reactive atomization and consolidation synthesis approach. The proposed model formulation is primarily based on the assumption that all of the strain energy in the oxides is used to create interfaces between the oxide dispersoids and the matrix. The following predictions are made, based on the preceding analytical model. First, the diameter or thickness of oxide discs (the oxide dispersoids are assumed to have a disc geometry) constantly decreases with increasing strain. However, when exposed to the range of strain levels that are present in conventional processes (*e.g.*, less than 100:1, 90 pct, and 90 pct of area, thickness, and height reduction ratio in extrusion, rolling, and forging, respectively), the oxide discs will fracture into sizes that are on the order of tens of nanometers in both diameter and thickness. Ultra-high strain levels (*e.g.*, more than 18.5 of total strain) are required to obtain ultra-fine oxide discs whose diameter and thickness are on the order of nanometers. Second, working temperature appears to exert only limited influence on the final diameter or thickness of the oxide discs. The size scale of oxide dispersoids predicted on the basis of the analytical model presented herein is in good agreement with the available experimental observations.

I. INTRODUCTION

IN spray forming, a stream of molten metal is disintegrated into a dispersion of micrometer-sized droplets by energetic gas jets (typically inert), and then the droplets are directed toward a substrate where they accumulate into a bulk material of predetermined geometry.^[1,2] Convective cooling of the droplets during flight, in combination with the presence of a limited amount of liquid phase during impingement, generally promote the formation of a microstructure that is characterized by limited segregation, as well as relatively fine equiaxed grains, in the 10 to 100 μ m range.^[1,2] Noteworthy is the observation that these microstructural characteristics have been widely reported for numerous alloy systems, regardless of the spray forming parameters or apparatus employed.^[1,2]

Reactive atomization and deposition (RAD) was originally developed in an effort to take advantage of the kinetic conditions that are present during spray processes (e.g., high surface area and elevated temperatures) to promote the formation of *in-situ* dispersoids.^[1,3-6] In RAD, a reactive gas mixture is used instead of an inert gas, depending on the thermodynamics of the relevant system; target dispersoids include oxides, nitrides, and carbides. Oxide dispersoids are of particular interest given the affinity for oxygen of most metal systems, in combination with their inherent stability. One of the primary motivations to study this synthesis approach is to improve thermal stability and strength of spray-deposited materials. The strength, as well as other characteristics (e.g., thermal stability) of deposited materials, can be improved via dispersion strengthening and grain size refinement arising from fine oxide dispersoids. The presence of these particles can also enhance thermal stability via retardation of recrystallization and grain growth at elevated temperatures.^[7,8,9]

Inspection of the available literature, however, shows that the oxides that are typically present in as-spray-deposited materials exhibit size scales that range from tenths of micrometers to a few micrometers,^[6,10] leading to a limited effectiveness in retarding grain boundary migration and providing dispersion strengthening. One mechanism that may be invoked to refine the size scale of the dispersoids further is strain-induced fracture during forming. This suggestion is particularly applicable in the case of spray-formed materials given the presence of porosity that typically necessitates elimination *via* some type of forming (*e.g.*, extrusion, rolling, forging, *etc.*).

In related work, Dai et al.^[3] and Kim et al.^[11] investigated the size and distribution of oxide phases in 5083 Al processed by RAD followed by subsequent extrusion and rolling and in 7079 Al processed by powder metallurgy followed by extrusion/rolling, respectively. However, despite the availability of preliminary information, no quantitative analysis has heretofore been attempted to establish a relationship between the oxide size and working parameters. Accordingly, the objective of the present study is to formulate an analytical model that can be used to predict the final dispersoid size in RAD Al alloys under various working parameters. In the present study, 5083 A1 (Al-4.4Mg-0.7Mn-0.15Cr (in wt pct)) is selected as the model material. The oxide phases that are present in 5083 Al processed by RAD using N₂-O₂ gas mixtures are identified using transmission electron microscope (TEM). The present article departs from the premise that there is a finite volume fraction of dispersed oxide phases in the RAD processed material. The kinetic and thermodynamic considerations that led to the formation of the oxide phases during RAD are discussed in other publications.^[12,13]

II. FORMULATION

A. States of Stress and Strain in the Matrix

As mechanical working processes, rolling, extrusion, and forging are widely used to manufacture products with various geometries. However, in order to maintain the problem tractable, input and output geometries selected in the present

YAOJUN LIN, Postgraduate Researcher, YIZHANG ZHOU, Associate Researcher, and ENRIQUE J. LAVERNIA, Professor, are with the Department of Chemical Engineering and Materials Science, University of California–Davis, Davis, CA 95616. Contact e-mail: yjlin@ucdavis.edu

Manuscript submitted July 2, 2004.

_	Extrusion, and Forging	
Working Process	Input Geometry	Output Geometry
Rolling	plate/strip	plate/strip
Extrusion Forging	round billet/disc	round bar round billet/disc

Table I. Input and Output Geometry during Rolling,

study are listed in Table I. During any one of rolling, extrusion, and forging, three-dimensional states of stress and strain are present in the deformed metal. The spatial orientational relationships between the three principal stresses^[14] and the corresponding working tools (*i.e.*, rolls in rolling, die in extrusion, and hammer and anvil in forging) are illustrated in Figure 1.^[15] In actual practice, the width of a rolled plate is much





 σ_{zm}

 $\sigma_{\rm ym}$

Anvil

Eym

 \mathcal{E}_{zm}

larger than the thickness, leading to negligible lateral spread. As a consequence, the rolled material exhibits a plane-strain state. During forging, the friction between the deformed metal and the tools (anvil and hammer) results in the vertical profile to become barrel shaped.^[15] For simplicity, it is assumed that, at different points inside the deformed metal, the corresponding strain is the same. Moreover, at any one point inside the deformed metal, $d\varepsilon_{xm} = d\varepsilon_{zm}$. Since the value of plastic strain is much larger than that of elastic strain in a deformed metal, elastic deformation can be safely neglected. For plastic deformation of the metal matrix, the volume change is nearly zero.^[16] As a result, the algebraic sum of the normal strains corresponding to the three principal planes equals zero; *i.e.*, $d\varepsilon_{xm} + d\varepsilon_{ym} + d\varepsilon_{zm} = 0$.^[15] The relationships of the normal strains in the metal matrix during rolling, extrusion, and forging are listed in Table II.

