Journal of the European Ceramic Society 22 (2002) 1061–1066

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Optimization of an aqueous, commercial silicon nitride slurry for colloidal isopressing

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Received 21 March 2001; received in revised form 10 July 2001; accepted 17 July 2001

Abstract

A commercial Si_3N_4-based aqueous slurry (AS800) was processed to enable the forming of shapes via a new method called colloidal isopressing. The as-received slurry was reformulated at pH 9–10 to contain 2 wt.% PEG-silane (*N*-[(triethoxysilyl)propyl]-*O*-polyethylene oxide urethane) and 0.5 M of either tetramethylammonium chloride or tetramethylammonium nitrate. The addition of the salt to an AS800 slurry formulated in the dispersed state at pH 9–10 changes the interparticle pair potential from fully repulsive to weakly attractive. These coagulated slurries were consolidated by pressure filtration at 2 MPa to a relative density of ≈0.51. It was shown that the consolidated bodies could be fluidized and used to fill a rubber mold. By isopressing a specific amount of consolidated slurry contained within a rubber mold at 200 MPa for one minute, bar-shaped powder compacts with a relative density of ≈0.60 were formed.

Keywords: Colloidal isopressing; Pressing; Si_3N_4; Suspensions

1. Introduction

Silicon nitride-based ceramics are strong, resistant to wear, and due to their moderate elastic modulus and low thermal expansion coefficient, they are very resistant to thermal shock. Hence silicon nitride is generally the material of choice for high temperature applications.[1] Despite this unique combination of properties, components made of silicon nitride are still prone to occasional, unpredictable failure from a flaw that was present in the initial powder. One method to improve the reliability is to remove the flaw producing heterogeneities greater than a given size by passing a slurry, made from the powder, through a filter.[2] Pujari et al. demonstrated the increased reliability of silicon nitride tensile specimens processed from a slurry passed through a 5 μm filter prior to forming via slip casting.[3]

Here, we show that a commercial silicon nitride slurry, containing the additives needed for densification and grain growth control, can be rapidly converted into a shape using a method called colloidal isopressing, recently introduced by Yu and Lange.[4] The primary advantages of shape forming using colloidal isopressing are: (1) strength degrading heterogeneities can first be removed by filtering a dispersed slurry, (2) a short forming period, (3) high relative density and complex shapes, (4) no shrinkage during drying, (5) uniform relative density, and thus no shape distortion during densification, and (6) the use of conventional dewatering presses and cold isostatic presses.

Colloidal isopressing relies on a weakly attractive interparticle pair potential which enables a plastic-to-elastic consolidation phenomenon discovered by Franks and Lange.[5] A weakly attractive (coagulated) particle network can be produced by developing a short-range repulsive potential that is summed with the always-present van der Waals attractive potential.[6] There are two general ways of producing a short-range repulsive potential. The first method, used by Yu and Lange to first demonstrate the colloidal isopressing method for alumina powders, is based on the electrostatic double layer phenomenon to produce a repulsive potential. In

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0955-2219/02/$ - see front matter
PII: S0955-2219(01)00423-X

this method, a highly repulsive interparticle potential is produced with a surface charge that causes the particles to be shrouded with counterions. The long-range repulsive potential is transformed into a short-range repulsive potential by adding excess counterions (i.e. adding salt) to reduce the effective thickness of the counterion cloud, and thus, reduce the interparticle separation distance where the particles become strongly repulsive.

In the second method, small molecules are attached to the surface of the particles to produce a steric repulsion at short separation distances when the particles are attracted to one another via the van der Waals potential.

The method used here is a combined electro-steric effect where the molecules adsorbed onto the surface may ionize and create an effective surface charge. Aqueous processing of silicon nitride requires special consideration due to both the oxidation of silicon nitride in water and the dissolution of the silanol groups on the surface of silicon nitride.[7] Colic et al.[8] showed that the reaction of water with the silicon nitride surface can be decreased substantially by chemisorbing organofunctional silanes at the silanol sites. The aminosilane molecules used for this task also develop a charge,[8] which can also be used to impart a repulsive potential due to an electrostatic double layer in addition to the steric repulsion imparted by the 'brush' configuration of the molecules on the surface.

