High-temperature Nanoindentation: New Developments and Ongoing Challenges

Zhi Chao Duan and Andrea M. Hodge

High-temperature or elevated-temperature nanoindentation testing presents an additional capability in nanoindentation techniques, which have demonstrated tremendous potential in the study of nanoscale mechanical behavior. However, to be able to conduct nanoindentation under relevant service temperatures and to gain a better understanding of the fundamental materials physics, high-temperature nanoindentation must overcome such technical issues as heat management, thermal drift, and sample oxidation. This article presents the current state and history of high-temperature nanoindentation with a focus on recent research topics and available testing systems.

INTRODUCTION

Nanoindentation has proven to be a powerful tool for testing small sizes as well as to study small-scale deformation.[1–4] In 1995 Poisl, Oliver, and Fabes introduced the notion of elevated-temperature nanoindentation by placing a commercial nanoindenter in a temperature-controlled room and increasing the room temperature to 32°C –34°C in order to test amorphous selenium.[5] Two years later, Suzuki and Ohmura (to the authors' knowledge) developed the first prototype of a high-temperature indentation instrument,[6] which could be used for fast indentations up to 600°C. However, the test sensitivity was affected by the high testing rates. Since then, many researchers have made improvements to both the instrumentation and the techniques themselves. A summary of the instrumented nanoindentation studies conducted at elevated temperatures is listed in Table I categorized by testing systems. It should be pointed out this summary covers only nanoindentation and mainly metallic and amorphous materials; research on polymers and microindentation studies are not included.[6–33]

BACKGROUND

At the early development stage of high-temperature nanoindentation, most

systems were custom made;[6–8] later on major modifications were implemented to existing commercial nanoindenters in order to conduct high-temperature nanoindentation.[15,16,18] High-temperature testing at the nanoscale has many additional requirements as compared to room-temperature nanoindentation, especially since the temperature must be stable and the thermal drift must be minimal to avoid the influence on displacements in the nanometer range.

While early high-temperature studies mainly focused on the development of techniques to validate the testing methods,[9,13] currently the research covers a wide range of topics including: extraction of high-temperature hardness and Young's modulus values,[28,24] incipient plasticity and indentation creep studies to reveal dislocation activities under loading,[15,20,24] and glass transition and phase transformation studies of specialized materials.[25,31,32] Details about these topics will be elaborated upon later in this article.

More than a decade after the introduction of this technique, it has been vastly improved and the results obtained have been validated as the maximum testing temperature keeps increasing. However, there still are limitations and issues which multiply as the temperature increases. Therefore, improvements and broader applications of this unique technique are of great interest to study nanoscale materials behavior.

SYSTEM SETUP

There are some commercially available high-temperature nanoindentation testing systems from different companies. While the main idea remains to minimize the temperature influence on the apparatus and measurement accu-

Table I. Summary of the Instrumented Nanoindentation at Elevated Temperature*

1994	1996	1997	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Amorphous Se 34°C [5]	Si 600°C [6]	W,GaAs,In 50°C [7]	Fe-3Si 106°C [8]	Au,Si, Soda lime glass 200°C [9]	Y-Mg-Zn 120°C [10]	Au,Fused silica,polymide 200°C [12]	Various 500°C [13]	Pt 200°C [15]	NiTi 78°C [19]	Fused silica 405°C [23]	Au-Metallic glass 140°C [25]	Au/Sn Solder 150°C [26]	Ni alloy 200°C [29]
					W,Fe-3Si 200°C [11]		Fe-40Al 400°C [14]	Pd-,Mg-Metallic glass 200°C [16]	Pt 200°C [20]	Pt 200°C [24]	Ti-Al-N 500°C[54]	Al-Ni-Si 200°C [27]	Au-based Metallic glass 128°C [30]
								Zr-based Metallic glass 450°C [17]	NiTi 200°C [21]	Ti-Al-N/Al-Cr-N 500°C[53]		Ni-based Super alloy 200°C [28]	Si 200°C [31]
								Au,Pt/Cu 130°C [18]	AlN/CrN 400°C [22]				Au-based Metallic glass 125°C [32]
													$MgAl_2O_4$ 200°C [33]

*Filled boxes denote custom apparatus, open boxes denote commercial apparatus.

racy, there are differences between the systems developed by various companies. Figure 1 presents a schematic of a typical high-temperature indentation setup. Keep in mind that location and heating/cooling mechanisms are different from company to company.