B. Behavior of Oxide Dispersoids

First, oxide dispersoids are fragmented in the stress and strain fields generated during a working process. Once the oxides are fractured, the shape of the fragmented oxide dispersoids will be irregular. In the present formulation, the oxide particles are assumed to fragment into disc-shaped dispersoids. Given this assumption, the fragmentation process is described as follows. Initially, prior to working (*i.e.*, in the as-deposited material), the diameter of a disc-shaped oxide, L_0 (approximately tenths of a micrometer to a few micrometers^[13]), is larger than the cor-

responding thickness l (approximately tens of nanometers^[12]). Under this condition, it is assumed that (1) cracks in the oxide discs propagate along the direction normal to the surfaces of the oxide discs, and (2) after fracture, new oxide dispersoids still exhibit a disc-shaped geometry with a diameter smaller than that of previous oxide discs and with the same thickness as that of the previous oxide discs (l). Fragmentation of oxide dispersoids in RAD 5083 Al described in Section III can be used to verify this fracture mode. In this material, diameters of oxide dispersoids are about 0.5 to 5 μ m at the beginning of extrusion (*i.e.*, in the as-deposited material)^[10] and about 20 to 100 nm after extrusion, as shown in Figures 4(a) and (c), indicating a decrease in the diameter of oxide dispersoids. The decrease in diameter of oxide dispersoids occurs under larger diameter of oxide dispersoids than thickness of oxide dispersoids (13.0 to 18.4 nm, as shown in Table V). From a theoretical standpoint, this fracture mode minimizes the increase in oxide/matrix interfacial area when the diameter of oxide discs is larger than the thickness of oxide discs. This fracture mode is termed as mode I fracture, as shown in Figure 2.

The diameter of oxide discs decreases with further fragmentation (*i.e.*, increasing amount of strain in the matrix) until the diameter of the oxide discs becomes smaller than the thickness (*l*). After this instant, it is then assumed that (1) fracture occurs along the planes normal to the axes of the oxide discs at the central points of the axes, *i.e.*, the thickness of the new oxide discs (l/2) is a half of that of the previous oxide discs; and (2) after fracture, the diameter of new oxide discs remains

Table II. Characteristics of Stress and Strain during Rolling, Extrusion, and Forging

Working Process	Relationship between Strains in the Matrix and the Oxide	Relationship between Stress and Strain in the Oxide
Rolling	$\varepsilon_{xm} = -\varepsilon_{ym}, \varepsilon_{zm} = 0; \varepsilon_{xo} = -\varepsilon_{yo}, \varepsilon_{zo} = 0$	$\sigma_{xo} = \frac{E_o}{1+v} \varepsilon_{xo}, \sigma_{yo} = \frac{E_o}{1+v} \varepsilon_{yo}, \sigma_{zo} = 0$
Extrusion	$\varepsilon_{ym} = \varepsilon_{zm} = -\varepsilon_{xm}/2; \ \varepsilon_{yo} = \varepsilon_{zo} = -\varepsilon_{xo}/2$	$\sigma_{xo} = \frac{E_o}{1+v} \varepsilon_{xo}, \sigma_{yo} = \frac{E_o}{1+v} \varepsilon_{yo}, \sigma_{zo} = \frac{E_o}{1+v} \varepsilon_{zo}$
Forging	$\varepsilon_{xm} = \varepsilon_{zm} = -\varepsilon_{ym}/2; \ \varepsilon_{xo} = \varepsilon_{zo} = -\varepsilon_{yo}/2$	$\sigma_{xo} = \frac{E_o}{1+v} \varepsilon_{xo}, \sigma_{yo} = \frac{E_o}{1+v} \varepsilon_{yo}, \sigma_{zo} = \frac{E_o}{1+v} \varepsilon_{zo}$



Steps 1) The diameter of oxide discs, L, is larger than the thickness of oxide discs, l; 2) the fragmentation of oxide discs occurs according to the following mode: diameter, L, is reduced to diameter, L', while the thickness remains unchanged, l.

Fig. 2-Schematic of the fracture mechanism of the oxide discs during mode I fracture.

unchanged before all of the previous oxide discs experience fracture normal to the axes. Experimental support of this fracture mode is provided by reports of fragmentation of the carbide network during forging of as-cast high-speed steels,^[17] where dendritic carbides (larger length than diameter) are fragmented into granular carbides, indicating a decrease in the length of carbides. In addition, the validity of this fracture mode is supported by the fact that this fracture mode minimizes the increase in oxide/matrix interfacial area when the diameter of oxide discs is smaller than the thickness of oxide discs. This fracture mode is termed "mode II" fracture, as shown by steps 1 and 2 in Figure 3. If the amount of strain is sufficient, all previous oxide discs (thickness of l) will experience fracture normal to the axes (step 3 in Figure 3). Then, the diameter of oxide discs becomes larger than the new thickness (l/2) and mode I fracture starts once again (step 4 in Figure 3).