The 'coated' silicon nitride particles need to be fully dispersed prior to removing heterogeneities by filtration and then coagulated prior to consolidation. The silicon nitride slurry formulated with the aminosilane can be dispersed by controlling the pH. The addition of salt to a dispersed slurry then changes the long range repulsive potential to a short range repulsive potential. In this paper, we apply the colloidal isopressing forming technology to a commercial silicon nitride aqueous slurry from Allied Signal. The silicon nitride particles are coated with an ionizable organofunctional silane and coagulated with salt. This system provides for the protective coating to keep the silicon nitride from reacting with water, the long range repulsive potential needed to remove the heterogeneities, and then, the weakly attractive interparticle interaction required for colloidal isopressing.

2. Experimental procedure

All the experiments were carried out with a commercial slurry supplied by Allied Signal, Inc. (called AS800). The solid content of the slurry was primarily silicon nitride (0.42 volume fraction) plus small fractions of proprietary densification additives. Slurries from three different batches (A, B, and C) were used. An organosilane, *N*-[(triethoxysilyl)propyl]-*O*-polyethylene oxide urethane (abbreviated here as PEG-silane) with the chemical formula $C_{10}H_{21}NO_4SiO(CH_2CH_2O)_{4–6}H$ (Gelest Inc., Tullytown, PA), was added to the slurry (2 wt.% based on the silicon nitride content). Two different salts were added to different slurries: tetramethylammonium chloride (TMACl, 97%) and tetramethylammonium nitrate ($TMANO_3$, 96%) (Sigma Aldrich, Milwaukee, WI). The pH was adjusted by adding either nitric acid (HNO_3) or tetramethylammonium hydroxide (TMAOH).

The zeta potential (Zeta Meter System 3.0, Zeta Meter Inc., Long Island City, NY) of an AS800 slurry containing 2 wt.% PEG-silane was measured after dilution with deionized water to a powder concentration of 0.025 g/l. The solution was solicited at pH 11 using an ultrasonic horn (Model W-380, Heat Systems-Ultrasonics Inc., Piscataway, NJ). The velocity of the particles under an applied electric field was first measured at the pH 11, then the pH was decreased stepwise by adding HNO_3.

Viscosity measurements were made with a stress-controlled rheometer (Model DSR, Rheometrics Inc., Farmingdale, NY) using slurries diluted to 20 vol.% solid using a cup and couette cell (cup diameter 32.0 mm, bob diameter 29.5 mm, bob length 44.0 mm). The dependence of the viscosity on the strain rate was measured for dispersed (pH 9–10) slurries with different salt concentrations (0.0, 0.1, 0.25, 0.50, 0.75 and 1.0 M). All measurements were initiated at the highest strain rate.

The slurries were consolidated by pressure filtration. Two different cylindrical dies were used, having an internal diameter of 25.4 and 45.0 mm. Using a hydraulic press (Carver Laboratory Press, Fred S. Carver Inc., Menomonee Falls, WI), a constant pressure was applied to the particle network in the slurry until the consolidation was terminated. The applied pressures ranged from 0.5 to 50 MPa. The equilibrium relative density was reached when the plunger stopped moving with no detectable movement of the plunger for at least 1 h.

After pressure filtration, some consolidated slurries were fluidized and then characterized via dynamic rheology using the DSR rheometer. The high relative density and high viscosity consolidated slurry required the use of a 4-blade vane tool (cup diameter 32.0 mm, bob diameter 16.0 mm, bob length 31.0 mm) to avoid slip.[9,10] To prevent the fluidized body from drying during the rheology measurements, it was covered with a layer of mineral oil. Dynamic frequency sweep experiments were performed to measure the shear modulus, and dynamic stress sweep tests to determine the yield stress. The yield stress was defined as the point at which the storage modulus, G′, starts to decrease substantially as the shear stress increased. The shear modulus was determined by measuring G' at a stress much lower than the yield stress, at which the network exhibits elastic behavior. The measurements were taken after designated periods in order to study the time-dependence of the shear modulus.

