Winter 2004

CISP

Center for Innovative Sintered Products

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Densification of Iron Powders: *The Attraction of Full-Density Steel*

Rand German – Director

Full-density sintered products are around us everywhere, in high-intensity light bulbs (indeed Coolidge patented tungsten wire made via a sintering technology in 1910), automotive connecting rods, watch cases, and cutting tools.

When CISP meets with the user community (often a large, multinational firm with significant market access) the consistent theme is very different from when we meet with the sintered materials community. The users usually approach sintered materials at the end of the design process. They start with a definition of the market and its needs, and design a product with targeted performance. From the performance emerges a specification of the material and some consideration of fabrication routes. Fundamentally, this means that consideration of sinter powders occurs near the end of the design cycle, after function, form, properties, tolerances, and materials are selected. At this point design engineers have two major questions:

1) Can you make it to my specifications?
2) How much will it cost?

When this happens, the competition is over a wide range of material fabrication processes, not just between vendors of sintered materials.

The perception in the sintered materials community is that more projects could be won if only performance could be improved. Since performance derives from density, the immediate conclusion is that market growth is inhibited by lack of densification. This is true for one portion of the sintered materials field – ferrous powder metallurgy. However, generally such a conclusion is not true for other materials, since small powders are available and can be sintered to full density in refractory metals, technical ceramics, cemented carbides, and even polymers.

For CISP, our quest is to help remove the boundaries on sintered products. Hence, we have investigated the subject of full-density sintered iron and steel. The statistics for the past decade show that major growth has been in applications of 7.6 g/cm^3 and higher, while applications below 7.0 g/cm^3 appear to be in decline (plastics again). So what is the research agenda to support the transition to full-density steel? Here are some important facts.

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Consortia – A Business Model

Since CISP began operation in June 2000, the business focus of the industry has shifted. Companies are being reconfigured to take advantage of partnering and alliances to produce the best return on assets. The practise of leveraging internal and external networks and taking advantage of collaborative platforms to address emerging customer needs is now a business model. A strong interest in the formation of consortia has emerged. To serve this need, we intend to bring together strategic groupings of members and non-members to focus on such subjects as water-soluble binders for injection molding, full-density ferrous PM, controlled porosity, titanium–biomedical–porous, green machining, injection molding and accelerated debinding, and microwave sintering. These measures should help companies to propagate new capabilities and offerings for competing in this global environment. Contact Sharon Elder: cisp@psu.edu.

Upcoming Events

March 21, 2004
PIM Tutorial
Orlando, FL

March 22-24, 2004
PIM04
Orlando, FL

May 10-11, 2004
Industry Member Meeting
University Park, PA

June 13-17, 2004
PM^2TEC
Chicago, IL

Densification of Iron Powders... continued from pg1

First

Sintering iron and steel to full density is possible, as evident by powder metal injection molding. Also in the past few years there have been several reports on using boron or carbon additions for full-density sintering, even using prealloyed powders. This is not new. First demonstrations of sintering a –150 mesh powder to full density were reported in1962, so it is hard to say that sintering to full density is a barrier. Over the past few years several groups have demonstrated that water-atomized iron powder mixed with nickel, molybdenum, carbon, and other alloying additions can be sintered to 97% density over 7.6 g/cm^3) at 1200°C (2200°F) in 30 min., giving a material with a strength over 700 MPa (100 ksi).

Second

Iron and steel powders have been compacted to essentially full density, making sintering a trivial activity. Sample parts made at IBM were shown in 1964. Today, special presses are used to achieve high pressures in the 1600 MPa (120 tsi) range – and even higher with tetrahedral presses. The conventional limit of 700 MPa (50 tsi) results in a lower density, but longer tool life. Dynamic compaction of iron powder to full density using gas guns was demonstrated by 1976. Further, many of us remember the "cold sintering" technology out of Israel, which simply used high pressures to take steels, including tool steels, to full density at high pressures. Hence, the new wave of technologies does not tease iron or steel powders into any new behavior, but simply puts the deformation work into the powder in multiple strokes or higher velocities or warmer temperatures.

