Development of high temperature nanoindentation methodology and its application in the nanoindentation of polycrystalline tungsten in vacuum to 950 ºC

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Abstract

The capability for high temperature nanoindentation measurements to 950 ºC in high vacuum has been demonstrated on polycrystalline tungsten, a material of great importance for nuclear fusion and spallation applications and as a potential high temperature nanomechanics reference sample. It was possible to produce measurements with minimal thermal drift (typically ~0.05 nm/s at 750-950 ºC) and no visible oxidative damage. The temperature dependence of the hardness, elastic modulus, plasticity index, creep, creep strain, and creep recovery were investigated over the temperature range, testing at 25, 750, 800, 850, 900 and 950 ºC. The nanoindentation hardness measurements were found to be consistent with previous determinations by hot microhardness. Above 800 ºC the hardness changes relatively little but more pronounced time-dependent deformation and plasticity were observed from 850 ºC. Plasticity index, indentation creep and creep recovery all increase with temperature. The importance of increased time-dependent deformation and pile-up on the accuracy of the

elastic modulus measurements are discussed. Elastic modulus measurements determined from elastic analysis of the unloading curves at 750-800 ºC are close to literature bulk values (to within ~11%). The high temperature modulus measurements deviate more from bulk values determined taking account of the high temperature properties of the indenter material at the point (850 ºC) at which more significant time-dependent deformation is observed. This is thought to be due to the dual influence of increased time-dependency and pile-up that are not being accounted for in the elastic unloading analysis. Accounting for this time-dependency by applying a viscoelastic compliance correction developed by G. Feng and A.H.W. Ngan (J. Mater. Res. (2002) 17:660-668) greatly reduces the values of the elastic modulus, so they are agree to within 6% of literature values at 950 ºC.

1. Introduction

Whilst nanomechanical testing is routinely performed at room temperature, for many applications involving high temperatures in the aerospace, automotive, cutting tool and nuclear sectors it is the mechanical properties at elevated temperature that are more relevant. Characterising the elevated temperature mechanical properties of materials used in these applications with high temperature nanomechanics is becoming increasingly popular [1-4]. Examples of temperature-dependent materials properties studied by high temperature nanoindentation with maximum test temperatures ≥400 ºC are given in Table 1. In almost all of these reports the sample and tip were heated independently to achieve an isothermal contact employing a dual active heating approach previously shown to provide an improvement in data accuracy in high temperature microhardness tests [5]. Accurate temperature matching avoids heat flow on contact between indenter and sample during indentation by minimising/removal of the thermal gradient between them resulting in minimal thermal drift.

[Table 1 about here]

Table 1 Applications of high temperature nanomechanics

Materials	Indenter material	Properties investigated	Max. Test temp. (ºC) [reference]
Silicon	Diamond	phase transitions, deformation mechanisms	400 [6], 500 [7]
Bulk metallic glass	Diamond	glass transitions, recrystallization, activation energies	400 [8]
Spinel	Diamond	yield stress and modulus from micropillar compression	400 [9]
Al alloys	Diamond	high temperature creep, dislocation mechanisms	560 [10]
Silicon	Diamond	yield stress from micropillar compression	500 [11]
Copper	Diamond	hardness and modulus	400 [12]
Fused silica	Diamond, cBN	hardness and modulus	400 [12, 13], 600 [14]
ultrahigh strength corrosion resistant steel	cBN	hardness	500 [15]
Ion irradiated ODS steels	cBN	high temperature creep and yield stress	600 [16]

Silicon	cBN	deformation mechanisms	650 [17]
PVD cutting tool coatings	Diamond, cBN	hardness and modulus, hardness/modulus ratio	500 [18-19], 600 [20-21], 750 [2]
CVD cutting tool coatings	cBN	hardness and modulus	700 [22]
Ion irradiated tungsten	cBN	ion irradiation effects on hardness	750 [23]
Ni-based superalloys	Diamond, Sapphire	creep compliance correction, modulus	400 [24-25], 665 [3]
G18 glass-ceramic seal material	cBN	hardness and modulus, creep, glass transitions	750 [26]
Silicon	cBN	elastic modulus from micro-cantilever bends	770 [27]

ODS = oxide-dispersion strengthened; PVD = physical vapour deposition; CVD = chemical vapour deposition.