Uniaxial compression tests were carried out on consolidated powder compacts saturated with water (diameter 25.4 mm, lengths varying from 25.3 to 27.4 mm, depending on the applied pressure). The specimens were stored in a plastic bag containing a wet paper towel in order to prevent them from drying. A mechanical testing machine (Instron 1123, Instron Co., Canton, MA) with a 5000 lb load cell was used for these measurements. All specimens were tested with a displacement rate of 1 mm/min and within 1 h after the consolidation. Nominal stresses and engineering strains were calculated from the recorded load-displacement data. The engineering strain was calculated by dividing the displacement by the initial specimen height; the nominal stress was determined by dividing the load by the instantaneous cross-sectional area of the specimen. The instantaneous cross-sectional area was estimated by assuming that the volume of the specimen was unchanged during the experiment. The maximum observed nominal stress was considered to be the peak stress.

Consolidated bodies were liquefied either by hand pressure or with a vibrator table (CM-30, Cleveland Vibrator Company, Cleveland, OH). The liquefied bodies were then injected into silicone molds, containing a rectangular cavity. The filled molds were placed into an isostatic press (Model No. IP-2-22-60, Autoclave Engineers Inc., Erie, PA) under 200 MPa for 1 min. Partially sintered alumina pieces, placed within the silicone mold, were used as porous bodies to remove excess water from the fluidized bodies during isopressing.

The relative densities of the specimens in the filter-pressed and the isopressed state were determined with the weight difference method. To determine the residual amount of water after isopressing, the specimens were weighed before and after drying at 70 °C. They were then heated to 500 °C to estimate the amount of residual organic additives.

3. Results

The zeta potential for the AS800 (see Fig. 1), reacted with 2 wt.% PEG-silane, measured 2 and 7 weeks (aged as dispersed slurries at pH ≈10) after its commercial preparation, were different at pH values greater than the iso-electric point (iep) by nearly a factor of 2 (larger after 7 weeks), whereas their iep was nearly identical (pH = 5.5 ± 0.3). The zeta potential for batch A and batch B measured two weeks after their preparation were also different at pH > iep; both had a similar iep.

Fig. 2 reports the viscosity versus strain rate data (batch A) for slurries prepared at the iep, in the dispersed state (at pH 10.1), and at pH 10.1 with the addition of different concentrations of either TMACl (Fig. 2a) or $TMANO_3$ (Fig. 2b). The slurry in the dispersed state (pH = 10.1) without added salt exhibited a

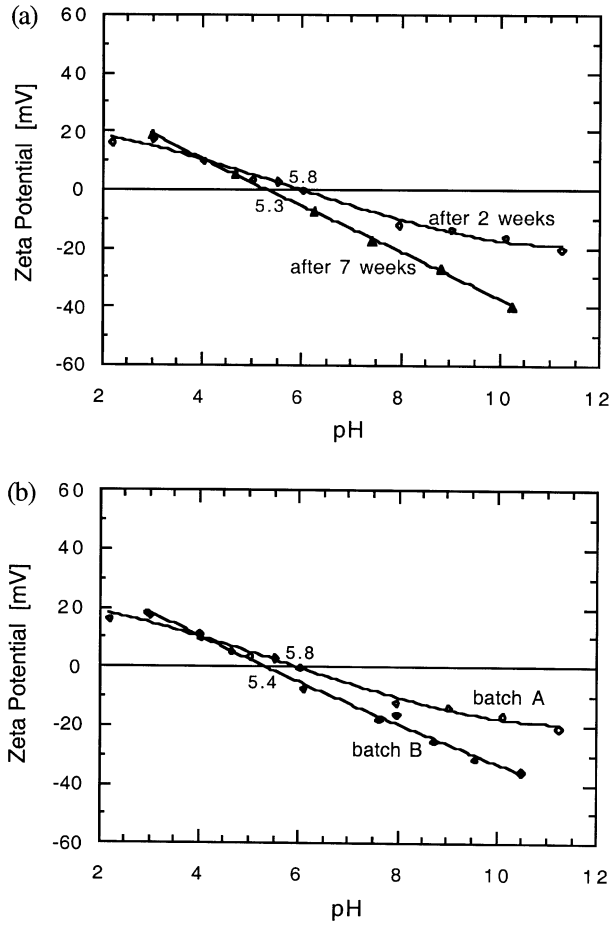

Fig. 1. (a) Zeta potential of AS800 powder reacted with 2 wt.% PEG-silane aged (pH ≈10) for two periods (batch A) and (b) for two different batches (aged less than two weeks).

very low viscosity and a nearly Newtonian behavior. In the flocced state, the AS800 slurry had a very high viscosity and exhibited strong shear rate thinning behavior. The addition of salt to a dispersed system caused an increase in the viscosity and a change from a nearly Newtonian behavior to a shear rate thinning behavior which is typical for attractive particle networks. No further changes in viscosity were observed for salt addition in excess of 0.5 M.

