

Application of Pre ceramic Polymers in Powder Metallurgy: Their Use as Low-Loss Binders and for the in Situ Formation of Dispersed Ceramic Phases in the Metal Matrix

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Powder metallurgy requires the use of polymers as binders and lubricants. During powder mixing high interparticle friction is introduced due to shape, size and coefficient of friction of the mixed material. Organic polymers such as Acrawax, stearate salts,^{1a} or microcrystalline cellulose² are being used to improve the flow and packing properties of metal powders. It also is essential to use polymeric lubricants in injection molding of metal powders to minimize die wear.³ The following prerequisites are usually met for a commercial organic lubricant/binder: low melting temperature (150–200 °C), chemical inertness, and low temperature for complete decomposition (400 °C). Before sintering of the molded part, the organic binder must be removed, a process which is costly and complex. Unless this is done exactly right, cracking, deformation, or bloating of the part can occur.

Pre ceramic polymers⁴ serve excellently as binders for ceramic powders in the fabrication of shaped ceramic parts. For example, Semen and Loop at the Ethyl Corp. laboratories⁵ demonstrated strengths of over 650 MPa for parts made from submicron SiC particles bonded with an amorphous silicon carbonitride matrix generated by pyrolysis of a polysilazane of the type $[(CH_3Si(H)NH)_a(CH_3SiN)_b]_n$.⁶ These parts were found to exhibit excellent oxidation resistance and strength retention at temperatures up to 1300 °C.

Prior to this work (and still today) organic polymers (e.g., poly(vinyl alcohol), poly(vinyl butyral), etc.) have been used as binders for ceramic powders such as SiC and Si₃N₄.^{1b} This, however, brings some disadvantages: (1) evolution of volatiles due to binder burnout during the firing of the ceramic part will, in the absence of suitable open porosity, cause a flawed microstructure (cracks and voids), and (2) thermolysis of the organic binder can leave behind carbonaceous residues. Pre ceramic polymers, if properly chosen, avoid these problems. First, provided that their pyrolysis gives high ceramic residue yields,⁴ evolution of volatiles will be minimal, and second, if the

right pre ceramic polymer is used, the retention of free carbon in the residual solid will be minimal or zero.

Since organic polymers also are used as binders in the consolidation of metal powders by injection molding, it follows that the benefits of using pre ceramic polymers as binders for ceramic powders may be translatable to metal (and metallic alloy) powders.

In 1976, Yajima et al.⁷ described experiments in which a polycarbosilane (the Nicalon ceramic fiber precursor⁸) was used as a binder for a Fe/Cr alloy powder. Fabrication by hot pressing to 1100 °C followed and gave a Fe/Cr alloy part containing uniformly distributed particles of Cr carbide and silicide (by XRD and TEM). The resulting composite was resistant to oxidation at 1000 °C and was harder than the base alloy. This work appears not to have been followed up, very likely because the main focus of the materials scientists working in the pre ceramic polymer area has been (and continues to be) on the preparation of continuous ceramic fibers and coatings.

In the expectation that this approach should be broadly applicable to powder metallurgy and to the production of discontinuously reinforced metal matrix composites, we have initiated an investigation of the use of pre ceramic polymers in the consolidation of metal and metallic alloy powders. We report some initial results to show that this is indeed the case.

