

Development Progress: Sintered Tough-Coated Hard Powders (TCHPs)

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ABSTRACT

Allomet has demonstrated it can produce a novel family of sintered designed-microstructure pseudoalloys that combine extremely high hardness with fracture toughness of tungsten carbide and weight approximately of titanium. This paper describes progress in developing processes for creating TCHP particulates and for consolidating them as we industrialize and commercialize this new family called Tough-Coated Hard Powders (TCHPs, or EternAloy[®]). Emerging from small-scale development to real world applicability, TCHPs have demonstrated the potential to significantly exceed the property extremes of conventional materials.

Consolidation of TCHP powders has been achieved by hot press, sinter-HIP, and sinter-forge. Recently, liquid phase sintering of TCHPs was demonstrated as a viable and highly robust consolidation option. TCHP coatings thermally-applied by HVOF, plasma spray, and by several types of laser have demonstrated outstanding results. Based on successful development progress, a TCHP manufacturing plant with proprietary process equipment became operational in mid-2004 in North Huntingdon, PA, USA.

Keywords: hardmetal, nano-composite, CVD coated powder, particle encapsulation, TCHP

INTRODUCTION

Tough-Coated Hard Powders (TCHPs) are hard micron and submicron scale refractory particles CVD coated with tough nanolayers of WC or TaC and Co or Ni binders (see Figure 1). Contrary to conventional hardmetals [1, 2, 3] in TCHP, the near-perfect atom-by-atom CVD distribution of the binder phase increases the range of consolidation parameters while avoiding undesirable Ostwald grain growth. It appears that almost any sintering method will consolidate TCHPs. Consolidation of TCHP creates an engineered highly homogeneous cellular structure whose interconnected tough WC-Co “shells” each contain a wear-resistant core (*e.g.*, Al₂O₃).

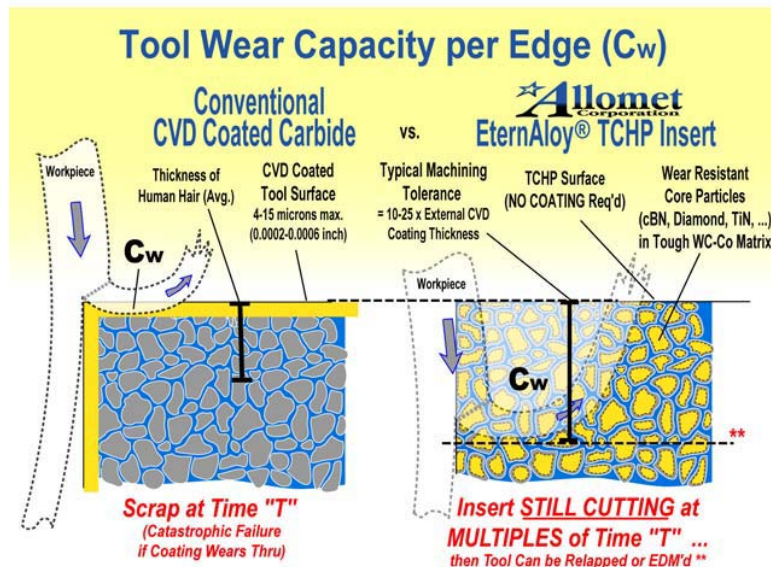


Figure 1. Comparison of conventional thin-coated and TCHP tool inserts during cutting. TCHP tool remains operating significantly longer until the machining tolerance is reached.

machining (EDM). (See **Figure 1**).

ADVANTAGE OF PARTICLE ENCAPSULATION

Encapsulating fine particles having one set of desirable properties with grain boundary modifiers having other properties allows us to blend heretofore-uncombinable material-property combinations prior to sintering. This merging of multiple property extremes into nanocoated submicron all-in-one “designer particles” enables an unprecedented near-atomic scale integration of thermodynamically incompatible materials and properties so that they operate simultaneously and seamlessly at the finest possible scale at working surfaces and cutting edges of tools. TCHPs, super- to ultra-hard particles uniformly distributed in a WC-Co matrix, already combine high hardness and high fracture toughness combinations. The thermal conductivity can be engineered to be significantly lower than in comparable filler-particle-free hardmetals, depending on the alloys of the matrix, on the

In TCHPs, the wear resistant material is distributed throughout the article, not only at the surface, combining the strength, heat resistance, and toughness of contiguous cemented carbide phases with the chemical and abrasion wear resistance of orders of magnitude harder materials. As wear progresses, new wear-resistant material continuously replaces (self-heals) the working surfaces and edges of the tool or article until its geometry reaches its maximum limits. Worn TCHP articles are then reusable many times by relapping or electro-discharge

