

SHORT TERM MOBILITY 2011 PROGRAM REPORT

FOR

ANDREAS M. GLAESER

UNIVERSITY OF CALIFORNIA, BERKELEY

DATES: JUNE 13TH, 2011 TO JUNE 24TH, 2011

LOCATION: CNR/ISTEC (FAENZA)

PRIMARY CONTACT: DR. GOFFREDO DE PORTU

EXECUTIVE SUMMARY:

This report summarizes the research activities of Professor Andreas. M. Glaeser supported by a Short-Term Mobility Program grant. The objectives of the proposed work were to establish selected properties of metallic interlayers that are used to join high-performance advanced ceramic materials. Consistent with these objectives, a number of mechanical properties of several distinct multicomponent interlayers were tested using nanohardness indentation tests. The researchers at ISTEC who collaborated on the project overcame complications that were encountered. A full assessment of interlayer and joined assembly properties will require the completion of additional independent tests being conducted on identical sets of samples in Kyoto Japan. In addition to the work on the project, a number of other interactions with CNR researchers at ISTEC and also from CNR-IENI (Genova) were facilitated, and these will have additional longer-term positive impacts such as joint publications, joint presentations, and joint proposals that could generate external funding for both collaborative projects and research exchanges that would expand and enrich CNR's research footprint.

INTRODUCTION AND BACKGROUND

The following report will outline the terms of the contract and the work that was done to fulfill the contractual obligations. An appendix is provided that discusses other interactions that occurred during the full period at ISTEC, and the potential benefits to CNR, ISTEC, and IENI from those additional interactions.

TERMS OF VISIT

The contract stipulated a ten-day period of work, and agreed upon dates for the official research stay were from June 13th, 2011 to June 24th, 2011. The actual dates at ISTEC were from June 8th, 2011 to June 29th, 2011, essentially fifteen days. This extra time was very valuable, enabling additional interactions that are described in the appendix.

SCIENTIFIC MOTIVATION, GOALS, AND RESULTS

As was described in the original STM proposal, the goal of the stay at ISTEC was to perform a detailed set of measurements on selected mechanical properties/characteristics of metallic interlayers that are being used to bond or join together small pieces of high-performance advanced ceramics into a larger more complex assembly. The difficulties of making large complex shape assemblies out of advanced ceramic materials are well-documented in the literature, and thus developing easy and reliable methods to make such structures from smaller and more easily made components is essential to more widespread use of advanced ceramics in a wide range of applications. ISTEC is the lead CNR lab in terms of fabricating high-performance structural ceramics, and has a history of outstanding contributions in this area. These contributions reflect the efforts and talents of many gifted researchers, and the development over the years of specialized facilities for both the fabrication and testing of candidate ceramic materials. Researchers such as Dr. de Portu, my host and primary collaborator on this project, and other well-known and highly regarded researchers such as Dr. Bellosi, Dr. Guicciardi, Dr. Sciti, Dr. Monteverde, Dr. Silvestroni, and Dr. Esposito made CNR-ISTEC a natural venue for this collaboration. Dr. De Portu, through his international network of associates and colleagues, was also able to secure the assistance and cooperation of Professor Giuseppe Pezzotti (Kyoto Institute of Technology, Kyoto Japan) to further enrich the information that we could obtain and thereby “add value” to the grant.