All bodies consolidated from coagulated slurries at 2 MPa (conditions shown in Table 1) could be easily fluidized by vibration. Table 1 shows the values for the initial shear moduli and the average yield stresses of AS800 for these fluidized bodies. All data in Table 1 were obtained by dynamic stress sweep experiments at a frequency of 1.0 rad/s. The shear moduli shown in Table 1 were measured immediately after the vane tool had been plunged into the slurry. The shear moduli were also determined after increasing rest periods within the instrument by performing frequency sweep tests at a stress of 50 MPa. The time-dependence of the shear modulus for a specimen from batch C, which contained 2 wt.% PEG-silane and 0.5 M $TMANO_3$ (consolidated

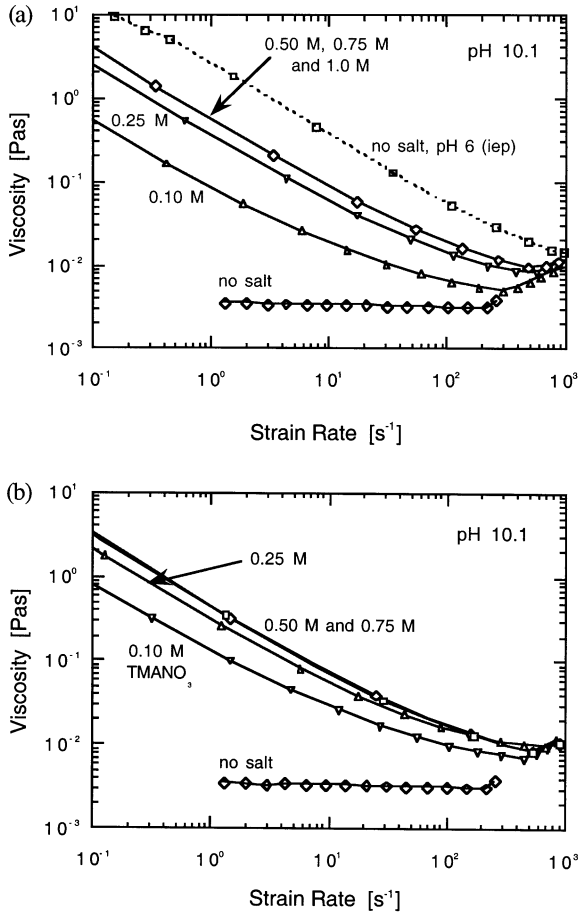

Fig. 2. Viscosity of AS800 (batch A, 2 wt.% PEG-silane) diluted to 20 vol.%: (a) in the flocced state (at pH 6), in the dispersed state (at pH 10.1), and for slurries formulated at pH 10.1 containing different concentrations of TMACl; and (b) in the dispersed state (at pH 10.1), and for slurries formulated at pH 10.1 containing different concentrations of $TMANO_3$.

at 2 MPa, then fluidized by vibration) is shown in Fig. 3. After sequentially determining the elastic modulus of the network for 21 h, the slurry was stirred again by oscillating the vane at a large amplitude. The shear modulus dropped again to the initial value and showed a similar increase with time (shown as the 2nd run in Fig. 3).

Although the specimens consolidated at 2 MPa could be liquefied by vibration, as shown in Fig. 4, they did not exhibit a low flow stress when the consolidated

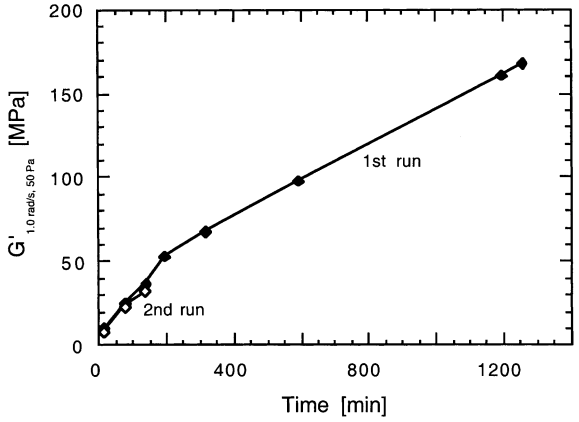

Fig. 3. Increase of the elastic modulus with time for a consolidated body of AS800 (dispersed slurry formulated at pH 10) with 2 wt.% PEG-silane and 0.5 M $TMANO_3$ (consolidation pressure: 2 MPa).