The experimental procedure is quite simple. A 100-mL round-bottomed flask was charged with 2–3 cm³ of the metal powder (generally –325 mesh) and 3–15 mol % of the polymer (based on silicon atom when an organosilicon polymer is used) and 30 mL of anhydrous toluene. The resulting suspension of the metal powder in a toluene solution of the polymer was ultrasonicated for 20–24 h. The sonic activation is necessary to clean the surface of the metal particles and to ensure homogeneous dispersion. Subsequently, the volatiles were removed at reduced pressure on a high-vacuum line with vigorous agitation. The heavy solid residue was dried *in vacuo* at 50 °C overnight and ground to a fine powder. Uniaxial pressing in a rectangular die at 13.5 kpsi for 1 h and isostatic pressing at 40 kpsi for 10 min, usually at room temperature, gave the green bar (3.5 × 1.2 × 0.5 cm). Subsequent heating under argon in a tube furnace to temperatures below the mp of the metal for ~2 h (temperature ramp rate of 5 °C/min) gave the final bar. The organosilicon polymers used to date in this study are our poly(methylsilane) (PMS) which had been cross-linked with $((\eta^5-C_5H_5)_2ZrH_2)_n$,⁹ the Nicalon polycarbosilane (PCS),⁸ our polysilazane (PSZ),⁶ and a polysilane containing methyl, vinyl, and hydrogen substituents (PVS).¹⁰ Our investigations thus far have focused on the consolidation of titanium, zirconium, vanadium, tungsten, copper, and aluminum powders. Experiments with other metal and alloy powders and with other polymers, including appropriate high carbon residue yield organic polymers, are in progress. Not every polymer gave satisfactory results with a given metal. Which polymer is best and at what loading must be determined by experiment. For instance, in the case of aluminum powder, the PMS gave excellent results, but use of the PCS and the PSZ resulted in brittle and “spongy” bodies.

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Figure 1. SEM of Ti/PMS pyrolyzed at 600 °C in Ar for 3 h.

In any case, a general requirement was found to be that the ceramic residue yield when the pure polymer is pyrolyzed in argon to 1000 °C should be above 60%.

During the heating of the green bodies, there appear to be two main chemical stages: (1) pyrolysis of the pre-ceramic polymer to give the amorphous ceramic product;¹¹ (2) solid-state reaction of this ceramic with the metal powder matrix to give new ceramic phases that are dispersed throughout the metal matrix, i.e., a ceramic dispersoid metal matrix composite is the end result. What ceramic phases result from such reactions of organosilicon polymers with metal powders had been established in our earlier studies of stoichiometric preceramic polymer/metal powder high-temperature, solid-state reactions.¹²

A consideration of the changes that occur as a given green body is heated in stages to the final temperature is instructive. We give as an example a composite of -325 mesh titanium powder with 10 mol % (based on Si; 9 wt %) of PMS binder. The green bar was heated in stages in argon to the final temperature of 1200 °C. Powder X-ray diffraction (XRD) examination of the bars heated to 600, 800, and 1200 °C showed progressive development of crystalline TiC and Ti₅Si₃. The development of the morphology with temperature is shown in Figures 1-3. At 600 °C a composite is present that shows Ti particles with their original shapes retained that are "glued" together with an amorphous ceramic (Figure 1). This bar has a density only slightly greater than that of the original green body (2.94 vs 2.89 g/cm³, respectively), has a large number of voids and is brittle. At 800 °C (Figure 2) the number of voids has diminished and, judging from the backscattering electron image, the Ti metal particles have begun to lose their original shape, probably due to surface reactions with the amorphous SiC which occludes the pores. The ceramic phases are becoming more pronounced. At 1200 °C (Figure 3) a composite with minimal flaws (density = 4.2 g/cm³) is present that contains relatively well-dispersed ceramic phases, Ti₅Si₃ and TiC (by XRD

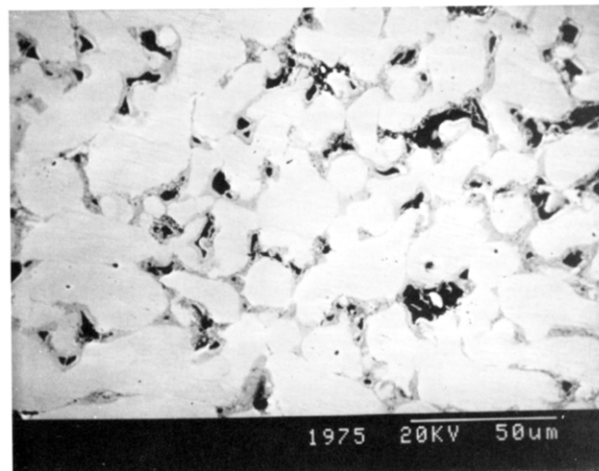


Figure 2. SEM of Ti/PMS pyrolyzed at 600 °C in Ar for 3 h. Backscattering electron image (note the development of gray ceramic phase between metal particles).