With high temperature nanomechanics becoming a more established technique it is timely to develop and refine the test methodology, particularly with the advent of elevated temperature nanomechanics in high vacuum. At room temperature, there has been an international standard for depth-sensing indentation, ISO14577(1-4), since 2002, with the latest revision being in 2007 [28]. In adapting the approach taken in the ISO standard to high temperature nanomechanics it is necessary that (i) the instrumentation is designed for thermal stability such that any thermal gradients are minimised/eliminated and tests can be performed without thermal drift or other instrumental factors influencing the raw data (ii) contact mechanics can

successfully be applied to high temperature measurements where appreciable time-dependent non-elastic deformation more commonly occurs (iii) oxidative wear of tip and sample does not occur (iv) the accuracy of instrument calibration is validated on reference materials with known elastic properties at the temperatures of interest.

At room temperature ISO14577 has highlighted the importance of removing time-dependent effects on the accuracy of elastic modulus determination [28]. In summarising round-robin intercomparison data from the INDICOAT project [29] that informed the ISO standard, Jennett and Bushby [30] noted that for ductile coatings such as Al on BK7 glass, the elastic modulus could be over-estimated by a factor of 2 if the hold period was too short. This over-estimation of the modulus is due to continuing anelastic deformation during unloading, i.e. poor experimental design can result in the creep rate during unloading being too high for meaningful measurements to be made [31] without accounting for this by a viscoelastic compliance correction as proposed by Feng and Ngan [32]. With improved experimental design, Chen and co-workers have recently shown that with the inclusion of a sufficiently long hold at peak load before unloading, it is possible with a sufficiently thermally stable instrument to use the approach to obtain loading-rate insensitive values of the elastic modulus of a polycrystalline copper sample over a x1000 difference in loading rate [33]. The greater time-dependency at elevated temperature necessarily extends the overall time required for the creep rate to reduce sufficiently that any continuing time-dependent deformation during unloading is minimal, putting a consequently greater requirement on the thermal stability of the instrumentation.

Sufficient care must be taken to ensure that oxidative wear of indenter and/or sample does not compromise the accuracy of the results. The choice of indenter materials for high temperature nanoindentation has been comprehensively reviewed by Wheeler and Michler [4] who noted that diamond and boron carbide show the best high temperature hardness while tungsten

carbide the lowest reactivity to the widest range of elements. Indenter wear at temperature is an important consideration. AFM images of Berkovich diamond indenters show that they remain undamaged even after prolonged usage at temperatures below 400 °C. However, diamond oxidises in air at >400-500 °C and this leads to chemical interactions and tip degradation. SEM images of a diamond indenter in contact with steel at 500 °C reveal dramatic damage due to chemical reaction, with carbon dissolution into the steel to form Fe_3C carbides [4]. In practice diamond, sapphire and cBN have all been used, with the choice being due to the maximum temperature, chemical reactivity at temperature and choice of test environment. Diamond has been used in the majority of published studies with a maximum temperature of 400-500 °C, whilst for testing at higher temperatures and/or for reasons of reactivity cubic boron nitride (e.g. testing solid oxide fuel cell glass-ceramic seal material [25], steels [15-16], PVD hard nitride coatings [18-21] and CVD alumina coatings [22]) and sapphire (steel, superalloys [3] and thermal barrier coatings) are more commonly used. Tests at higher temperatures are commonly performed in argon (or vacuum) atmosphere to minimise oxidation of test samples which can otherwise be extreme. For example, tungsten oxidises at >500 ºC in air [4]. Lofaj and Kaganovskii reported that oxidation of tungsten in tungsten carbide at >650 ºC resulted in dramatic swelling of samples with the formation of a brittle porous WO_3 layer [34]. However, in a reduced oxygen environment such as argon, nitrogen or forming gas, the oxygen is not completely eliminated and the limitations to testing have led to the development of high temperature nanoindentation in high vacuum. Thermal management in vacuum is inherently more difficult than in either air or inert atmospheres as convection cannot be used to equilibrate temperatures [1]. Korte and co-workers noted [3] that this was a particular problem in the experiments in vacuum reported by Trenkle et al [12] using sample-only heating (the indenter being only passively heated) on thermally conductive samples such as copper and aluminium.