The three main commercially available systems are by Hysitron, Inc., MTS (now Agilent Nanoindenter), and MicroMaterials. The Triboindenter system from Hysitron, (Minneapolis, MN) is widely used in many studies. Hysitron's temperature control stage uses a Peltier thermal element and a resistive heating element. The Peltier thermal element allows for a temperature range from –10°C up to 120°C; with the addition of the resistive element, this range could be expanded up to 200°C. A new model is now available for temperatures up to 400°C and the set-up has been successfully implemented into a vacuum/controlled atmosphere chamber.

MTS Nanoindenter (now Agilent Nanoindenter) has a similar setup as the Triboindenter system; the heating stage combined with argon environmental atmosphere has capabilities to the maximum temperature of 350°C. However, the shield is not actively cooled, and higher test loads are available due to a different load cell set-up.

Another popular testing system (NanoTest system) developed by MicroMaterials Inc. (Wrexham, U.K.), presents an indentation instrument which operates with a horizontal loading configuration with a maximum allowable temperature of up to 750°C.

The displacement transducer is placed below the heated area to minimize the influence of convection currents. A similar thermal shield as in the Hysitron setup is placed between the loading head and the hot stage to insulate the direct radiant heating of the capacitor. A significant design difference in the NanoTest setup is the heating elements for the indentation tip, where a small heater and a miniature thermocouple are attached to the diamond stub. This design will heat up the specimen and the indentation tip simultaneously to the testing temperature to prevent the heat flow upon the first diamond-specimen contact.

It should be noted that there are further options including products from other companies and additional accessories which could be used for high-temperature nanoindentation (e.g., a high-temperature indentation testing system from ONERA, France).[55]

TESTING PROTOCOLS

Instrumental drift is always a concern, even in the standard room-temperature nanoindentation test. Thermal drift is augmented in the high-temperature testing setup. The first contact of the room-temperature (RT) tip to the heated specimen would create substantial heat flow due to the temperature gradient. Thermal expansion of the tip as well as thermal contraction of the specimen at the tip contacting area consequently lead to fluctuations of the load and displacement signals. Even after contact of the tip with the specimen, there are significant poten-

tial sources of thermal drift. Schuh et al. pointed out that a thermal fluctuation of 1 K can lead to an artificial drift displacement on the order of 100 nm or more in a typical test setup.[23]

A standardized testing protocol should be followed, especially to maintain the contacting area of the tip and the specimen in equilibrium throughout the indentation process. A popular testing protocol is to heat the sample to the selected temperature for a certain period of time, usually 30 minutes to an hour, before starting any measurement. Once the sample is at thermal equilibrium, the tip is brought in contact with the sample surface with a low set-point load and equilibrated at the temperature for 1 hour. The tip will remain in contact with the specimen surface for the entire duration of all tests performed at the given temperature to reduce the overall thermal drift.[15,20,24,30–32] A careful study performed by Schuh et al. collected thermal drift data correlated to equilibration time and temperature which revealed that acceptable drift rates could be achieved at temperatures up to 405°C given that enough time had passed for the system to equilibrate.[23] This protocol is widely adopted in high-temperature nanoindentation testing[24,25,32] and appears to be effective at controlling the impact on the results. Figure 2 shows thermal drifts at RT and 200°C after over 8 hours of testing by following the protocol previously described. It is noted that even though the typical drift at 200°C is higher than at RT, overall it is well within accepted values.

RESEARCH TOPICS

Early works using high-temperature nanoindentation methods mainly covered derivations of hardness and Young's modulus of the materials. Later, the focus shifted to the study on incipient plasticity, elasticity-plasticity transitions (pop-ins), glass transition of bulk metallic glass (BMG) materials as well as indentation creep and phase transformations.