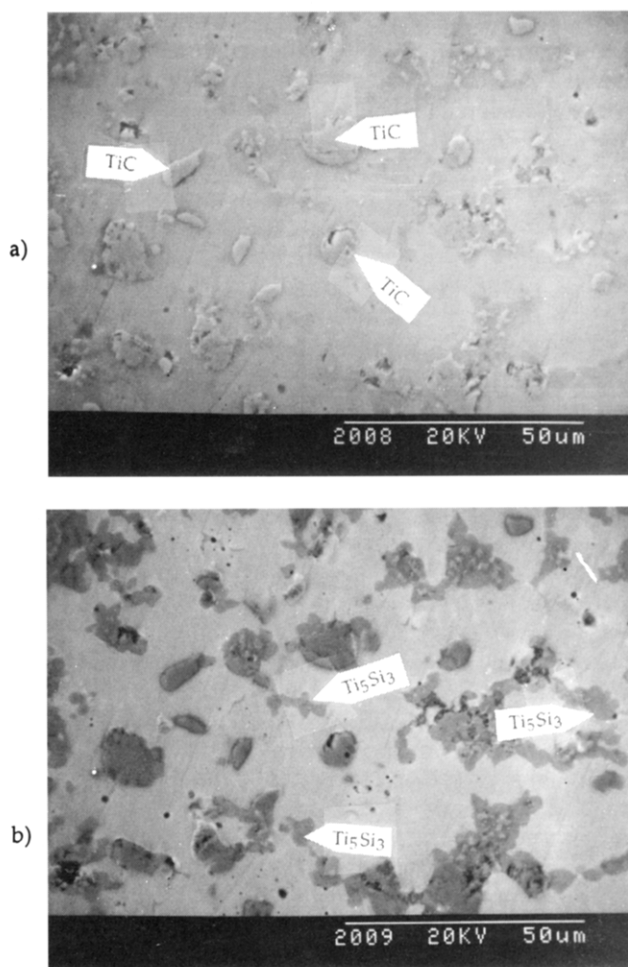


Figure 3. SEM of Ti/PMS pyrolyzed at 1200 °C in Ar for 3 h: (a) secondary electron image depicting convex TiC rich regions, (b) backscattering electron image with well-visible Ti₅Si₃-rich regions. The EDX patterns of Si-rich regions confirm the assignment.

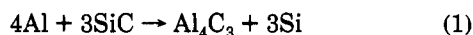
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and energy dispersive X-ray diffraction (EDX), Figure 3). The shrinkage in volume after firing (at 1200 °C) is 30%, and no other distortions are present. Although the ceramic phase dispersion increases with higher temperature, it appears that the dispersion is governed mostly by the metal particle size.

Metallic aluminum appears to be a special case. Pyrolysis of an Al powder/10 mol % (16 wt %) PMS composite

bar to 550 °C yields an amorphous silicon carbide dispersed in the Al matrix. The volume shrinkage on pyrolysis is 10% without any other defects. The ceramic phase appears to be poorly dispersed in the Al matrix. Examination by Vickers microhardness tests showed soft metal regions of 46.8 HV (44 HB) and hard metal/ceramic regions of 75.5 HV (66 HB). When this bar was heated to 1000 °C (above the mp of pure Al, 660 °C), it retained its shape and became stronger and hard (75.3 HV) throughout. At that temperature the ceramic phase had dispersed, probably as a result of the solid-state reaction that had taken place between SiC and Al (eq 1).¹³ XRD analysis showed



elemental Si and Al₄C₃ to be present, so the final result was an aluminum-silicon alloy that contained dispersed Al₄C₃ ceramic phase.