Several materials are potential candidates for reference samples for high temperature nanoindentation. Although fused silica is the most common reference sample for room temperature nanomechanics, it is an anomalous glass with complex indentation behaviour including densification under the indenter [35], a very high hardness/modulus (H/E) ratio with susceptibility to lateral dilation [36], an elastic modulus that increases with temperature [12-14] while its hardness decreases [12-14, 37], susceptibility to cracking depending on water content [38], cracking at high load, dependent on the acuity of the indenter [39] with temperature-dependent cone and radial cracking thresholds [37]. Other candidate materials are being explored, either to replace fused silica, or to be used as part of multiple reference sample calibration. Being elastically isotropic, polycrystalline tungsten may have potential as a reference sample for high temperature vacuum nanoindentation with its high melting temperature (3422 ºC) and readily available bulk data on hardness and elastic modulus [40]. Its hardness does not decrease monotonically with temperature, since bcc metals such as W and Mo show a pronounced "knee" in their hardness vs. temperature dependence at ~0.2 T_m at the boundary between "cold" and "warm" deformation (the characteristic temperature T*) [40-45]. Below this temperature hardness increases as the temperature is lowered. Its elastic modulus decreases from 411 GPa at 25 ºC to 370 GPa at 1000 ºC [40,46]. High temperature mechanical properties of tungsten are also important for the nuclear industry since tungsten and its alloys [23,45,47] are being considered as the main plasma-facing material in a fusion reactor, with expected operating conditions of up to 700 ºC at the first wall and 500 ºC at the divertor [18]. These components will be subject to irradiation damage by alpha particles and fast neutrons and as vacancy mobility in tungsten is more significant over 530 ºC [23,47] this may influence damage structures and mechanical properties. In a recent review Wheeler and co-workers showed optical micrographs of the surface of tungsten samples after exposure to different high temperature environments [1]. After heating at 750 ºC for 1 h in Argon the

surface showed the presence of a thick oxide layer so that any nanomechanical testing would be impossible. The oxidation rate was reduced significantly after heating at 750 ºC in reducing Ar-5% H_2 atmosphere but the oxidation of some grains was observed. After testing at 750 ºC in high vacuum for an extended period of 21 days the tungsten surface showed no visible surface degradation, with the characteristic colour change due to tungsten oxide being completely absent [1]. Gibson and co-workers recently reported the elevated temperature properties of unimplanted and He-implanted tungsten by nanoindentation in high vacuum from 25 to 750 ºC [23]. The characteristic slope change in H vs. T previously seen in hot hardness measurements was observed. Depth-profiles of the hardness vs. temperature trends obtained by performing multi-cycle load-hold-unload tests showed the hardening effect of the implantation present at lower temperatures was found to be negligible above 450 ºC.

In this current work a similar sample of polycrystalline tungsten has been tested with the temperature range extended by 200 ºC to 950 ºC and conventional load-hold-unload experiments were performed rather than multi-cycle load-hold-unload tests reported in reference 23. This approach enables the temperature dependence of the plasticity index defined by equation 1 to be determined:-

$$\text{Plasticity index} = \text{plastic work/total work} \approx 1\text{-}x(H/E_r) \approx h_r/h_{max} \qquad \text{[Eqn. 1]}$$

Cheng and Cheng have shown by FEA that the energy-based plasticity index is very strongly correlated with h_r/h_{max} (Eqn. 1) [48,49]. The temperature dependence of the hardness, elastic modulus, plasticity index, creep, and indentation creep strain (increase in creep depth/depth at start of the creep period) in polycrystalline tungsten have been studied over the temperature range (25, 750, 800, 850, 900 and 950 ºC). The results have been used to validate the high temperature nanoindentation methodology and to determine critical issues for further investigation.

2. Experimental

2.1 Instrumentation operation in vacuum

Measurements were performed with a high temperature vacuum nanoindentation system (NanoTest Xtreme, Micro Materials, UK). Modifications to the standard NanoTest design for high temperature nanomechanical measurements in argon purging include the exchange of sample stage motors and capacitive displacement sensor for vacuum compatible equivalents. The instrument was housed within a high vacuum chamber with roughing and ultra-low vibration turbo-molecular pumps equipped with magnetically levitated bearings (Leybold/Oerlikon, UK) to achieve an ultimate vacuum level of 10^{-7} mbar. It has been shown elsewhere that the high vacuum is sufficient to avoid visible signs of oxidation to 750 ºC [1] and that tests can be performed reliably at low depths over this temperature range [23]. Figure 1 shows internal and external views of the instrumentation. Elimination of gaseous atmosphere in the chamber avoids convection, allowing faster stabilisation than is possible in an enclosed gas environment. Radiative heating above ~600 ºC provides an additional mechanism for equalisation of tip and sample temperatures, becoming increasingly effective above 850 ºC.