It is difficult to accurately evaluate the local stresses and strains associated with the fragmentation in the oxides. In order to render this problem tractable, it is assumed that the corresponding strain increments in the matrix and in the oxide are inversely proportional to the modulus of elasticity of the matrix and of the oxide. The assumption is based on the fact that the material with a lower stiffness is deformed more easily than that with a higher stiffness. On the basis of this assumption, the relationships between strains in the oxides (*i.e.*, ε_{xo} , ε_{yo} , and ε_{zo} , corresponding to strains in x-, y-, and z-axis directions) can be obtained, as shown in Table II. Because the oxides are brittle materials, the "maximum normal strain theory of failure" can be used as a criterion to predict when fracture of the oxides occurs.^[16] Typically, the tensile strength of an oxide is approximately one order of magnitude lower than its compressive strength.^[18] In other words, the fracture tensile strain is approximately one order of magnitude lower than the fracture compressive strain. Moreover, Table II shows that there exist the following relationships between tensile and compressive strains inside the oxides: (a) tensile strain equals the compressive strain during rolling, (b) tensile strains are twice the value of the compressive strains during extrusion, and (c) tensile strains are half of the value of the compressive strains during forging. As a result, oxide fracture occurs once the tensile strain reaches the fracture strain during forming (i.e., during the working process), safely neglecting plastic deformation in the oxides (brittle materials). Once fracture occurs, the strain will begin to cumulate in the oxide particles until the next fracture process is triggered.



Steps 1) The diameter of oxide discs, L, is smaller than the thickness of oxide discs, l; 2) a part of oxide discs are fragmented along the planes normal to the axes of the oxide discs at the central points of the axes, leading to L > l/2, while the diameter remains unchanged, L; 3) all of oxide discs are fragmented along the planes normal to the axes of the oxide discs at the central points of the axes while the diameter remains unchanged, L; 4) diameter, L, is fragmented into diameter, L', while the thickness remains unchanged, l/2.

Fig. 3-Schematic of the fracture mechanism of the oxide discs during mode II fracture.

Second, coarsening may occur for the fragmented oxide dispersoids during a working process. There are two possible approaches for the oxide dispersoids to coarsen during a working process: dissolution-precipitation^[19] and bonding of dispersoids that collide with each other.^[20] The oxides usually have so low a solubility in the matrix AI^[21] that they are unlikely to dissolve in the matrix. As a result, the fragmented oxides will not coarsen through a dissolution-precipitation mechanism. The oxides selected as the reinforcements for dispersion strengthening have much higher melting points (e.g., 2053 °C, 2800 °C, 2334 °C, 2420 °C, and 3050 °C for Al_2O_3 , MgO, Cr_2O_3 , Yb₂O₃, and ThO₂, respectively^[18]) than the working temperature range of Al alloys (less than 600 °C^[22]). In the range of the above working temperatures (*i.e.*, less than 0.5 T_{om} , where T_{om} is the melting point of an oxide), bonding of collided oxide dispersoids with a conventional size (e.g., more than 1 μ m) cannot occur.^[20] However, for extremely fine dispersoids (*e.g.*, less than $100 \text{ nm}^{[23]}$), a significant percentage of atoms are associated with disordered surface regions, leading to an increase in the chemical activity of dispersoids and a significant decrease in the bonding temperature (so called "scaling effect"). For oxide dispersoids less than 100 nm, an equation developed by Alymov et al.^[23] can be used to describe the dependence of the bonding temperature, T_b (K), on the average size of dispersoids, $\overline{d}(m)$:

$$T_b = 0.3T_{om}[1 - 4\gamma_{sl}H^{-1}\rho_o^{-1}(\bar{d} - 2h)^{-1}] \qquad [1]$$

where γ_{sl} (J m⁻²) is the interfacial tension between the solid and liquid oxide, $H(J kg^{-1})$ is the latent heat of fusion of the oxide, ρ_0 (kg m⁻³) is the density of the oxide, and $h = 2 \times$ 10^{-9} m is the thickness of melted layer on a oxide dispersoid's surface. Hence, corresponding to a working temperature, there exists an average size of oxide dispersoids for bonding. At the average size, bonding of collided oxide dispersoids makes it impossible to further decrease the dispersoid size. In other words, the average size is also the minimum average size of oxide dispersoids at a given temperature. The strain corresponding to the minimum average size is the maximum efficient strain to break oxide dispersoids. Thus, the strain during a working process should be selected to be lower than the strain corresponding to the minimum average size in order to ensure the efficiency of the working process. According to the preceding analysis, the fragmented oxide dispersoids will not coarsen in the range of strain values selected herein.

C. Size Scale of Oxide Discs vs Strain

Fragmentation of the oxide particles leads to an increase of interfacial area between the metal matrix and the oxides. During a working process, the increment of interfacial area per unit volume of oxides relative to that prior to working (*i.e.*, in the as-deposited material), ΔS (m²/m³), can be evaluated using the following equation (Appendix):

$$\Delta S = \frac{2^n (1+f_n)}{l} + \frac{4}{L} - \frac{4}{L_0} - \frac{2}{l}$$
[2]

where l (m) and L_0 (m) are the thickness and the diameter of oxide discs initially prior to working (*i.e.*, in the as-deposited material), n is fracture times along the planes normal to the

axes of oxide discs, f_n is the volume fraction of oxide discs with thickness of $l/2^n$ (the volume fraction and the thickness of the rest oxide discs are $(1-f_n)$ and $l/2^{n-1}$, respectively), and L (m) is the diameter of the oxide discs during working. The increased interfacial energy is converted from strain energy input in the oxide. In the present study, it is assumed that all of the strain energy in the oxide during working is used to create the new interface between the matrix and oxides. Since the oxide dispersoids do not coarsen in the range of selected strains, the following relationship between the strain energy per unit volume of the oxide, $\Delta U (J m^{-3})$, and the increment of interfacial area per unit volume of the oxides (ΔS) can be obtained: $\Delta U = \gamma_{m-o} \Delta S$, where γ_{m-o} (J m⁻²) is the interfacial energy between the oxide and the metal matrix ($\Delta U >$ $\gamma_{m-o}\Delta S$ if oxide dispersoids coarsen). Combining with Eq. [2], the relationship between the size scale of oxide dispersoids (*i.e.*, n, f_n , and L) and the strain energy per unit volume of the oxide (ΔU) is given by

$$\frac{2^{n}(1+f_{n})}{l} + \frac{4}{L} - \frac{4}{L_{0}} - \frac{2}{l} = \frac{\Delta U}{\gamma_{m-o}}$$
[3]

During a working process, strain energy per unit volume of the oxide (ΔU) as a function of strain will be analyzed in detail as follows.