Incipient plasticity refers to the very earliest stage of the mechanical contact where the transition from elastic to plastic deformation occurs. With the theoretical expectations for the elastic response given by the Hertzian theory, the onset of plastic deformation during nanoindentation can nominally be identified by the first point at which the experimental data deviates from the elastic curve. In many cases, this yield point appears in the load-depth curve (P-h curve) as a discontinuity, termed as a "pop-in." The discontinuity denotes the indenter travels without a measured increase in applied load in a load-controlled experiment or the load is rapidly released at a constant displacement in a displacement-controlled setup. Numerous investigations on this topic have been conducted at RT[35–40] and correlate the initial pop-in to the homogeneous dislocation nucleation. Temperature variation is believed
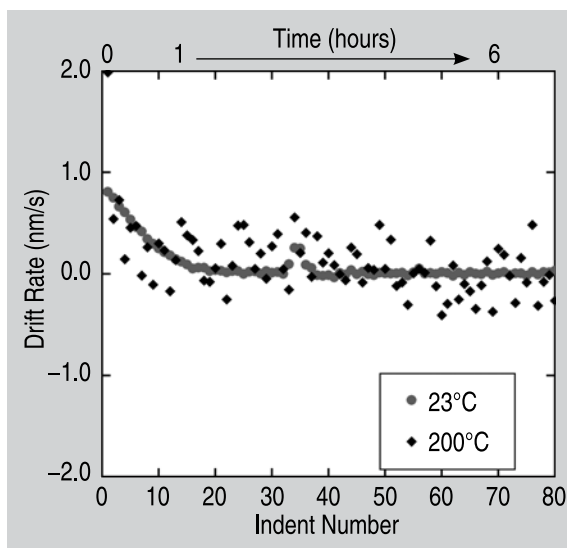

Figure 2. Representative drift rate curves at 23°C and 200°C following the testing protocol which includes an hour temperature settling time.

to be able to induce obvious changes in experimental P-h curves and provide important experimental support for the interpretation of incipient plasticity as a dislocation nucleation event.

Studies by Lund et al.[15] and Mason et al.[24] on single-crystalline platinum focused in the relationship of the onset of pop-ins to the test temperature as well as indentation rate. The experimental results were consistent with a thermally activated mechanism of incipient plasticity, where higher time-at-temperature under load promotes yield. The onset of plasticity is believed to be associated with a heterogeneous process of dislocation nucleation.

To date, most of the studies on the effect of thermally activated process on initial defect formation were conducted on face-centered-cubic (f.c.c.) metals, very few reports on body-centered-cubic (b.c.c.) materials are available. In a recent work on a b.c.c. (001) tantalum single crystal, nanoindentation at temperatures ranging from 25–200°C, different shapes of the load-displacement curves were revealed.[41] Only one large discontinuity marking the onset of plasticity is observed in RT experiments, while multiple pop-ins separated by elastic reloading segments were observed at 200°C. The distinction of the P-h curves is believed to be related to the critical temperature T_C above which screw dislocations become mobile and the material behavior looks more like an f.c.c. material. This is consistent with the stress-biased thermal activated dislocation nucleation model proposed by Mason et al.[24] Figure 3 shows typical RT and 200°C curves for f.c.c. and b.c.c. materials.

Bulk metallic glasses have been a hot topic in the last decade and draw much attention from researchers for their superior strength at low temperatures (<0.8 T_g, with T_g being the glass transition temperature),[42–45] formability, and good geometrical transferability in the supercooled liquid region (>0.75 T_g).[46,47] As temperature is a critical factor in the mechanical properties as well as atomic structures of these special materials, deformation at elevated temperatures is of great interest.