So what is the bottom line for CISP research? We know iron and steel powder work-harden during pressing, so the low starting density and work-hardening are major limitations on pressing to full density. Higher temperatures, higher strain rates, higher packing densities, and higher compaction pressures increase the pressed density, but these come with cost penalties. Full-density sintering likewise comes with cost penalties associated with the higher sintering temperatures, dimensional variation, and microstructure effects (grain size growth). Thus, when we look in detail at the options, we find that full density is possible

1) via high-compaction pressures with concerns over tool wear and press cost

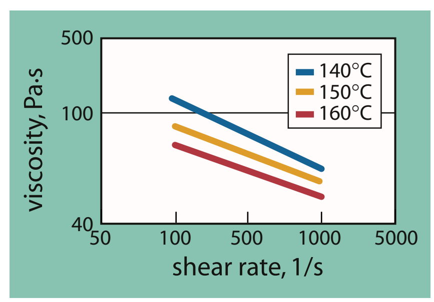
2) via high-sintering temperatures with concerns over furnace cost and dimensional precision.

CISP remains active in both areas. One project is building constitutive models for full-density iron pressing by examining combinations of powder size, powder shape, powder purity, apparent density, temperature, strain rate, peak pressure, and number of pressure pulses. A second project is examining means to improve lubrication and tool life, including selection of new binders and lubricants, all geared to sintering to full density with minimized distortion. Next May we hope to have full reports on both approaches, with basic information that will allow CISP members to make informed decisions for the future.

PIM of Niobium

Niobium has excellent formability and the lowest specific weight among the refractory metal family (Nb, Ta, Mo, W, and Re). Unlike ferrous materials, refractory metals do not incur a powder cost penalty, since they are already formed from small powders. Currently, the majority of Nb is used as an alloying element in steels and nickel-base superalloys. Only 1-2% of the global niobium is used in pure form and niobium-based alloys. These are employed in a variety of high-temperature applications ranging from light bulbs to rocket engines.

Powder injection molding of pure niobium powder is being investigated at CISP for the efficiency of the process. Due to the high reactivity of niobium, impurity pickup occurs during the processing. This study aims to identify an operating window for consolidation and sintering of pure niobium and niobium-based alloys. Alloying elements are added to reduce pickup and subsequently increase the high-temperature strength. Further, a quaternary Nb-Ti-Mo-W system will be investigated with respect to its effect on strength, oxidation resistance, and processability.



In the experiments performed, niobium feedstock exhibited pseudoplastic flow behavior. Viscosities of the feedstock at all working temperatures were smaller than 200 Pa.s, which matches the requirements for injection molding. Ninety-eight percent density was achieved in molded tensile bars after sintering at 2000°C in high vacuum. Gaurav Aggarwal: gza103@psu.edu.

Industry Member Meeting Recap

CISP's most successful member meeting to date took place on October 20–21, during which more than 100 attendees were treated to a diversity of technical presentations and given the opportunity to network with colleagues from industry and academia. The overarching theme of this meeting was "Globalization – threat or opportunity?" It was evident that the business climate had improved since our previous meeting in February. Dr. Michael Wargo, Enterprise Chief Information Officer for NASA's Office of Biological and Physical Research, outlined the current space program. NASA has developed from providing support for basic research to laying in place the stepping-stones for new space exploration and survival. In-space fabrication and the ability to sustain life for extended periods of time and return humans safely to earth are all critical issues for continued exploration.

A further special topic, on spray deposition as a new technique in cold spray, was given by Dr. Maurice Amateau, Head of the Materials Processing Division at the Applied Research Lab of Penn State. Dr. Digby Macdonald, Director of the Center for Electrochemical Science and Technology at Penn State, presented an update of the new thermoelectric chemistry synthetic approach to titanium powder. CISP Director Dr. Randall German presented a status report on new trends in sintering.

Technical updates included a project report on full-density iron pressing. We now have the first computer model of the sintering processes graduated to 3-D – non axi-symmetric component predictions of final size and shapes. There was also a report on the support of the first implications of the master sintering curve for commercial practice that now involves several companies.

If you are interested in joining this diverse group of companies, contact Sharon Elder: cisp@psu.edu.

Online Calculation of Pressure Buildup During Thermal Debinding

A software that enables the calculation of the pressure buildup in a powder component during thermal debinding is now available. You can download the software, called "Debindo," by clicking "Numerical Simulation of Binder Burnout and Stress Formation" on the CISP web page at *http://www.cisp.psu.edu/resdev/research_proj.htm*. This link brings you to a tutorial that teaches how to work with the software. Companies are invited to look at Debindo and to evaluate pressure buildup in their own components. Studies performed at CISP for alumina injection molded bars showed that critical pressure leading to the formation of cracks and defects is very small (1.0055* atmospheric pressure). Companies that would like to know more about the software and the possibility of improving the thermal debinding cycle should contact Chantal Binet: cub9@psu.edu.