Because the oxides are brittle materials, plastic deformation can be safely neglected and only elastic deformation occurs in the oxide particles. As a result, three-dimensional stresses and strains in oxides generally satisfy Hooke's law. Assuming that oxides are isotropic materials, the following equations give the relationships between stresses and strains:^[16]

$$\sigma_{xo} = \frac{E_o}{(1+v)(1-2v)} [(1-v)\varepsilon_{xo} + v(\varepsilon_{yo} + \varepsilon_{zo})] \quad [4a]$$

$$\sigma_{yo} = \frac{E_o}{(1+v)(1-2v)} [(1-v)\varepsilon_{yo} + v(\varepsilon_{zo} + \varepsilon_{xo})]$$
 [4b]
$$E_o$$

$$\sigma_{zo} = \frac{E_o}{(1+v)(1-2v)} [(1-v)\varepsilon_{zo} + v(\varepsilon_{xo} + \varepsilon_{yo})] \quad [4c]$$

where σ_{xo} , σ_{yo} , and σ_{zo} (Pa) are the three normal stresses in the oxide, and E_o (Pa) and v are the modulus of elasticity and Poisson's ratio of the oxide. Inserting the relationships among strains in Table I into Eqs. [4a] through [c], the stress-strain relationships for rolling, extrusion, and forging can be obtained, as listed in Table II.

Taking extrusion as an example, the input strain energy per unit volume of the oxide during the working process is analyzed as follows. When ε_{xo} reaches the fracture tensile strain of the oxide (ε_{tl}), fracture of oxides occurs. The strain energy per unit volume of the oxide during the cycle of $\varepsilon_{xo} = 0$ to $\varepsilon_{xo} = \varepsilon_{tl} (u_e)$ is given by

$$u_{e} = \int_{0}^{-\varepsilon_{d}/2} \sigma_{yo} d\varepsilon_{xo} + \int_{0}^{-\varepsilon_{d}/2} \sigma_{zo} d\varepsilon_{zo} + \int_{0}^{\varepsilon_{d}} \sigma_{xo} d\varepsilon_{yo} = \frac{3E_{o}\varepsilon_{ll}^{2}}{4(1+v)}$$
$$= \frac{3\sigma_{l}^{2}}{4(1+v)E_{o}}$$
[5]

During the cycle of $\varepsilon_{xo} = 0$ to $\varepsilon_{xo} = \varepsilon_{tl}$, the increment of the corresponding strain in the matrix (ε_{xm}) is estimated in terms of the aforementioned assumption between strain and modulus

of elasticity: $d\varepsilon_{xm} = (E_o/E_m)d\varepsilon_{xo}$, where E_m (Pa) is the modulus of elasticity of the metal matrix. By integrating the two sides of this equation, the following relationship can be obtained: $\Delta \varepsilon_{xm} = (E_o/E_m)\varepsilon_{tl}$. For the matrix, the total strain in the *x*-axis (elongation direction), $\varepsilon_{xm,t}$ is given by $\varepsilon_{xm,t} = \ln \psi$, where ψ is the area reduction ratio. The total fracture times $N_{\text{total}} = \varepsilon_{xm,t}/\Delta \varepsilon_{xm}$. The total strain energy per unit volume of the oxide during extrusion $(U_e \text{ (J m}^{-3}))$ is given by

$$U_e = N_{\text{total}} u_e = \frac{3\sigma_t E_m}{4(1+\nu)E_o} \ln \psi$$
 [6a]

Using arguments similar to those presented previously for extrusion, the total strain energy per unit volume of the oxide for rolling (U_r (J m⁻³)) and for forging (U_f (J m⁻³)) can be obtained as

$$U_r = -\frac{\sigma_t E_m}{(1+\nu)E_o} \ln (1-\omega)$$
 [6b]

$$U_f = -\frac{3\sigma_t E_m}{2(1+\nu)E_o} \ln \left(1-\delta\right)$$
 [6c]

where ω and δ are the thickness and height reduction ratio during rolling and forging, respectively.

III. EXPERIMENTAL

The experimental procedure can be described as follows. First, 5083 Al deposits were produced *via* RAD under the processing parameters listed in Table III. Details of the RAD experiments can be found in References 3 and 24. Then, the deposited materials were extruded with area reduction ratio of 9:1 at 400 °C. Extruded bars were then annealed at 565 °C to 570 °C for 1 hour and water quenched, in order to allow any intermetallic phases present (*i.e.*, Al₃Mg₂, Al₆Mn, and Al₁₈Cr₂Mg₃^[25]) to dissolve into 5083 Al matrix^[24] and to facilitate identification of oxide phases. Oxides in the extruded and annealed 5083 Al were investigated using a transmission electron microscope (PHILIPS* CM20 TEM) operated at 200 kV.

*PHILIPS is a trademark of Philips Electronic Instruments Corp., Mahwah, NJ.