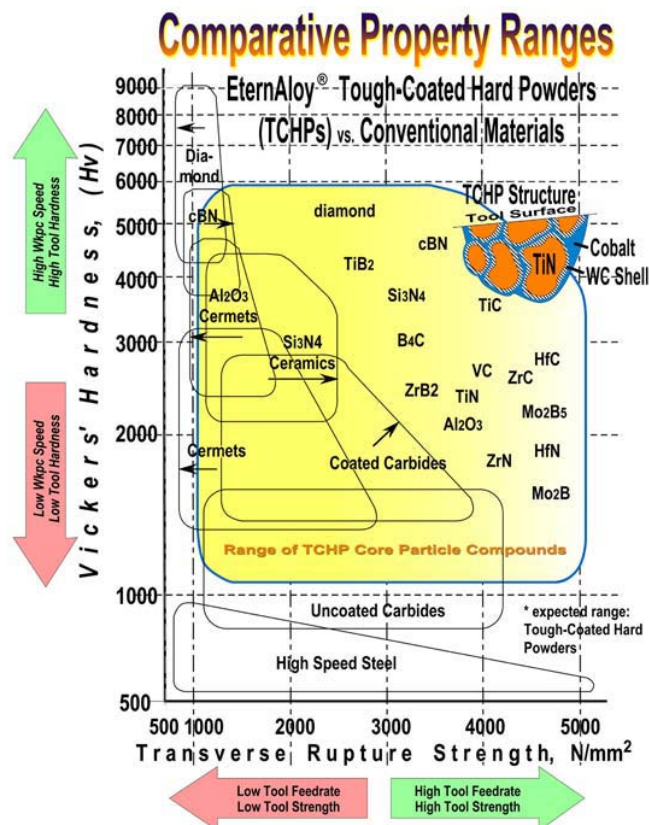


Figure 2. Hardness and strength combination ranges for common tool materials compared with those for several TCHP variants. The theoretical TCHP composite structure is shown (inset) at upper right.

amount of residual porosity, and interfacial thermal barrier. Since TCHPs typically consist of a high amount (~40-80 vol%) of refractory compound particles, the thermal insulation properties can be further enhanced by using (i) ultra-fine, (ii) low-conductivity core particles, *e.g.*, Al_2O_3 . Thus a higher volume fraction of the cores, together with a reduction in filler-particle size, translate to a decreased composite conductivity for improved HS machining.

In addition to the improved insulation properties, higher strength and hardness are achieved with a finer microstructure. No matter to what heat treatment TCHPs are subjected, the core particles will remain uniformly distributed. Such, during consolidation, the WC-Co-matrix can be selectively designed and optimized for toughness, density, and/or retention of the fine microstructure. See **Figure 2** for a hardness vs. strength comparison of tool materials, and **Figure 3** for typical fully dense TCHP microstructure.

With TCHP's maximum combinations of hardness, toughness, and other engineered properties (*e.g.*, thermal conductivity or resistivity, coefficient of friction, etc.) unavailable in any other materials, better combinations of cutting speeds and feeds are virtually assured.

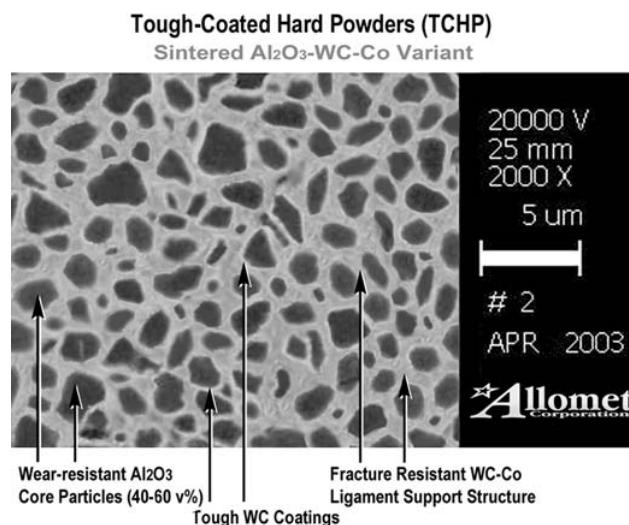


Figure 3. SEM microphoto of fully dense Al_2O_3 -core TCHP. Other particles (cBN, diamond, TiN ,...) can be substituted or mixed in combinations with targeted property combinations.

BUILT-IN LUBRICANTS

Since the precursors are combined through chemical vapor deposition of the tough matrix onto hard filler particles, TCHPs don't need milling or blending at any stage of processing, or segregation prevention during storage. Additional features not readily available in conventional processing, such as inclusion of low-friction particles for self-lubrication, can be implemented during particle encapsulation by blending with another powder for a special functional property, and/or by mixing before consolidation.