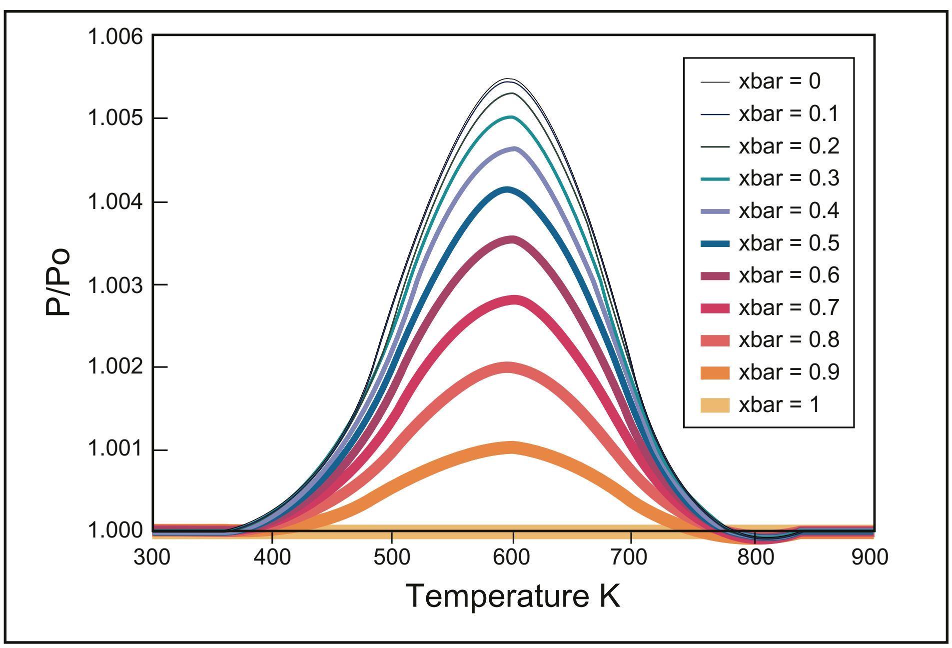


Figure 1. Pressure that develops during thermal debinding of an alumina injected molded part with 56.6 wt% solid, and 15.2wt% polyethylene at 60°C/min debinding rate. Polymer wax was previously removed by solvent debinding.

Corrosion Resistant MIM Components

Many MIM components are produced from stainless steels because of their corrosion resistance under oxidizing conditions, which include exposure to nitric acid, phosphoric acid, and concentrated sulfuric acid. However, other corrosive environments encountered in the chemical processing industry require different material solutions. Alloys with higher Ni contents have greater resistance to reducing environments, such as exposure to hydrochloric acid, hydrofluoric acid, dilute or intermediate strength sulfuric acid, caustic soda, and dry chlorine.

Advanced Materials Technologies Pte Ltd and CISP have been evaluating the corrosion resistance of MIM superalloys (HX, 718, and 625) and commercially pure Ni (270) in comparison to 316L stainless steel. These alloys were injection molded and sintered to densities of 95% of wrought or better. The general corrosion resistance of the sintered parts to 1M nitric acid, 1M hydrochloric acid, bleach (5.25% sodium hypochlorite solution), 40% sodium hydroxide, and 50% sulfuric acid was measured according to ASTM G 31.

Corrosion rates for the various MIM alloys	Corrosive media	316L mpy	HX mpy	718 mpy	625 mpy	270 mpy
	Nitric acid	0.0	-	0.0	0.0	160
	Hydrochloric acid	8.8	3.8	16	0.3	5.5
	Bleach	0.0	-	0.1	0.1	79
	Sodium hydroxide	0.8	-	0.0	0.0	0.0
	Sulfuric acid	36	1.7	42	0.0	0.3

The 316L performed well in the oxidizing media – bleach and nitric acid – and the results compare favorably with wrought material. As expected, these media attacked the commercially pure Ni much more severely than the 316L. On the other hand, the Ni had better performance over 316L in the reducing media – sulfuric acid and sodium hydroxide. Both Ni and 316L had moderate corrosion resistance against hydrochloric acid while the 625 showed excellent corrosion resistance to both oxidizing and reducing media, including hydrochloric acid. The 718 was more susceptible to attack by hydrochloric acid and sulfuric acid. HX had relatively good corrosion resistance to these media. These results confirm the capability of MIM to produce corrosion resistant components for the range of conditions found in the chemical processing industry. Contact John L. Johnson: john@amtellect.com, or Pavan Suri: pavans@psu.edu.