Works by Yang et al.,[25] Song et al.,[30] and Li et al.[32] studied the deformation behavior of various BMGs and
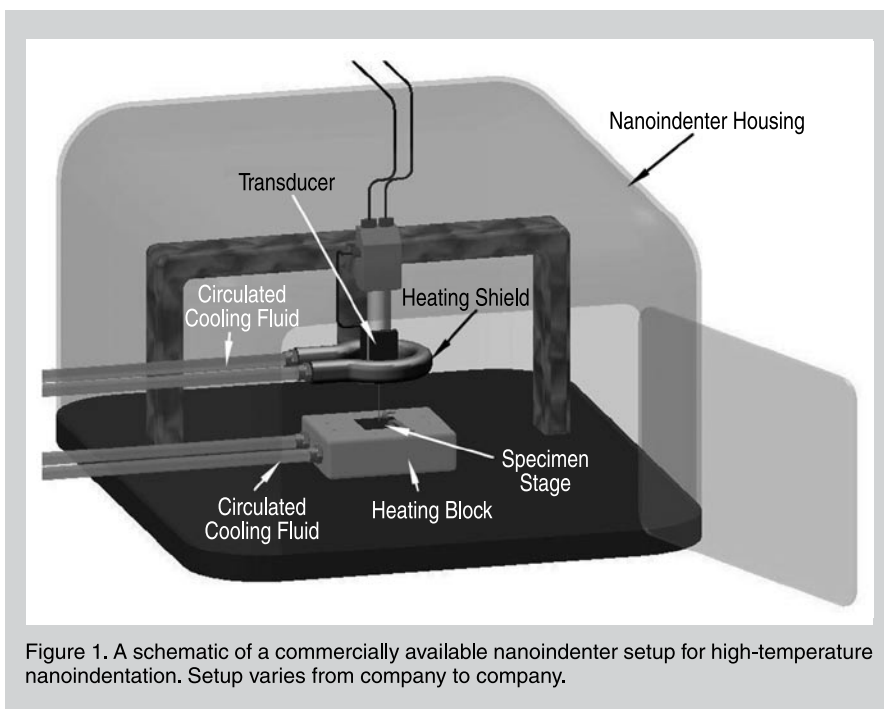

Figure 1. A schematic of a commercially available nanoindenter setup for high-temperature nanoindentation. Setup varies from company to company.

focused on the inhomogeneous-to-homogeneous flow transition and indentation size effect (ISE) at elevated temperature. The experimental results suggested that the inhomogeneous-to-homogeneous transition temperature of BMGs is strain-rate dependent and could be predicted using the free-volume model and deduced size of the basic flow units and activation energies.

The time-dependent behavior of materials under load during indentation is commonly observed in indentation experiments and sometimes considered a problem in extracting hardness and Young's modulus of the materials.[48] This behavior is defined as indentation creep and being widely investigated for its advantages in local assessment and/or if there is not enough material available to machine tensile or compression creep specimens.

Initial work on indentation creep was mainly performed at RT to better understand the creep factor during normal indentation testing in order to quantitatively calculate the hardness and Young's modulus. Recently indentation creep studies have expanded to the elevated-temperature range. Sawant and Tin[28] studied the high-temperature nanoindentation of a single-crystal nickel-based superalloy and evaluated the creep compliance of the material at temperatures ranging from 303 K to 673 K for a dwell time of 1,500 s. The extracted creep compliance was used to correct the elastic compliance at different temperatures and was shown to be in close agreement with other values recorded in the literature.[34,49] Wang et al. systematically studied the nanoindentation creep of electrodeposited nanocrystalline nickel at elevated temperature ranging from 348 K to 448 K. Using a load holding time of 30 s at the peak value, the stress and temperature dependence of the creep rate were characterized and based on the calculated activation energy the dominant creep mechanism was concluded to be grain boundary diffusion.[50]