2.2 Thermal control strategy

For high temperature operation, the NanoTest system employs active dual heating of the sample and the indenter with a patented design of heated indenter, novel stage design and thermal control method involving the following steps for the indenter heating control side: i) the indenter is heated to the target temperature by feedback control ii) once the target temperature is reached the controller measures the average power supplied to maintain the

target temperature iii) the indenter is then supplied with this constant power during indentation [2]. More details on the experimental configuration are given in [1,2]. This "power lock" method has previously been shown to be able to effectively compensate for the differing thermal masses of the indenter and sample sides of the contact and provide accurate drift minimisation at high temperature, with thermal drift rates as low as 0.01 nm/s being reported in vacuum at 750 ºC [23]. The thermal stability is sufficient for nanopositioning/imaging at high temperature using the Berkovich as a stylus to image the surface at low (~1 μN) force without noticeable thermal or positional drift to 770 ºC [27]. The design of the heated indenter involves a novel direct ceramic bonding that avoids brazing making higher temperatures accessible.

2.3 Nanoindentation experiment design

Nanoindentation measurements were performed under high vacuum on a sample of polycrystalline tungsten at 25, 750, 800, 850, 900 and 950 °C using a well-worn cubic boron nitride Berkovich indenter ($A_c = 4000h + 24.5h^2$). The tests at room temperature were performed to maximum loads of 90-300 mN, loading in 15 s, holding at maximum load for 20 s, unloading in 5 s, 60 s hold at 90 % unload for thermal drift correction. The tests at elevated temperature had the same conditions except with a 30 s hold at peak load. Power law fitting was over 90-40 % of the unloading curve. This loading and analysis protocol was designed to combat the influence of time-dependency on the accuracy of modulus measurements and minimise any strain-rate effects. In practice due to the low thermal drift there was no difference in the measured values of H and E whether the data were corrected for thermal drift or not. In a separate set of experiments, after cooling the sample back to room temperature and reheating, additional tests were performed with a 60 s or 300 s hold at peak load at up to 945 ºC.

3. Results

Typical indentation curves at 900 °C are shown in figure 2 (a). The creep during the hold at peak load is significant and increases with load as shown in figure 2 (b). The indentation creep strain is relatively invariant with load (fig. 2(c)). The slight increase (~1-5%) at lower load is considered to be due indenter geometry (the blunt Berkovich is not quite self-similar at the lower depths). During the 60 s hold period at 90% unloading, creep recovery was observed at higher temperature. Thermal drift assessed from the last 60% of the 60 s hold period at 90% unloading was typically ~0.05 nm/s and it did not vary significantly with load or temperature.

The polycrystalline tungsten softened dramatically over the temperature range studied. It showed an indentation size effect which persists at high temperature. Hardness from measurements to 150-300 mN decreased from ~ 6 GPa at 25 ºC to 2 GPa at 950 ºC. Figure 3 shows typical indentation behaviour at 25, 750, 850 and 950 °C. Time-dependent plasticity is more pronounced at >750 ºC. Optical microscopy showed no visible signs of oxidation (the thickness of its native oxide is ~1 nm) after cooling from 950 ºC, with the sample looking identical as prior to testing. Significant pile-up was observed in the high temperature indentations. The surface had a non-equiaxed granular structure after testing at 950 °C and the hardness measured at 25 ºC after cooling was unchanged. The softening at high temperature was accompanied by more pronounced time-dependent deformation. The mean indentation creep strain from indents at 90-300 mN is shown in figure 4. There was a gradual increase to 800 °C followed by a more pronounced increase above that temperature. The indentation creep strain at room temperature is extrapolated to 30 s to allow direct comparison with the high temperature data.

There was no indentation size effect in elastic modulus. The modulus calculated from the unloading slope was virtually constant vs. temperature in the range 25 ºC (E_r = 287 ± 10 GPa) to 800 ºC (E_r = 291 ± 9 GPa at 750 ºC; E_r = 288 ± 9 GPa at 800 ºC) but above this slightly higher values were found with E_r = 311 ± 11 GPa at 950 ºC. This rise was coincident with the onset of more significant time-dependent deformation and greater plasticity index. The plasticity index increased with temperature from 0.85 at 25 ºC to 0.95 at 900 and 950 ºC (figure 5).

Figure 6 (a, b) shows illustrative depth vs. time data from the hold at 90% unload. All the curves show some initial creep recovery the rate of which is virtually negligible after ~20 s so that the subsequent data (20-60 s of the hold at 90% unload) can be used to assess the underlying thermal drift in contact. The underlying thermal drift assessed from the last 60% of the 60 s hold period was ~0.04 nm/s in the tests at 230 nm at 850-950 ºC and ~0.06 nm/s for the tests at a range of loads at 850 and 900 ºC.

4. Discussion

To the best of the authors' knowledge the data in this work are the first reported nanomechanical measurements to 950 ºC. To avoid oxidation of the tungsten sample [1,23,34] it was necessary to employ high vacuum. The appearance of the samples was unchanged after testing at 950 ºC.