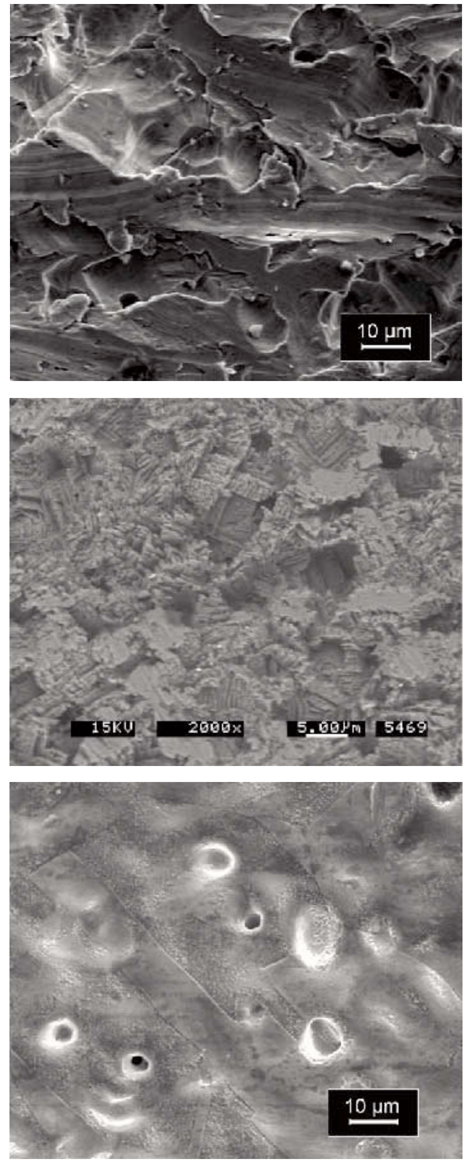
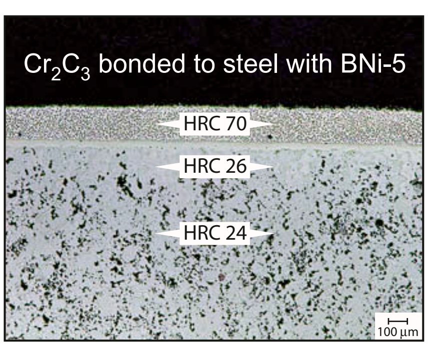


Figure 1. Backscatter SEMs of the surfaces of (a) 316L (b) 718 and (c) 270 after corrosion testing in H_2SO_4.