When ceramic materials are joined to metals or to ceramics using metallic interlayers (foils) as the “glue”, failures often occur preferentially in the joint region. With the joining method that we have developed, the failures more often occur away from the joint. Understanding fully why this is the case provides the fundamental information that would allow the extension of this successful approach to other material systems. Failures at the joint can be due to the development of highly flawed or defective interfaces, or due to the development of high stresses near the metal-ceramic interface, or both. We have collaborated with CNR-IENI to better understand how the liquids that develop during joining will flow into and fill gaps along the metal-ceramic interface. Further details on this are in the appendix. Stresses that can cause failure can be applied or can be residual. The residual stresses are caused by differences in the rates at which the metal and ceramic expand and contract during heating and cooling. Several factors affect the magnitudes of the residual stresses, and the work at ISTEC was designed to quantitatively assess several factors that would be required in modeling/predicting these residual stresses. The interaction with Dr. Pezzotti would provide a direct measurement of the residual stresses. The work at ISTEC, in combination with work done at Berkeley was designed to provide a fundamental understanding of the origins of these stresses and also how they might change as a result of changes in the chemistry design of the joining media used. In the particular joining method we use, we begin with an interlayer or foil that has multiple chemically distinct

layers. For example, the interlayer would have a thick central layer of one material, call it B. Each surface would then be coated by one (or more) much thinner layers of a second material, call it A. At the start of joining, the interlayer has an A/B/A structure. During joining, the "A" layer causes the formation of a liquid at reduced temperature. With time, the interlayer material becomes more chemically uniform, but the A:B ratio can vary, and with it, the thermal expansion, the hardness, and the elastic modulus, factors that affect the magnitude of the residual stresses. It is possible to estimate how the thermal expansion varies for a known variation of composition. Thus, the relevant unknown parameters of interest are the variation of composition within the joining layer, and how this compositional variation affects the elastic modulus of the material and the hardness of the material. Measurements using a nanohardness indenter at ISTECH provided insights on the interrelationship between these three parameters.

Three distinct ceramic-interlayer combinations were evaluated at ISTECH. Two samples were made using a 99.9% pure, >98% dense, fine-grain-size polycrystalline alumina, "SSA-999W" grade produced by Nikkato Corporation in Osaka Japan. For one sample, the interlayer involved deposition of a 1- μm -thick layer of Ni and a 1- μm -thick deposition of Mo, onto each side of a 125- μm thick Nb foil. The interlayer was then Ni/Mo/Nb/Mo/Ni. The second alumina sample was bonded using a Ni/Nb/V/Nb/Ni interlayer. A 2- μm -thick layer of Ni and a 2- μm -thick layer of Nb, with both thickness determined by the mass increase of the samples were deposited onto each side of a 125- μm thick V foil. The third sample is based on a 15 wt% zirconia-85 wt% alumina material for the ceramic. Here the interlayer was simply a 2- μm thick layer of Ni deposited on both sides of a 125- μm thick Nb foil (Ni/Nb/Ni). All three samples were processed using the same bonding conditions: 2.4 MPa load at 1400°C with a 6 h hold under high vacuum with a 4°/min heating rate to the bonding temperature and a 2°/min cooling rate. The three samples have unique characteristics. The Ni/Mo/Nb/Mo/Ni interlayer will have a small thermal expansion mismatch with alumina, but Mo should be disproportionately higher in concentration near the interface and prior work shows that Ni-Mo liquid have poor wetting behavior; this leads to the potential for a poorly bonded and weak interface. The Ni/Nb/V/Nb/Ni interlayer should produce a liquid with good wetting properties, but the thermal expansion mismatch is large. Therefore, the interface should be flaw-free but the residual stresses could be large. The Ni/Nb/Ni interlayer should have a small thermal expansion mismatch and thus low residual stresses, and the good wetting characteristics of the Ni-Nb liquid should produce a well-bonded interface. This is consistent with the observation that in bonded samples failures occur primarily in the ceramic, and not in the joint region.

The nanohardness scans performed at ISTECH began in the ceramic material (alumina or zirconia-toughened alumina) traversed the metallic interlayer, and then extended into the other ceramic component. Calibration runs were necessary to establish the proper loads for the hardness measurements. The measurements are delicate and extremely time consuming, are best repeated multiple times to assure accuracy, and each individual data point within a scan set must be carefully checked to assure that the measurements are not affected by anomalies on the sample surface. The researchers at ISTECH are to be commended for their care and attention to the measurements and for identifying individual data points that were affected by extraneous factors and not representative of the actual material. Examples would include situations where the indent interacted with a pre-existing flaw in the ceramic, or perhaps a particle of polishing media that had become embedded in the soft metal.