Other studies that employed the high-temperature nanoindentation technique include: a study on the phase transformation of silicon by investigating the effect of elevated temperatures on the formation of Si-III/Si-XII during unloading of indentation at various temperatures;[31] studies on shape memory alloys by Wood et al.[51] and Zhang et al.,[21] respectively, using the P-h data as evidence of the presence of a martensitic phase transformation; as well as studies on polymeric materials.[52]
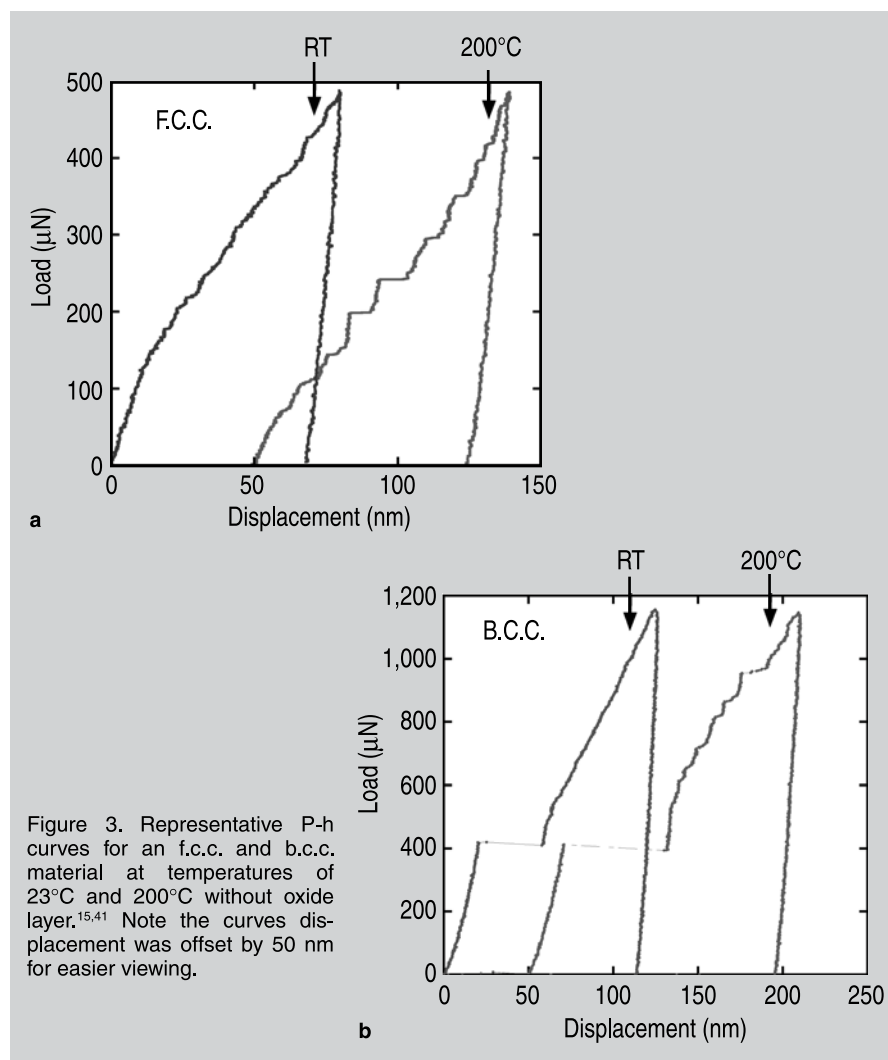
FUTURE OUTLOOK

In order to implement high-temperature nanoindentation as a standard testing technique, which will then allow new studies in nanomechanics, there are several key issues that must be addressed. In what follows we note the current limitations and improvements.

Oxide Formation

The development of oxidation layers on the sample surface has always been a problem for high-temperature nanoindentation testing. Given the typical testing depth range, an oxide layer can have a significant contribution to the overall behavior, thus complicating the data analysis. As nanoindentation is a precise depth-sensing technology usually with the indentation depth on the order of nanometers to a few micrometers, even a thin oxide layer could have deleterious influence on the data obtained. At relatively low temperature (<200°C), oxidation is minimal, especially for high-melting-point materials with a stable native oxide layer (e.g., tantalum or noble metals, such as gold). In the study on single-crystal (100) Ta, room-temperature nanoindentation testing conducted before and after heating to 200°C provided results suggesting the negligibility of further oxidation occurring during the thermal duration as verified by XPS results.[41]

However, in other materials, significant oxidation may still occur even within a low temperature range. Hence, special treatments are essential for correct measurement of the materials properties. One approach is to introduce an oxidation-proof coating; for

Figure 3. Representative P-h curves for an f.c.c. and b.c.c. material at temperatures of 23°C and 200°C without oxide layer.[15,41] Note the curves displacement was offset by 50 nm for easier viewing.

example, when Volinsky et al. conducted nanoindentation studies on copper films at 130°C, a thin platinum layer was deposited on top of the copper film to prevent surface oxidation.[18] The addition of the platinum layer does not affect the measurements of the mechanical properties of copper films as the thickness of the platinum layer is substantially smaller than the indentation depth.