IV. RESULTS

A. Experimental Results

Figures 4(a) and (b) show a bright-field image and the corresponding selected area diffraction (SAD) pattern, respectively. Figure 4(c) is the TEM dark-field image from the spots on the second ring in Figure 4(b). By indexing the diffraction pattern in Figure 4(b), the oxide phase is identified as MgO. No other types of oxides (*e.g.*, Al₂O₃, MnO, and Cr₂O₃) can be detected. This result is consistent with published studies,^[26,27] which demonstrate that oxides in Al-Mg alloys with Mg concentration above 3.2 wt pct consist primarily of MgO. On the basis of the line intercept length in a series of TEM brightfield (*e.g.*, Figure 4(a)) and dark-field (*e.g.*, Figure 4(c)) images, the average size of MgO dispersoids is approximately 50 nm.

B. Simulation Results

The mechanical and physical properties of MgO and 5083 Al used in the following simulation are given in Table IV. In the calculation that follows in Sections 1 and 2, the oxide discs from 40 μ m droplets in the as-deposited material (the calculated diameter $L_0 = 253.0$ nm and the calculated thickness l = 15.6 nm^[12,13]) are chosen for the study of further fragmentation during working processes. Forty micrometers is the calculated medium diameter of atomized droplets under the conditions listed in Table III.^[12] According to the aforementioned analysis, strain during a working process should be selected such that the calculated sizes of fragmented oxide discs are larger than the average size for bonding (determined by Eq. [1]). In order to compare the calculated size of an oxide disc with the average size for bonding to determine the strain range, the effective diameter of the oxide disc is assumed to represent the size of the oxide disc. The effective diameter of an oxide disc is defined as a diameter of a sphere with a volume equivalent to the oxide disc.

1. The calculated size scale of oxide discs vs strain

Figure 5 shows the calculated diameter and thickness of oxide discs as a function of area, thickness, and height reduction ratio in extrusion, rolling, and forging at a process temperature 400 °C (a typical hot-working temperature for Al alloys^[22]). The calculated diameter of oxide discs is seen to monotonically decrease with increasing strain, whereas the calculated thickness of oxide discs remains the same as the calculated initial thickness (l = 15.6 nm) and mode II fracture does not occur in the following range of strains: up to 100:1, 90 pct, and 90 pct of area, thickness, and height reduction ratio in extrusion, rolling, and forging, respectively. Even at room temperature (20 °C), which should favor the formation of a small diameter/thickness (as discussed in the subsequent text), mode II fracture does not occur and both the calculated diameter and thickness of oxide discs exceed 10 nm (27.7, 39.4, and 27.7 nm in diameter corresponding to extrusion, rolling, and forging, respectively, and 15.6 nm in thickness for the three processes) at the aforementioned maximum strains. At room temperature (20 °C), when mode II fracture starts in the oxide discs, the calculated thickness, area, and height reduction ratio in rolling, extrusion, and forging are approximately 99.85 pct, 5800:1, and 98.7 pct, respectively. For extrusion and forging, the preceding ultra-high strains are impractical. However, for rolling, a newly developed technique called accumulative roll bonding (ARB), where the thickness reduction ratio per single-step rolling is 50 pct, can reach this extent of ultra-high strain.^[32]

Figure 6 shows the calculated diameter and thickness of oxide discs as a function of total strain and rolling cycle during an ARB process at 400 °C. At the beginning, mode I fracture occurs. The calculated diameter of oxide discs decreases with increasing strain, and the calculated thickness of oxide

Table III. RAD Processing Parameters in the Experiments

Atomization Gas Mixture	Atomization Pressure	Superheat Temperature	Melt Flow Rate	Deposition Distance
16O ₂ -84N ₂ (vol pct)	1.51 MPa	1000 °C	0.012 kg s^{-1}	0.34 m



Fig. 4—(*a*) TEM bright-field image showing oxide dispersoids; (*b*) corresponding SAD pattern indicative of MgO; and (*c*) TEM dark-field image from the spots on the second ring.

Table IV. Michanical and Thysical Troperties of Migo and 5005 A	Table IV.	anical and Physical Properties of N	MgO and 5083	Al
---	-----------	-------------------------------------	--------------	----

Quantity	Symbol	Value	Unit	References
5083 Al/MgO interfacial energy	γ_{m-o}	$1.0 + 6.09 \times 10^{-5} (T-273)$	$\mathrm{J}~\mathrm{m}^{-2}$	28, 29, and 30
Compressive strength of MgO	σ_c	1377 - 0.25 (T-273)	MPa	18
Tensile strength of MgO	σ_t	146.8 - 0.061 (T-273)	MPa	30
Modulus of elasticity of MgO	$\dot{E_o}$	213.2 - 0.143 (T-273)	GPa	30
Poisson's ratio of MgO	v	0.34		30
Modulus of elasticity of 5083 Al	E_m	$72.2-3.56 \times 10^{-3}$	GPa	31
,	m	$(T-273) - 9.2 \times 10^{-5}$		
		$(T-273)^2$		

discs remains the same as the calculated initial thickness (l = 15.6 nm). When the total strain approaches approximately 8.71 (between 10 and 11 rolling cycles), the calculated diameter of oxide discs is close to the calculated initial thickness ($\approx 15.6 \text{ nm}$) and mode II fracture starts. When the total strain increases from approximately 8.71 to 13.34 (from

10 to 17 rolling cycles) during mode II fracture, the calculated diameter of oxide discs remains unchanged (\approx 15.6 nm) and the calculated volume fraction of oxide discs with half of the calculated initial thickness (l/2 = 7.8 nm) increases from 0.0 to 1.0. Then, the secondary mode I fracture occurs with increasing strain. The calculated diameter of oxide discs



Fig. 5—The calculated diameter and thickness of oxide discs as a function of strain during extrusion, rolling, and forging.



(1) The calculated diameter of oxide discs.

(2) The calculated volume fraction of oxide dises with thickness l/2.

(3) The calculated volume fraction of oxide discs with thickness *l*/4.(4) The calculated initial thickness of oxide discs *l*.