An example of the type of results obtained is shown in the attached figure, which presents information on the compositional variation, the Young's modulus variation, and the hardness variation as one traverses the interlayer. The original structure of this particular interlayer was Ni/Mo/Nb/Mo/Ni as described previously. Processing at high temperature smooths the compositional variation, as shown in Figure 1a. The experiments showed quite clearly that although that the composition of the interlayer still varies spatially after processing, and this could be expected to result in variations in the hardness and Young's

modulus, no such variations were actually detected in the material. These results, and parallel results for the other two interlayers examined thus serve two purposes. First, they quantify the Young's modulus and hardness for the interlayers of interest. Although the Young's modulus is not expected to exhibit large spatial variations in the systems we have examined, a constant value makes modeling of interlayer response easier. Substantial variations in the hardness could in principle have been encountered due to variations in solution hardening, precipitation hardening, microstructure, or some combination thereof. The lack of any obvious variation in this material again will simplify modeling. The remaining two interlayers had distinct Young's moduli and hardness values, but also showed little variation in either parameter as the interlayer was traversed. In these two cases, this was consistent with the development of a uniform composition across the entire interlayer. A full assessment of the results must await the completion of the residual stress measurements being performed at the Kyoto Institute of Technology.

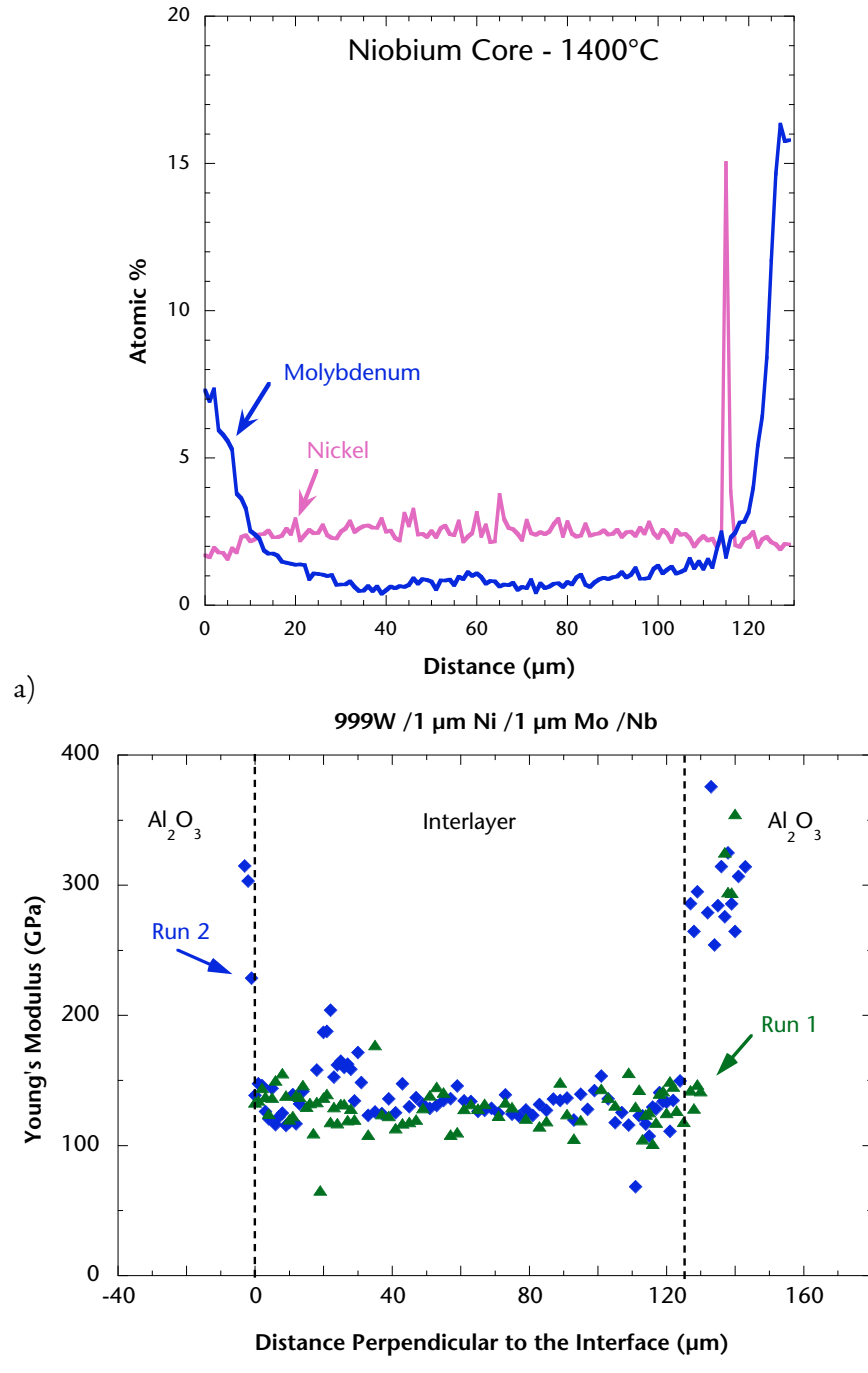


Figure 1 Spatial variation of (a) the interlayer composition, (b) the Young's modulus and (c) the hardness in a Ni/Mo/Nb/Mo/Ni (B3) interlayer and adjoining alumina after processing and partial homogenization.

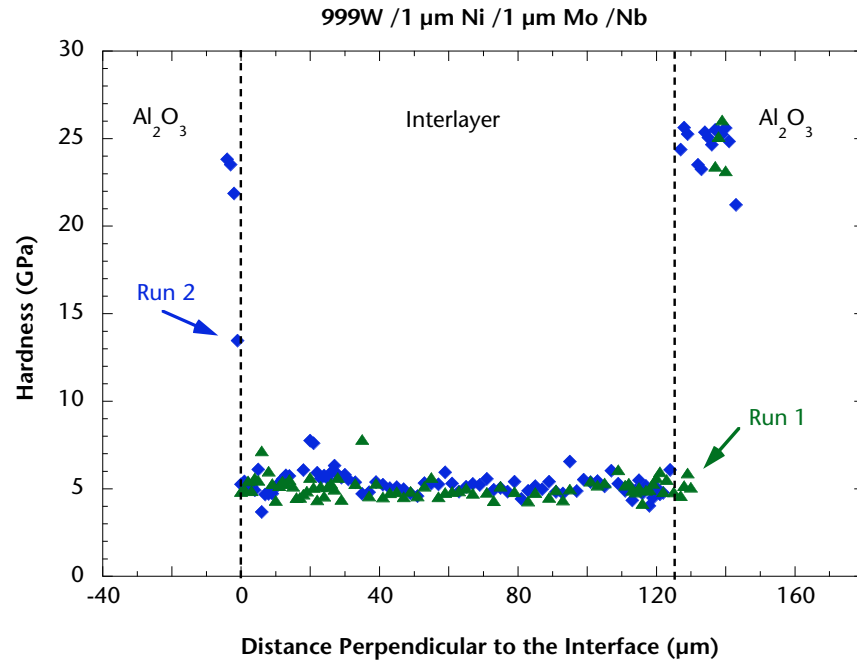


Figure 1 (continued) Spatial variation of (c) the hardness in a Ni/Mo/Nb/Mo/Ni (B3) interlayer and adjoining alumina after processing and partial homogenization.