High Temperatures (>200°C)

For even higher testing temperatures, controlled atmosphere must be introduced in order to minimize the oxidation; however, this requires extensive modification of the nanoindentation system. In addition, thermal drift becomes more notable as the testing temperature increases, as studied by Schuh et al.[23] and Rajulapati et al.[41] However, there are some successful studies at these higher temperatures. For example, Schuh et al. presented a technique for elevated temperatures up to 405°C showing good temperature equilibration and thermal drift control. The tests focused on the dependence of hardness and Young's modulus of fused silica on the temperature range from 23°C to 405°C and demonstrated quantitative agreement with the literature data for these properties.[23] Sawant and Tin[28] tested nickel-based superalloy at a temperature up to 600°C. An environmental chamber purged with high-purity argon and <0.01% O_2 level was used in the study. However, at the extreme temperatures, oxidation occurred at the sample's surface and also at the indenter tip. Therefore, for their study a diamond tip was used for tests conducted at temperatures <773 K, and a sapphire tip was used for temperatures above 773 K.

CONCLUSIONS

Nanoindentation is a powerful tool for mechanical testing at small scales which has attracted much attention in the last decade for its unique advantages such as testing of small sample sizes.[1-4] New additions to the nanoindentation repertoire such as in-situ testing and high-temperature testing provide new insights into mechanisms that are difficult to or not previously observed. In this paper we have included the current available research in the area and highlighted research trends. As was presented in Table I, steady progress has been made. However, the field is still growing and expansion of both equipment and topics are expected.