Further, controlled encapsulation of ultra-fine, *i.e.* nanosized particles – same as is done with TCHPs – is a very promising approach to overcome agglomeration and segregation hurdles on the way to nanocomposites.

MECHANICAL PROPERTIES

A major breakthrough of TCHPs was proving that cobalt does not come close to penetrating the protective WC coating during sintering. This avoids dissolution and chemical alloying of WC and Co with many core particle materials such as TiN . (Chemical involvement of TiN would greatly reduce the maximum toughness of the matrix phases to that of conventional brittle cermets). In TCHP, there is a natural and powerful “protective symbiosis” between the core particles and the WC coating. First, during sintering, especially in the “soluble core” group, the very robust WC coating protects the core particles from dissolution by the binder metal and thus protects the matrix from harmful pollution by TiN , ZrN , NbC , and the like [4, 5]. During use, the highly wear resistant TCHP core particles protect the WC-Co support matrix from wear after sintering while the support matrix protects the brittle phases from fracture and pullout.

The second major breakthrough was demonstrating that TCHP powders can readily be pressed and liquid-phase sintered or sinter-HIPped like ordinary carbides in commonly-available equipment [7]. An inherent advantage of TCHP powders over classical WC-Co mixes is that the Co binder in TCHP is more homogeneously distributed throughout the powder than is possible by any known mixing process. During coating, the cobalt is added, atom-by-atom, to encapsulate the surface of each highly contiguously WC-coated TCHP particle with exactly the targeted Co:WC ratio. This continues until *the desired Co:WC ratio is nearly perfectly uniformly distributed on every TCHP particle and throughout the powder*. This is a key feature of TCHP that has never been achieved in milling of conventional hardmetal powders.

The very uniform distribution of Co in TCHPs reduces concern about Ostwald grain growth. Thus, the TCHP sintering temperature has a margin for increase in order to attain the capillary attractive forces necessary for increasing interparticulate slip and WC mass transfer for fully dense conventional liquid phase sintering consolidation of TCHP. Because of minimized concerns about dissolution of the WC coating and about grain growth, *increased weight percentages of Co* in TCHP than are customary in WC-Co sintering become feasible as a means of providing the needed dissolution, capillarity, WC kinetics, and densification. It is to be remembered that in TCHP, the WC is present as a tough matrix material only because the real wear resistance is being provided by the core particles. Added cobalt will therefore add to the amount of liquid phase during sintering while at the same time increasing fracture toughness after cooling.

During liquid-phase sintering, ~90% of the protective WC coating remains as solidus to form preferred nucleation and reprecipitation “rim sites” of WC during cooling, reforming and maintaining the desirable core-rim structure after sintering. This has many advantages in developing a chemically inert substrate while assuring mechanical toughness through coating and particle uniformity and homogeneity that is inherently superior to that of any mixed powders.

DEAGGLOMERATION FOR COATING TCHPs

D. Geldart's Groups A, B, and D powders (generally particles larger than about 50-100 microns) have negligible interparticle cohesive forces compared with the forces fluidizing gases exert on the particles [8]. In Geldart's Group C classification of particles (which are the most useful in hardmetals), powder agglomeration increases exponentially as the particle size decreases below about 40 microns. Group C particles of low density are much more easily entrained by fluidizing gases but are more difficult to deagglomerate than are heavier particles. Because of high van der Waals and other interparticle cohesive forces, Group C particles are difficult to deagglomerate and fluidize at all. According to Rawle [6], these adhesive forces are about 100 g's for 10 micron particles, about 1000 g's for 1.0 micron particles, and about $10^4 - 10^5$ g's for 0.1 micron particles, where “g” is the force of gravity.

A TCHP particle coating apparatus must provide a means of continuously applying forces on the agglomerates high enough to fluidize, deagglomerate, and individually coat Geldart Group C particles with WC and Co. Because of these enormous attractor forces, few of the many powder coating methods disclosed in the public domain are remotely capable of coating contiguous and homogeneous coatings on Geldart Class C powders because they cannot apply sufficient breakup forces on the powder agglomerates to individualize the particles for 100% coating.

One of the most widely-used coating methods is the fluidized bed. Fluidized bed reactors are useful to operate because of the high exposure of solid surfaces to the carrier and coating source reactant gases. However, this is terminally offset by the principal limitations of all fluidized beds: (1) smallest core particles in the 4-5 micron range; (2) large and costly development lots; (3) inherently increasing particle weight requires continuous alteration of

process parameters and sophisticated modeling, monitoring, instrumentation, and control systems; (4) particle coating residence time inherently proportional to particle size and weight; (5) product quality variation with lot size; (6) thermodynamic inefficiency; and (7) prodigious consumption of expensive CVD process gases.