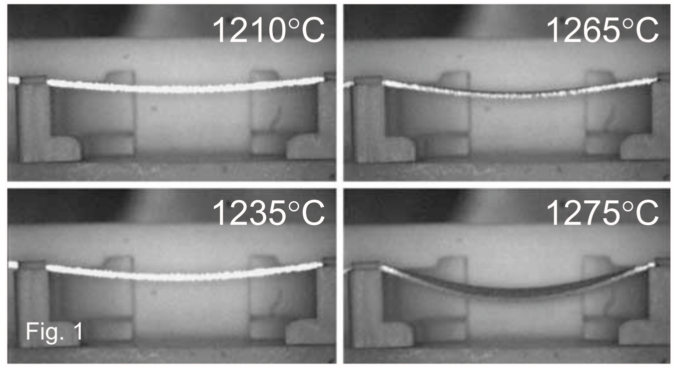
P/M Hardfacing

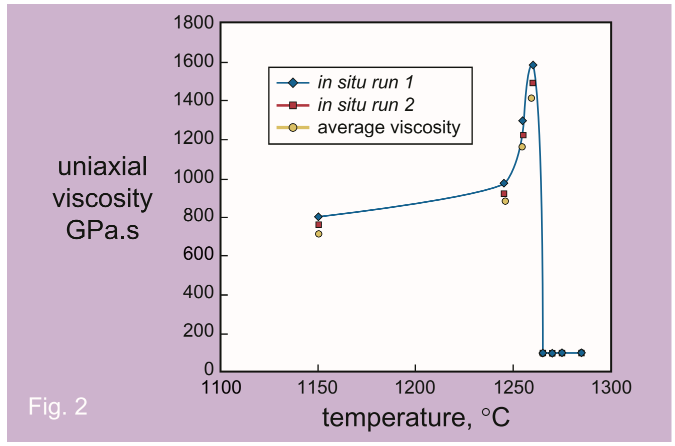
Our P/M Hardfacing project goal is to sinterbond a carbide layer to traditional iron-based P/M parts during the sintering process. Four braze alloys were investigated as candidates. Chromium carbide was chosen as the hard phase because the thermal expansion coefficient is closer to that of iron than other carbides. The chromium carbide layer was applied via a slurry and doctor blade at a thickness of 0.25 mm. The braze alloy powders were tape cast and set atop the carbide layer. Vacuum sintering at 1150°C for one hour produced successful brazed carbide layers with two of the braze alloys, resulting in a 70 HRC coating. Excess braze alloy infiltrated the porosity in the Fe base material. New focus for the project will be towards sinterbonding in N_2/H_2 atmosphere, and efficient application methods for the carbide and braze layers, including electrophoretic deposition, a popular method in automotive painting. In this process, the metal to be coated is immersed in a dilute solution of particles, binder, and solvent. Particles are drawn to the surface of the part by a DC charge, resulting in a coating of uniform thickness. The thickness is self-regulating because the particles create an insulating layer. This process may be applied to the coating of the carbide particles, while a method such as dip coating may be used for the braze layer. Contact Neal Myers: nsm104@psu.edu.



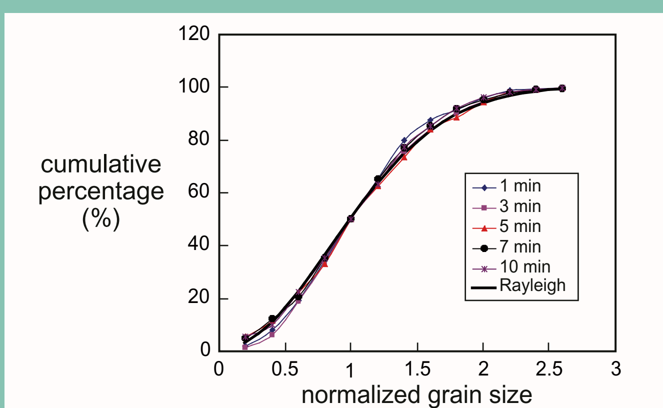
In Situ Viscosity Evaluation During Supersolidus Sintering

Supersolidus liquid phase sintering (SLPS) is an economical way to manufacture net-shaped components starting with coarse alloy powders. The evolution of viscosity plays a critical role in densification and distortion during the process. An *in situ* video-imaging technique (Synchrotron) was used to measure the bending deflections during SLPS. Bending beam theory was used to calculate the viscosities during sintering. Experiments have been performed with boron-doped stainless steel 316L bars. The *in situ* images showing the bending deflection with temperature are shown in Figure 1. Figure 2 shows the apparent viscosity evolution with temperature and, as can be seen, viscosity increases with temperature due to densification, after which the viscosity drops considerably. This viscosity decrease will lead to slumping and hence poor dimensional control. Efforts are under way to better understand how the viscosity evolves during sintering and to correlate that with microstructural evolution. This will help us to manipulate the processing conditions to achieve full densification without distortion. Contact Rand German: rmg4@psu.edu or Ravi Bollina: rxb901@psu.edu.

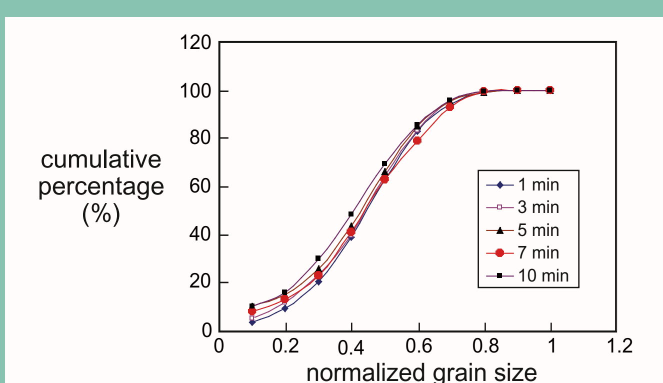




Quantitative Microstructure Analysis: Tungsten Heavy Alloys



Relative grain size distributions in 88W-9.6Ni-2.4Cu alloys sintered at 1412°C for different hold times (1, 3, 5, 7, and 10 min).