Fig. 6—The calculated diameter and thickness of oxide discs as a function of total strain and rolling cycle during an ARB process.

continues to be reduced until approximately 7.8 nm ($\approx l/2$) corresponding to a total strain of 22.61 (between 28 and 29 rolling cycles), and the calculated thickness of oxide discs remains constant (l/2 = 7.8 nm). Next, secondary mode II fracture occurs with increasing strains. In the range of total strain from approximately 22.61 to 31.88 (from 28 to 40 rolling cycles), the calculated diameter of oxide discs remains unchanged (\approx 7.8 nm) and the calculated volume fraction of oxide discs with a quarter of the calculated initial thickness (l/4 = 3.9 nm) increases from 0.0 to 1.0. After that, with the increase of strain, the calculated diameter of oxide discs continues to decrease, and the calculated thickness of the oxide discs remains unchanged (l/4 = 3.9 nm). In the range of strains selected in Figure 6 (less than 40 of total strain), the calculated effective diameter of oxide discs is smaller than 5.1 nm of the average size for bonding (determined by Eq. [1]).



Fig. 7—The calculated diameter and thickness of oxide discs as a function of process temperature during extrusion, forging, and rolling.



(4) The calculated initial thickness of oxide discs l_{i}

Fig. 8—The calculated diameter, thickness, and effective diameter of oxide discs as a function of process temperature during an ARB process.

2. The calculated size scale of oxide discs vs process temperature

Figure 7 shows the calculated diameter and thickness of oxide discs as a function of process temperature for extrusion (area reduction ratio 9:1), forging (height reduction ratio 75 pct), and rolling (thickness reduction ratio 90 pct). The calculated results show that thickness of oxide discs remains the same as the calculated initial thickness (l = 15.6 nm). When the process temperature is lower than 200 °C, the calculated diameter of oxide discs slowly increases with increasing process temperature. When the process temperature is higher than 200 °C, the increase in the calculated diameter of oxide discs with increasing process temperature is relatively rapid. However, the increase in the calculated diameter of oxide discs with increasing process temperature is limited to the temperature range of 20 (room temperature) to 570 °C (574 °C of the solidus temperature). For example, when the temperature increases from 20 °C to 570 °C, the calculated diameter increases from 51.9 to 70.8 nm for extrusion, from 42.9 to 59.6 nm for forging, and from 39.4 to 55.0 nm for rolling.

Figure 8 shows the calculated diameter, thickness, and effective diameter of oxide discs as a function of rolling

temperature during an ARB process at an ultra-high total strain of 8 (10 rolling cycles). Starting with 20 °C, the calculated diameter of oxide discs remains unchanged (≈ 15.6 nm), and the calculated volume fraction of the oxide discs with a half of the calculated initial thickness (l/2 = 7.8 nm) increases slightly with an increase of rolling temperature until approximately 60 °C, as shown in Figure 8. Then, the calculated volume fraction of the oxide discs with thickness of l/2decreases slowly with an increase of rolling temperature until approximately 120 °C. Next, the calculated volume fraction of the oxide discs with thickness of l/2 decreases rapidly with rolling temperature until approximately 296 °C. Finally, the calculated diameter of oxide discs rapidly increases with increasing rolling temperature, and the calculated thickness of oxide discs remains the same as the calculated initial thickness (l = 15.6 nm). The curve of the calculated effective diameter of oxide discs vs rolling temperature in Figure 8 exhibits a similar shape to the curves of the calculated diameter vs process temperature for extrusion, forging, and rolling in Figure 7. Similarly, the increase of the calculated effective diameter of oxide discs with an increase of rolling temperatures is limited in the temperature range from 20 °C to 570 °C (from 17.1 to 22.0 nm).

IV. DISCUSSION

A. Size Scale of Oxide Dispersoids vs Conventional Strain

According to Eqs. [6a] through [c], strain energy in oxide discs (ΔU) increases with increasing strain. As a result, the size scale (*i.e.*, diameter or thickness) of oxide discs decreases with increasing strain (Eq. [3]). However, in the range of conventional strains (up to 90 pct, 100:1, and 90 pct of thickness, area, and height reduction ratio in rolling, extrusion, and forging, respectively), the strain is so low that the calculated diameter of fragmented oxide discs is larger than the calculated thickness of oxide discs (Figure 5). Thus, the calculated diameter of the oxide discs is decreased and the calculated thickness of oxide discs remains unchanged with increasing strain (so-called "mode I fracture," as shown in Figure 2). Generally, both the calculated diameter and thickness of oxide discs exhibit a size scale on the order of tens of nanometers.

In an effort to validate the analytical model in the range of conventional strains, the size scale of oxide dispersoids calculated using the analytical model is compared to the TEM results from RAD 5083 Al that is conventionally formed (*i.e.*, without occurrence of mode II fracture) and the results are listed in Table V. Measured data in cases 1 and 2 are based on the experiments in the present study (RAD under the conditions in Table III followed by extrusion with the area reduction ratio

of 9:1) and in Reference 24 (RAD under the conditions reported in Reference 24 followed by extrusion with the area reduction ratio of 16:1 plus rolling with thickness reduction ratio of 41 pct). The average effective diameter of oxide discs in droplets from $D_{0.5}$ to $D_{99.5}$ (D_{i} is defined as a droplet size below which the cumulative mass percent is i) is used to represent the calculated average size of oxide discs. According to Table V, the calculated average effective diameters of oxide discs are smaller than the measured average sizes of the oxide dispersoids. The difference between the calculated and measured average sizes of oxide dispersoids may be attributed to the following two reasons. First, it is assumed that all of the strain energy is used to create the interface between the matrix and the oxides. In practice, the percent of strain energy to transfer into interfacial energy is likely to be less than 100 pct. Second, existence of slip between the matrix and the oxides reduces strain and thereby strain energy in the oxide dispersoids.