APPENDIX

In 2010 I elected to take a sabbatical leave in Italy, and divide my six months abroad between two CNR laboratories, IENI in Genova, and ISTEC in Faenza. IENI has facilities for performing high-temperature wetting studies, and such studies provide important information on how a liquid will interact with the solids in which it is in contact. This is highly relevant to the issue of joining using liquid-metal joining media, and the group at Genova, headed by Dr. Passerone, also had prior experience in applying such studies to selected ultrahigh temperature ceramics (UHTCs). The group at Faenza in turn is recognized as being among the world leaders in fabricating UHTCs, and indeed is responsible for many of the processing innovations that have transformed UHTCs from materials that have *potentially* interesting properties to materials that can now be fabricated in dense bulk form using much readily accessible processing conditions. The sabbatical provided an opportunity to learn more about wetting behavior in Genova, and processing in Faenza, and to initiate research interactions with both groups.

The three-month stay in Genova in 2010 was marked by the initiation of a collaborative program of wetting behavior relating to transient-liquid-phase (TLP) bonding of ceramics, an approach that I developed at Berkeley. The first publication stemming from this work is in draft form, and should be submitted within the next month or two. In addition, Dr. Valenza, a postdoctoral researcher at IENI has applied for a prestigious Curie Fellowship. If this is awarded, he will spend eighteen months in Berkeley, extending his knowledge of wetting behavior using unique facilities in Berkeley, and be exposed to the details of TLP bonding. Upon returning to Italy and CNR, he will be equipped to develop an independent program on TLP bonding of advanced ceramics at IENI. During my most recent visit, three of the principle collaborators from Genova came to Faenza and extensive discussions and valuable exchanges took place relating to the experimental results and the forthcoming paper. After my return to Berkeley I also assisted and advised Dr. Valenza in preparing his application for the Curie Fellowship.

The ensuing three months in 2010 were spent at ISTEC in Faenza. I was asked and happy to provide a six-week course on phase diagrams to about a dozen researchers who were interested in expanding their understanding of both phase diagrams and the underlying thermodynamics. The course I provided mirrored a course that I have been offering for nearly twenty years at Berkeley. I worked with three staff scientists on initiating a program on TLP bonding of UHTCs, sharing with Drs. Sciti, Silvestroni, and Esposito my ideas on proper interlayer design, arranged for preparation of foils in Berkeley, and helped with the interpretation of initial results. This initial interaction was limited in extent, but flourished during my brief June 2011 visit. In the past two months, some successful strategies for bonding these very challenging materials have been demonstrated; a joint paper is being prepared, and a presentation at an international meeting is now planned. In addition, I have been working with these three researchers on proposals that would help provide the resources needed to build upon these initial promising results, and enable more widespread use of UHTCs in a variety of energy-generating applications. My role in this proposed research is as a volunteer advisor, a role I am more than happy to fill. It has been very satisfying to work with multiple researchers at ISTEC. They are competent, knowledgeable, inquisitive and enthusiastic. ISTEC provided a very warm, friendly and productive environment in which to both do research and interact with researchers. It was during the 2010 visit that I had the chance to speak extensively with Dr. de Portu, and it was at that time that potential for future interactions and collaboration emerged. The kind and enthusiastic support of Dr. Bellosi during the stay was greatly appreciated.

Other minor contributions during my 2011 visit resolved around commenting and providing feedback on presentations that were going to be given at a major international meeting in Europe. I also was asked to

comment and help with the redesign of the English version of the ISTEC website. These are all activities that I was pleased to participate in, and hope benefitted CNR.

In the longer term, I hope to continue my interaction with both IENI and ISTEC, and collaborate with researchers in both labs. I am hopeful that Dr. de Portu, my host during this STM activity, will be able to come to Berkeley in 2012 so that we can extend the work that was initiated during my stay at ISTEC in Faenza. I am also using my connections with researchers elsewhere to try to arrange for access to facilities and instruments that ISTEC lacks, and that would allow researchers at ISTEC to conduct experiments and perform analyses that they are currently unable to perform in-house.