Contiguity distributions in 88W-9.6Ni-2.4Cu alloys sintered at 1412°C for different hold times (1, 3, 5, 7, and 10 min).

Image analysis and microstructural quantification of tungsten heavy alloys have been performed using the Clemex Image Pro system that was installed in summer 2003. The microstructural parameters quantified by this system include grain size, grain shape, connectivity, contiguity, dihedral angle, neck size, neck size ratio, and pore size. In contrast to previous measurements, statistical distributions of all these parameters can be measured simultaneously for further analysis. This is a powerful tool for microstructure analysis of liquid phase sintered samples and the study of liquid phase sintering under microgravity. The analysis results can be used to evaluate the fundamental mechanisms of sintering, and to model and predict the liquid phase sintering process. Currently, the pore size and porosity analysis can be conducted automatically, and it takes only about 10-15 min. to produce pore size, porosity, and pore size distribution for 5000 pores. The mean values and statistical distributions of grain size and all other microstructural parameters can be measured in a much shorter time than before. This work is supported by NASA-GEDS. To learn more on the capabilities of this system or have samples tested contact Lou Campbell: lgc102@psu.edu or Junwu Shen: jxs705@psu.edu.

Student's Corner

Raman Baijal

Raman Baijal is a master's student at CISP. He received his B.S. in Metallurgy and Materials Science from the Indian Institute of Technology (IIT) Bombay, India. He is currently working on the thermal cycle design for densification, microstructure control, and sintered property development in binder injection molded iron–nickel steel. He will be graduating this December and is seeking a job opportunity in the industry. E-mail: rub121@psu.edu.

Student Achievements

Guneet Sethi

Guneet Sethi, CISP master's degree student, has been selected as the receipient of an Innovation Potential of Students Projects Award 2003 from the Indian National Academy of Engineers (INAE) for his undergraduate project titled Experimental and Theoretical Study of Microwave and Conventional Sintered Bronze. Guneet is one of only five B.Tech. students from India who received this award for the year 2003. Guneet joined the CISP lab in August 2003 and is currently working on full-density iron and the conditions for densification. E-mail: gsethi@psu.edu.

Past Student

Dr. Anish Upadhyaya

Dr. Anish Upadhyaya obtained his Ph.D. degree here at the lab in 1998 with a thesis related to distortion during liquid phase sintering of tungsten alloys. He continued for a year in the P/M Lab (now part of CISP) as Director of Materials Development. In May 2000 he returned to India where he is now Assistant Professor in the Materials and Metallurgical Engineering department at the Indian Institute of Technology (IIT), Kanpur.

Dr. Upadhyaya has received several accolades for his research. He was recently selected for the prestigious Young Metallurgist of the Year Award (2003) by the Ministry of Steels and Mines, Government of India.

Dr. Upadhyaya has studied materials processing of varied nonferrous systems, metal–metal and metal–ceramic composites. His research specialization is powder metallurgy processing of materials. His research has attracted several sponsored projects both from government and non-government sources related to sintering aspects of major ferrous and non-ferrous systems, the results of which have been presented in major journals and conferences (over 70 papers). E-mail: anishu@iitk.ac.in.

Honorary Doctorate

CISP Director Randall M. German has been awarded an honorary doctorate degree from the University Carlos III of Madrid. Dr. German presented seminars on Introduction to PM, Sintering Theory and Application, and Powder Injection Molding at the university in spring 2003. We established a collaborative relationship with this university several years ago, and for each of the past two summers CISP has hosted a PhD student of theirs at our lab. We will continue this cooperation and plan to send one of our students to Spain on a reciprocal exchange in the near future.

Research Position

CISP is anticipating the need for a full-time senior researcher early next year. The successful candidate must have at least a master's degree in engineering or a closely related discipline, with a specific focus on the processing of sintered materials, plus at least three years' experience. The individual will build a research program that complements current programs with strengths in such areas as materials processing, powder and microstructure characterization, sintered biomaterials, thermal imaging, novel heating technologies, sintered hard materials, or electronic materials. The candidate must have an established track record of attracting research funds and publishing. Excellent written and oral communication skills are required. Submit cover letter, resume, one-page statement of research interests, and three professional references to Sharon Elder: cisp@psu.edu.

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