B. Size Scale of Oxide Dispersoids vs Ultra-High Strain

The calculated results in Figure 6 reveal fragmentation and size scale of oxide dispersoids under ultra-high strains. The calculated fragmentation behavior of oxide discs in Figure 6 can be summarized as follows. First, the calculated diameter or thickness of oxide discs constantly decreases with increasing strain, as a result of the consistent increase of strain energy in oxide discs with increasing strain (Eqs. [3] and [6a] through [c]). Second, both the calculated diameter and thickness of oxide discs are fragmented to less than 10 nm under an ultra-high deformation (*e.g.*, higher than 18.5 of total strain during an ARB process in Figure 6). On the basis of the two characteristics, other approaches capable of generating ultra-high strain (*e.g.*, ball milling (BM) for powders and equal channel angular pressing (ECAP)^[33] for bulk materials) may also be expected to generate ultra-fine dispersoids on the order of nanometers.

Inspection of the published literature reveals that oxide and nitride dispersoids with a size range from 2 to 10 nm have been observed in BM powders.^[34,35,36] These ultra-fine dispersoids originate from extensive fragmentation of oxides and nitrides caused by ultra-high strains that accumulate during BM. Those oxides and nitrides are produced *via in-situ* reactions between powders and oxygen/nitrogen from the environment or milling slurry under energetic milling states. These experimental observations confirm that ultra-high strain does lead to the formation of ultra-fine dispersoids on the order of nanometers.

C. Size Scale of Oxide Dispersoids vs Process Temperature

The calculated results in Figures 7 and 8 reveal that process temperature has a limited influence on the size scale of oxide

56.3

Tuble V. Comparison between measured and Calculated Sizes of Oxfae Dispersonas (http://						
(Calculated			
Measured	Average		$D_{0.5}$ to $D_{99.5}$			D_{50}
Average	Effective			Effective		
Size	Diameter	Diameter	Thickness	Diameter	Diameter	Thickness
50	44.5	55.0 to 70.9	13.0 to 18.4	41.0 to 51.5	58.3	15.6

10.4 to 16.1

37.5 to 42.5

Table V. Comparison between Measured and Calculated Sizes of Oxide Dispersoids (nm)

39.8

55.7 to 57.5

45

Case

1

2

13.1

Effective

Diameter

43.0

39.6

dispersoids, for both conventional (Figure 7) and ultra-high strains (Figure 8). The preceding results can be rationalized as follows. With the increasing process temperature, the tensile strength of MgO and the modulus of elasticity of 5083 Al and of MgO decrease. The decrease of the first two factors favors the increase of the calculated diameter/thickness of oxide discs, whereas the decrease of the third factor favors the decrease of the calculated diameter/thickness of oxide discs (Eqs. [3] and [6a] through [c]). The combination of these opposite effects leads to a slow change of the calculated diameter or thickness at low temperature, as well as a limited increase of the calculated diameter or thickness when the temperature increases from 20 °C to 570 °C.

V. CONCLUSIONS

An analytical model is established to predict the size scale of oxide dispersoids in Al alloys synthesized by RAD after rolling, extrusion, and forging. The calculated diameter or thickness of oxide discs decreases with decreasing the process temperature. However, the process temperature has a limited influence on the calculated diameter or thickness of oxide discs. The calculated diameters or thickness of oxide discs monotonously decrease with increasing strain. In the range of conventional strains (e.g., up to 90 pct, 100:1, and 90 pct of thickness, area and height reduction ratio in rolling, and extrusion and forging, respectively), only the calculated diameter of oxide discs is reduced and the calculated thickness of oxide discs remains unchanged. Generally, both the calculated diameters and thickness are more than 10 nm. Under ultra-high strains (e.g., during ARB, ECAP, and BM), both the calculated diameter and thickness of oxide discs can be reduced to less than 10 nm.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from the United States Army Research Office (Grant No. DAAD19-01-1-0627). In addition, the authors extend their appreciation to Drs. Jianhong He and Fei Zhou for their guidance with the TEM techniques.

APPENDIX

Increment of interfacial area between the oxide and the metal matrix

The volume of an oxide disc and the interfacial area between the matrix and an oxide disc with diameter *L* and thickness $l/2^n$ are $v_n = (\pi L^2/4)(l/2^n)$ and $s_n = \pi Ll/2^n + \pi L^2/2$, respectively. The volume of an oxide disc and the interfacial area between the matrix and an oxide disc with diameter *L* and thickness $l/2^{n-1}$ are $v_{n-1} = (\pi L^2/4)(l/2^{n-1})$ and $s_{n-1} = \pi Ll/2^{n-1} + \pi L^2/2$, respectively. In per unit volume of oxides, the total area between the matrix and the oxide discs is $S_t = N_n s_n + N_{n-1}s_{n-1}$, where $N_n = f_n/v_n$ and $N_{n-1} = (1 - f_n)/v_{n-1}$ are the number of oxide discs with thickness of $l/2^n$ and of $l/2^{n-1}$, respectively. Relative to the interfacial area per unit volume of the oxides prior to working (*i.e.*, in the as-deposited material),^[13] $S_0 = 2/l + 4/L_0$, the increment of interfacial area per unit volume of the oxides during a working process is $\Delta S = S_t - S_0$. Then, Eq. [1] can be obtained.