ACKNOWLEDGEMENTS

References

1. C.A. Schuh and T.G. Nieh, *J. Mater. Res.*, 19 (2004), pp. 46–57.
2. W.C. Oliver and G.M. Pharr, *J. Mater. Res.*, 19 (2004), pp. 3–20.
3. M.R. VanLandingham, *J. Res. NIST*, 108 (2003), pp. 249–265.
4. X.D. Li and B. Bhushan, *Mater. Char.*, 48 (2002), pp. 11–36.
5. W.H. Poisl, W.C. Oliver, and B.D. Fabes, *J. Mater. Res.*, 10 (1995), pp. 2024–2032.
6. T. Suzuki and T.Ohmura, *Philos. Mag. A*, 74 (1996), pp. 1073–1084.
7. S.A. Syed Asif and J.B. Pethica, *Philos. Mag. A*, 76 (1997), pp. 1105–1118.
8. D.F. Bahr, D.E. Wilson, and D.A. Crowson, *J. Mater. Res.*, 14 (1999), pp. 2269–2275.
9. J.F. Smith and S. Zheng, *Surf. Eng.*, 16 (2000), pp. 143–147.
10. B. Wolf, K.O. Bambauer, and P. Paufler, *Mater. Sci. Eng. A*, 298 (2001), pp. 284–295.
11. D.E. Kramer, K.B. Yoder, and W.W. Gerberich, *Philos. Mag. A*, 81 (2001), pp. 2033–2058.
12. B.D. Beake and J.F. Smith, *Philos. Mag. A*, 82 (2002), pp. 2179–2186.
13. B.D. Beake, S.R. Goodes, and J.F. Smith, *Z. Metallk.*, 94 (2003), pp. 798–801.
14. J. Xia, C.X. Li, and H. Dong, *Mater. Sci. Eng. A*, 354 (2003), pp. 112–120.
15. A.C. Lund, A.M. Hodge, and C.A. Schuh, *Appl. Phy. Lett.*, 85 (2004), pp. 1362–1364.
16. C.A. Schuh, A.C. Lund, and T.G. Nieh, *Acta Mater.*, 52 (2004), pp. 5879–5891.
17. T.G. Nieh et al., *Intermetallics*, 12 (2004), pp. 1183–1189.
18. A.A. Volinsky, N.R. Moody, and W.W. Gerberich, *J. Mater. Res.*, 19 (2004), pp. 2650–2657.
19. X.G. Ma and K. Komvopoulos, *J. Mater. Res.*, 20 (2005), pp. 1808–1813.
20. C.A. Schuh, J.K. Mason, and A.C. Lund, *Nat. Mater.*, 4 (2005), pp. 617–621.
21. Y. Zhang, Y.-T. Cheng, and D.S. Grummon, *J. Appl. Phys.*, 98 (2005), 033505.
22. F. Giuliani et al. *Mater. Sci. For.*, 492-493 (2005), pp. 335–340.
23. C.A. Schuh, C.E. Packard, and A.C. Lund, *J. Mater. Res.*, 21 (2006), pp. 725–736.
24. J.K. Mason, A.C. Lund, and C.A. Schuh, *Phys. Rev. B*, 73 (2006), 054102.
25. B. Yang, J. Wadsworth, and T.-G. Nieh, *Appl. Phys. Lett.*, 90 (2007), 061911.
26. Y.C. Liu et al., *J. Alloys Comp.*, 448 (2008), pp. 340–343.
27. A. Richter et al., *Mat. Sci. Eng. A*, 494 (2008), pp. 367–379.
28. A. Sawant and S. Tin, *Script. Mater.*, 58 (2008), pp. 275–278.
29. C.L. Wang, M. Zhang, and T.G. Nieh, *J. Phys. D*, 42 (2009), 115405.
30. S.X. Song et al., *Appl. Phys. Lett.*, 94 (2009), 061911.
31. S. Ruffell et al., *Nanotechnology*, 20 (2009), 135603.
32. N. Li et al., *Intermetallics*, 17 (2009), pp. 227–230.
33. S. Korte and W.J. Clegg, *Script. Mater.*, 60 (2009), pp. 807–810.
34. H. Takagi, M. Fujiwara, and K. Kakehi, *Mater. Sci. Eng. A*, 387-389 (2004), pp. 348–351.
35. D.F. Bahr, D.E. Kramer, and W.W. Gerberich, *Acta Mater.*, 46 (1998), pp. 3605–3617.
36. Y.L. Chiu and A.H.W. Ngan, *Acta Mater.*, 50 (2002), pp. 1599–1611.
37. W.W. Gerberich et al., *Acta Mater.*, 44 (1996), pp. 3585–3598.
38. J.D. Kiely and J.E. Houston, *Phys. Rev. B*, 57 (1998), pp. 12588–12594.
39. S. Suresh, T.G. Nieh, and B.W. Choi, *Script. Mater.*, 41 (1999), pp. 951–957.
40. A. Gouldstone et al., *Acta Mater.*, 48 (2000), pp. 2277–2295.
41. K.V. Rajulapati, Biener, and A.M. Hodge, *Philos. Mag. Lett.* (2009), in press.
42. R.W. Cahn, *Nature*, 341 (1989), pp. 183–184.
43. A.L. Greer, *Science*, 267 (1995), pp. 1947–1953.
44. C. Liu et al., *Metall. Mater. Trans. A*, 29 (1998), pp. 1811–1820.
45. W.L. Johnson, *MRS Bulletin*, 24 (1999), pp. 42–56.
46. T.G. Nieh and J. Wadsworth, *Script. Mater.*, 54 (2006), pp. 387–392.
47. J.P. Chu et al., *Appl. Phys. Lett.*, 90 (2007), 034101.
48. A.C. Fischer-Cripps, *Mater. Sci. Eng. A*, 385 (2004), pp. 74–82.
49. D. Sieborger, H. Knake, and U. Glatzel, *Mater. Sci. Eng. A*, 298 (2001), pp. 26–33.
50. W. Wang, C.B. Jiang, and K. Lu, *Acta Mater.*, 51 (2003), pp. 6169–6180.
51. A.J.M. Wood and T.W. Clyne, *Acta Mater.*, 54 (2006), pp. 5607–5615.
52. A. Gray and B.D. Beake, *J. Nanoscience and Nanotechnology*, 7 (2007), pp. 2530–2533.
53. G.S. Fox-Rabinovich et al., *Surface and Coatings Technology*, 200 (2006), pp. 5738–5742.
54. B.D. Beake et al., *Surface and Coatings Technology*, 201 (2007), pp. 4585–4593.
55. B. Passilly et al., *Philosophical Magazine*, 86 (2006), pp. 5739–5752.

Zhi Chao Duan is a postdoctoral researcher and Andrea M. Hodge is an assistant professor with the Aerospace and Mechanical Engineering Department, University of Southern California, Los Angeles. Prof. Hodge can be reached at ahodge@usc.edu.