To apply increased amounts of shear and tensile forces to break up the agglomerates, Allomet's rotary drum reactor employs a rotary drum furnace fitted with a nonrotating deagglomeration comb, homogenization guide, and a nonrotating shaft and comb/guide mounting assembly. The deagglomeration comb squeezes and compresses the agglomerated powder between the rotating drum and the stationary comb surfaces applying compression, shear, and tensile forces on the agglomerates to break them up as they reform. The powder flows, rolls, tumbles, fluidizes, and cascades by a combination of centrifugal force, gravity, compressive and shear forces, and rotational inertia imparted by the drum and comb.

Particle fluidization dynamics may be videotaped through a false glass/plexiglas end piece while rotating at room temperature.

During the deagglomeration tests viewed with plexiglas observation window, the deagglomerator conceptual design worked better than anticipated (see **Figure 4**). We were pleasantly surprised by the vortex of powder fines that was maintained (at position C), especially as there was a fine mist of powder cascading downwards at its center.

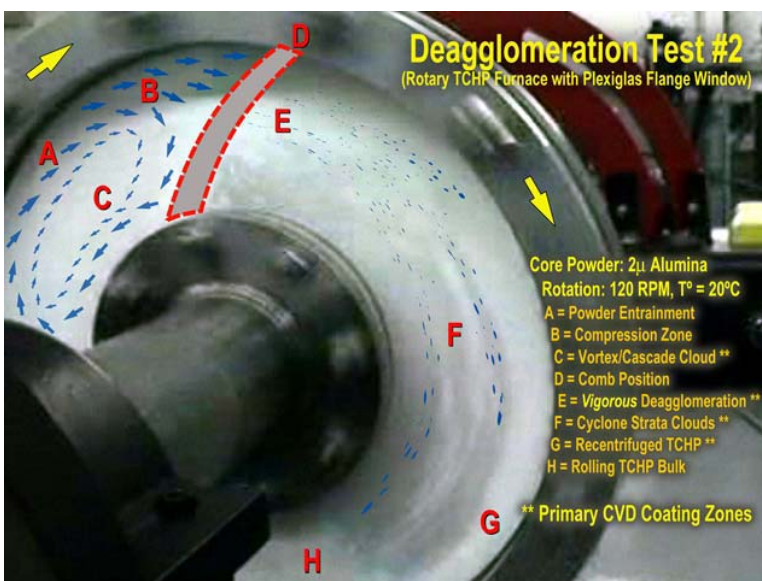


Figure 4. High speed plexiglas window view of successful shear/cyclonic deagglomeration of 2 µm Geldart Class C Al_2O_3 core powder in an Allomet Rotary TCHP furnace retort.

This adds considerably to the amount of deagglomerated particles that are exposed to the CVD coating vapors per unit of time, increasing the coating efficiency and precursor chemical utilization. The downward flow of powder at the comb face (from **B to C**) keeps powder from collecting there that could have created hard agglomerates.

It was expected that there would be insufficient kinetic energy left in the powder upon exiting the comb (see **D and E**) for it to do anything but fall straight downwards. Instead, the pressure expels the powder forcefully from between the comb teeth, creating a cyclonic blizzard of deagglomerated micron core powders inside the retort with CVD gases continually flowing through them. This pitches the moving powder such that the exposure to CVD vapors is increased. It was also expected that the rotating retort would re-centrifuge the deagglomerated TCHP along the retort wall (near position **G**), and indeed it does. However, by a cyclonic or gas phenomenon we don't yet understand, a large percentage of the deagglomerated TCHP remains uncentrifuged in stratified "clouds" of powder. The added benefit of this is that the particles remain deagglomerated and individualized for a longer time, again increasing the coating efficiency and precursor chemical utilization.

Allomet demonstrated its process will deagglomerate (and individualize for CVD coating) particles in the 500 nm – 2.0 micron range. The success of these trials validates a considerable number of our assumptions about coating Geldart Class C TCHP powders. As such, this is a *major* step forward. It is expected that particles in the 200-500 nm range can also be

deagglomerated and individualized for coating, something only done previously in liquid-based systems.

CONCLUSIONS

- TCHPs have the potential of achieving the highest combinations of toughness, hardness/wear-resistance, and designer properties of all known tool materials.
- Deagglomeration and coating of 500 nm – 2.0 micron particles in a rotary coating furnace has been achieved, something only done previously in liquid-based systems.
- Hot pressing has proven to be a valuable method to consolidate TCHPs to full density in one step. The consolidation cycle has been optimized; proof-of concept has been successfully demonstrated.
- Nanoengineered particulates (TCHPs) with net-shape manufacturing technologies offer opportunities for engineers to simultaneously design and optimize structures at the nano-, micro-, macro- and functional levels.
- The first generation of TCHP Products demonstrates better cutting performance than conventional hard metals or cermets. More process optimization is underway.

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