bodies were loaded in uniaxial compression at a displacement rate of 1 mm/min. Nevertheless, their behavior was different than truly brittle specimens. The bodies consolidated at a pressure higher than 5 MPa showed a steeper slope in the elastic regime, higher peak stresses, and much more cracking than those consolidated at a pressure $\leqslant 5$ MPa, as shown by the insert in Fig. 4. Pieces of the specimens consolidated at $\leqslant 5$ MPa could be liquefied after mechanical testing, whereas the fractured portions of the bodies consolidated at higher pressures only broke into smaller and smaller pieces during vibration.

The relative densities of the specimens used for the uniaxial compression tests are plotted as a function of the consolidation pressure in Fig. 5. A sudden increase in the relative density between 5 and 10 MPa can be recognized. Between these two pressures the behavior of the consolidated slurry changes from plastic to brittle as well.

The relative densities after pressure filtration at 2 MPa and after isopressing at 200 MPa are shown in Table 2. The relative density of the as-received AS800 was measured to be 0.405. The specimen with 2 wt.% PEG-silane, without added salt had a high packing density after the consolidation but exhibited a brittle behavior, and thus, could not be liquefied and extruded into the rubber cavity for isopressing. The bodies with 2 wt.% PEG-silane and 0.5 M salt could be liquefied for isopressing, and showed a moderate relative density. As

Table 1
Shear moduli and yield stresses of consolidated slurries for different compositions

Batch	A	A	A	B
PEG-silane (wt.%)	2	2	1	2
Salt	TMACl	$TMANO_3$	$TMANO_3$	$TMANO_3$
Salt concentration (M)	0.5	0.5	0.5	0.5
PH	10.1	10.1	10.1	8.7
Consolidation pressure (MPa)	2	2	2	2
Initial shear modulus (MPa)	1.3	0.9	13	4.5
Average yield stress (Pa)	294	406	213	684

Table 2
Relative densities after pressure filtration at 2 MPa and after isopressing at 200 MPa for 1 min

Batch	PEG-silane (wt.%)	Salt	Salt conc. (M)	pH	Rel. density filter-pressed (%)	Extrudable?	Rel. density isopressed (%)
A	2	–	–	10.1	57.9	No	
A	2	$TMANO_3$	0.5	10.1	51.8	Yes	60.1
B	2	$TMANO_3$	0.5	8.7	51.3	Yes	61.7

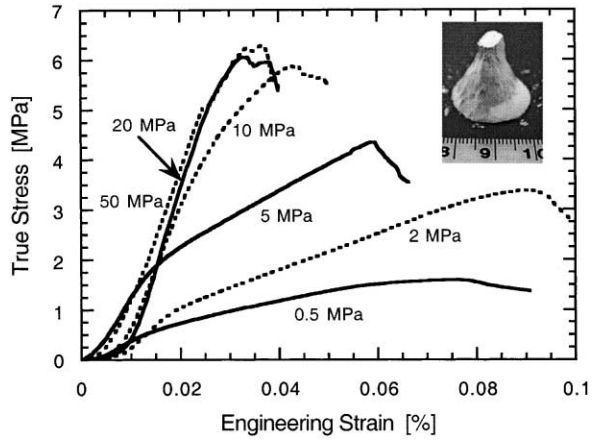

Fig. 4. True stress versus engineering strain curves for different consolidation pressures (AS800, batch B, 2 wt.% PEG-silane, 0.5 M $TMANO_3$, loading rate: 1 mm/min). The inset picture shows a body consolidated at 50 MPa after uniaxial compression.