The high-temperature reactions which result in a dispersion of ceramic phases throughout the metal matrix have useful consequences. Taking titanium powder as an example, it was found that when cross-linked PMS (a source of near-stoichiometric SiC) was used as binder, the final product (after heating to 1200 °C) had a Brinell hardness of 390 HB (vs 70–74 HB for pure ingot Ti). In contrast, use of the PCS and PVS polymer binders (whose pyrolysis results in substantial amounts of free carbon) gave a final composite much richer in TiC (via the Ti + C reaction) that was less hard (132 HB for the PCS bar, 222 HB for the PVS bar). On the other hand, these composites which were richer in TiC had a higher modulus of rupture (344.6 MPa for the bar in which PVS was used, 377.2 MPa for the bar in which PCS was used) than the bar in which PMS was used as binder (203.1 MPa).

In general, the melting temperatures of the final composite bars were lower than those of the pure metal. However, the aluminum composite bar mentioned above retained its shape without apparent melting up to 1300 °C. Differential calorimetry indicated some internal melting shortly before the melting point of aluminum, which, however, did not compromise the stability of the bar. This lack of *apparent* melting very likely is due to Al₄C₃ dispersoid reinforcement of the bar. It has been observed by some investigators¹⁴ that the presence of a nonmetallic dispersoid such as Al₄C₃ results in greatly improved high-temperature (500 °C) creep behavior, excellent thermal shock resistance and high sound damping capacity in aluminum matrix composites.

Enhanced resistance to high-temperature oxidation was seen in some cases. In particular, titanium composite bars consolidated using 10 mol % of PMS or PSZ as binder retained their rectangular shape on being heated in air at 1000 °C for 50 h. Surface oxidation (6% and 11% weight

gain, respectively) did occur, but removal of the outer oxide layer left a hard (421 HB and 487 HB, respectively) metallic bar. In contrast, the use as binders of organosilicon polymers whose pyrolysis gives a substantial amount of carbon in addition to SiC (PCS, PVS) did not result in such oxidation resistance in the final product.

In another example, an Al/10 mol % PMS composite bar that had been heated first to 550 °C in argon with a 2-h hold and then to 1000 °C with a 2-h hold survived very well 50 h heating in air at 1000 °C, showing a 2% weight increase, a 10% volume increase, and retaining its original preoxidation hardness of 75 MV (66 HB). Such Al/10 mol % PMS composite bars also were fairly resistant to boiling water. After such treatment for 1 month, a bar that had been heated only to 550 °C showed a 0.1% weight decrease, no change in volume, and undiminished hardness. A bar that had been heated to 1000 °C (i.e., containing Al₄C₃), on treatment with boiling water for 1 month, underwent surface corrosion as indicated by a 14% weight increase and a 26% volume increase. After removal of the surface layer, the hardness of the bulk body was found to be undiminished.

It is clear that preceramic polymers will find useful application in powder metallurgy. They serve well as low loss binders that facilitate shaping the green body. It may be expected that future research will lead to the development of metal powder/preceramic polymer formulations suitable for fabrication of parts by injection and compression molding. The preceramic polymer binders also serve as the *in situ* source of well-dispersed, discontinuous ceramic reinforcement phases, leading, in favorable cases, to stronger, harder, and more oxidation-resistant materials. Although our initial work has focused on the use of organosilicon polymers in this application, we have found that boron-containing polymers, such as the decaborane-diamine polymers,¹⁵ also may be used. These, when heated in a metal matrix, give metal borides as a ceramic phase.^{12b} Considering the many preceramic polymers that have been developed to date and the many metals and metallic alloys that may be used, this area of preceramic polymer application is a very broad one indeed. Much work remains to be done in order to obtain a good understanding of the chemical, ceramic and metallurgical aspects of this novel metal processing procedure. We report our early results at this time because we wish to call attention to this new variation of powder metallurgy/metal matrix composite fabrication which, we believe, has good potential in materials applications.

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Supplementary Material Available: XRD patterns of the Ti/PMS composite (4 pages). Ordering information is given on any current masthead page.

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