REFERENCES

- E.J. Lavernia and Y. Wu: Spray Atomization and Deposition, John Wiley & Sons Inc., New York, NY, 1996, pp. 7-9, 278-79, and 398-99.
- 2. P.S. Grant: Progr. Mater. Sci., 1995, vol. 39, pp. 497-545.
- S.L. Dai, J.-P. Delplanque, and E.J. Lavernia: <u>Metall. Mater. Trans.</u> <u>A</u>, 1998, vol. 29A, pp. 2597-2611.
- H. Liu, R.H. Rangel, and E.J. Lavernia: <u>Acta Metall. Mater.</u>, 1994, vol. 42, pp. 3277-89.
- X. Zeng, H. Liu, M. Chu, and E.J. Lavernia: <u>Metall. Trans. A, 1992</u>, vol. 23A, pp. 3394-99.
- X. Zeng, S. Nutt, and E.J. Lavernia: <u>Metall. Mater. Trans. A, 1995</u>, vol. 26A, pp. 817-27.
- 7. F.J. Humphreys and J.W. Martin: *Phil. Mag.*, 1968, vol. 17, pp. 365-80.
- 8. O. Preston and N.J. Grant: Trans. TMS-AIME, 1961, vol. 221, pp. 164-73.
- F.J. Humphreys and M. Hatherly: *Recrystallization and Related Annealing Phenomena*, Pergamon, Oxford, United Kingdom, 1995, pp. 78, 146, 256, and 306.
- Y.J. Lin, Y. Zhou, and E.J. Lavernia: <u>J. Mater. Res.</u>, 2004, vol. 19, pp. 3090-98.
- Y.W. Kim, W.M. Griffith, and F.H. Froes: <u>J. Met.</u>, 1985, vol. 37, pp. 27-33.
- Y.J. Lin, Y. Zhou, and E.J. Lavernia: <u>Metall. Mater. Trans. B</u>, 2004, vol. 35B, pp. 1173-85.
- Y.J. Lin, Y. Zhou, and E.J. Lavernia: <u>Metall. Mater. Trans. A. 2004</u>, vol. 35A, pp. 3265-73.
- G.W. Rowe: *Elements of Metalworking Theory*, Edward Arnold Ltd., London, 1979, pp. 23 and 37.
- J.N. Harris: Mechanical Working of Metals, Pergamon Press Ltd., Oxford, United Kingdom, 1983, pp. 53, 86-87, and 98.
- N.R. Bauld: *Mechanics of Materials*, Prindle, Weber & Schmidt Publisher, Boston, MA, 1986, pp. 54 and 567.
- 17. G.A. Roberts and R.A. Cary: *Tool Steels*, ASM, Materials Park, OH, 1980, pp. 633-40.
- G.V. Samsonov: Oxide Handbook, C.N. Turton, and T.I. Turton, translators, IFI/Plenum Data Corporation, New York, NY, 1973, pp. 105-14 and 235-42.
- D.A. Porter and K.E. Easterling: *Phase Transformations in Metals* and Alloys, Stanley Thorns (Publishers) Ltd., London, United Kingdom, 1992, p. 315.
- J.R. Groza: in *Nanostructured Materials*, C.C. Koch, ed., Noyes Publications, Norwich, NY, 2002, pp. 125 and 155-57.
- T.B. Massalski, H. Okamoto, P.R. Subramanian, and L. Kacprzak: Binary Alloy Phase Diagrams, ASM INTERNATIONAL, Materials Park, OH, 1990, pp. 1-3542.
- Y.V.R.K. Prasad and S. Sasidhara: *Hot Working Guide*, ASM INTERNATIONAL, Materials Park, OH, 1997, pp. 25-448.
- M.I. Alymov, E.I. Maltina, and Y.N. Stepanov: <u>Nanostr. Mater.</u>, 1994, vol. 4, pp. 737-42.
- S.L. Dai, J.-P. Delplanque, and E.J. Lavernia: <u>J. Mater. Res.</u>, 1999, vol. 14, pp. 2814-23.
- J.R. Davis: Aluminum and Aluminum Alloys, ASM INTERNATIONAL, Materials Park, OH, 1993, p. 494.
- 26. J.A.S. Tenorio and D.C.R. Espinosa: Oxid. Met., 2000, vol. 53, pp. 361-73.
- T.J. Carney, P. Tsakiropoulos, J.F. Watts, and J.E. Castle: <u>Int. J Rapid</u> Solidification, 1990, vol. 5, pp. 189-217.
- E.A. Brandes and G.B. Brook: *Smithells Metals Reference Book*, Butterworths-Heinemann, Oxford, United Kingdom, 1992, pp. 8-1, 8-2, 8-25, and 14-7.
- 29. R. Asthana: Metall. Mater. Trans. A, 1994, vol. 25A, pp. 225-30.
- G.V. Samsonov: Oxide Handbook, translated from Russian by C.N. Turton and T.I. Turton, IFI/Plenum Data Corporation, New York, NY, 1982, pp. 51, 173, 183, and 187-88.
- J.R. Newby: *Metals Handbook*, 9th ed., ASM, Metals Park, OH, 1985, vol. 8, p. 23.
- Y. Saito, H. Utsunomiya, N. Tsuji, and T. Sakai: <u>Acta Mater.</u>, 1999, vol. 47, pp. 579-83.
- 33. V.M. Segal: Mater. Sci. Eng. A, 1995, vol. 197, pp. 157-64.
- J. Lee, F. Zhou, K.H. Chung, N.J. Kim, and E.J. Lavernia: <u>Metall.</u> <u>Mater. Trans. A</u>, 2001, vol. 32, pp. 3109-15.
- M.J. Luton, C.S. Jayanth, M.M. Disco, S. Matras, and J. Vallone: in *Multicomponent Ultrafine Microstructures*, L.E. McCandlish, B.H. Kear, D.E. Polk, and R.W. Siegel, eds., Materials Research Society, Pittsburgh, PA, 1989, pp. 79-86.
- R.J. Perez, H.G. Jiang, C.P. Dogan, and E.J. Lavernia: <u>Metall. Mater.</u> <u>Trans. A. 1998, vol. 29, pp. 2469-75.</u>