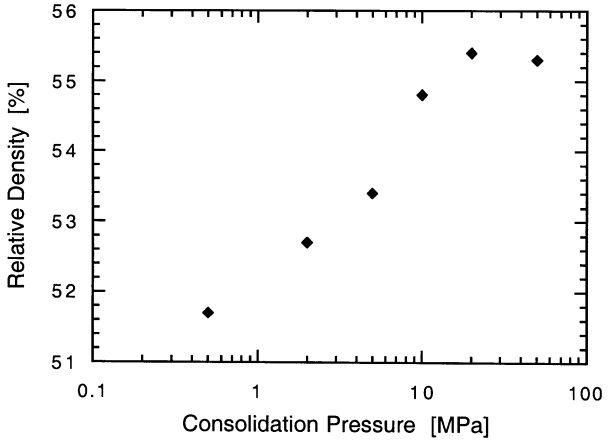

Fig. 5. Relative density versus consolidation pressure (AS800, batch B, 2 wt.% PEG-silane, 0.5 M $TMANO_3$).

shown, isopressing at 200 MPa for 1 min caused an increase in relative density from ≈0.51 to ≈0.60.

4. Discussion

As expected, the powder in the dispersed slurry formulated at a pH far from the iep without added salt, produced the highest relative density compacts that exhibited brittle behavior, consistent with observations of Franks and Lange.[5] Adding a modest amount of salt to the dispersed slurry resulted in a lower relative density after consolidation, but, when consolidated at pressures $\leqslant 5$ MPa, produced bodies that could be fluidized. The fluidized bodies could be injected into rectangular rubber molds and isopressed to a much higher relative density similar to that previously reported for alumina.[4]

Slurries formulated at the iep had higher viscosities relative to those formulated at pH 10 with added salt. At the iep, the particles are strongly attracted to each other by van der Waals forces. Hence, the force to pull the particles apart (to move them past each other in a shear flow field) is larger for slurries formulated at the iep, relative to the weakly attractive networks formed by adding salt to a dispersed slurry. According to Fig. 2(a) and (b) an addition of 0.5 M of either TMACl or $TMANO_3$ is sufficient to change the interparticle pair potential from fully repulsive to weakly attractive.

The elastic modulus of the fluidized, consolidated bodies was observed to increase with time (Fig. 3). When the body was stirred at a high shear strain, the low value of the modulus was recovered, and it retraced the same increase found for the first set of measurements. Our results show that the elastic modulus of the fluidized, consolidated bodies still increased after 20 h (Fig. 3). That is, the elastic modulus of the consolidated and fluidized body strongly depends on the shear history. The reason for this behavior has been recently discussed by Yu and Lange, who suggest that during shear flow, the particles align themselves with the flow field to produce an anisotropic particle network that relaxes to its isotropic structure when the shear strain is removed.[11] They showed that the time required to recover the isotropic network was dependent on the strength of the attractive pair potential.

5. Conclusions

AS800 is a commercial slurry formulated by Allied Signal. Its primary ingredient is silicon nitride; it also contains small fractions of other powders needed for densification and microstructure control. It has been demonstrated that the AS800 slurry can be reformulated to produce shapes via the new colloidal isopressing method. Measurements of the shear modulus and the relative density of consolidated AS800 slurries indicate

that increasing the PEG-silane content to 2 wt.% was sufficient to produce steric repulsion between the silicon nitride particles. Viscosity measurements showed that a salt concentration of either 0.5 M TMACl or $TMANO_3$ is sufficient to change the interparticle pair potential from fully repulsive to weakly attractive. Consolidation at a pressure of 2 MPa produced a relative density of $\approx$0.51. A plastic-to-brittle transition of the saturated AS800 powder compacts appears to occur between consolidation pressures of 5 and 10 MPa. Dynamic rheology experiments on AS800 slurries which were consolidated at a pressure $\leqslant$5 MPa and liquefied beforehand indicated in a time dependent network strength as observed via elastic modulus measurements. The relative density could be increased to $\approx$0.60 after shape forming via colloidal isopressing. Finally, isopressed bars were sintered to full density at Allied Signal via pressureless sintering.

Acknowledgements

We gratefully acknowledge the support for this research from the SRI/DARPA Solid Freeform Fabrication and Design Program, Award number 46-000123, Army Research Office, Contract Number, DAAG55-98-1-0455, and Ceramic Components Division, Allied Signal Aerospace, Torrance, CA.

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