In their recent review of the critical issues in high temperature nanoindentation, Wheeler et al emphasized that precise matching indenter and sample temperatures has been consistently shown to be essential for eliminating thermal drift in high temperature nanoindentation [1]. Published data at quite moderate temperatures [50] show that measurements using sample-

only heating may be subject to rather dramatic drift and instability. The thermal gradient increases at higher temperatures exacerbating the problem. A passively heated indenter will never completely reach the same temperature of the sample as it functions as a local heat sink [1], and testing in vacuum will exacerbate this [12]. Wheeler et al have noted that thermal drift may be separable into frame and contact drift [1] and that to obtain reliable data it is important to minimise both. In this current work the frame drift was minimised by the stabilisation period prior to the measurements and the contact drift minimised by the dual active heating of the indenter and sample.

At room temperature the approach taken in ISO 14577 is to correct data from the last period of a constant load hold segment either at initial contact or a 90% unload. The implicit assumption being that any creep rate or creep recovery rate would essentially be minimal after this period so that remaining change in displacement signal would be solely due to instrumental drift. Although a useful guide for many materials, practice has shown that it is inaccurate when testing very soft samples and/or strongly viscoelastic materials where the underlying drift rate is a tiny fraction of the contact creep or creep recovery rate. Where creep recovery dominates the data the displacement change rates are significant (e.g. >1 nm/s on strongly viscoelastic materials at high load) and also show a strong dependence on load so this rate should not be used to correct for thermal drift since it is a time-dependent materials effect completely unrelated to instrumental stability [51-53]. The initial creep recovery rates in figure 6 show a slight dependence on temperature (as expected from the increased creep shown in figures 3,4) the drift rate drops to ~0.05 nm/s after ~20 s. The data in the last 60% of the hold period at 90% unload do not vary with load, confirming that the thermal drift is very low and being accurately corrected. The enhanced creep observed at higher temperatures is not an artefact of an incorrect thermal drift correction being applied to the data. Due to the

low thermal drift the measured values of hardness and modulus in the high temperature tests were unaffected by whether the data were corrected for thermal drift or not.

It is possible to compare the results of this study with existing hot hardness (i.e. non-depth-sensing) measurements at higher load and elevated temperature elastic modulus measurements obtained by other techniques. The data showed a small indentation size effect in hardness, which was ~0.4 GPa higher at 90 mN than at 300 mN, but the elastic modulus data across the load range were quite constant and showed no obvious trend. To improve the statistics, the mean hardness results from 150-300 mN were combined with the results of additional tests with 60 s hold at peak load. Values of hardness were relatively constant over the range 750-950 ºC. These averaged values have small error bars and are plotted in figure 7(a) together with microhardness and hardness results on single crystal and polycrystalline tungsten taken from the literature. To provide a more direct comparison to studies at different applied load the data have been normalised by the hardness at 25 ºC in figure 7(b). There is generally good agreement between the data with the inflexion at ~0.2 T_m being clear.

In the range 25 ºC to 800 ºC the reduced elastic modulus, E_r, was relatively constant vs. temperature. Higher values at 850-950 ºC were coincident with the onset of more significant time-dependent deformation (figure 4). These values have been compared against bulk measurements. The reduced elastic moduli expected at elevated temperature were estimated using the elastic moduli of tungsten and the cubic boron nitride indenter material at the temperatures in question. Wheeler and Michler noted that the use of room temperature indenter material moduli can cause significant error in Young's modulus measurements [4], although for diamond, cBN and WC indenters, it is relatively small; for a cBN indenter and sample with E_r = 200 GPa and ν = 0.33 this was calculated to be ~2 % at 950 ºC [4]. The elastic modulus of cBN decreases by 4% between 25 and 950 ºC [54] and the elastic modulus of tungsten decreases by 9.5 % between 25 and 950 ºC [46]. The Poisson's ratio of tungsten

increases marginally with temperature [40], but both the magnitude of the change and its effect on indentation results are considered to be negligible [4]. Indenter geometry variation with temperature due to thermal expansion is considered negligible [4].

At 750-800 ºC the calculated elastic modulus of tungsten was in broad agreement with the expected values (~11% high), but at 850-950 ºC the measured values are greater than the expected values by ~30-35 %. It is likely that the onset of increased time-dependent behaviour at 850 ºC (~0.3 T_m) is at least partly responsible for this. It occurs in the temperature range where Milman et al have reported an upward inflexion in the trend of h_r/h_{max} (h_r = residual indentation depth, h_{max} = maximum indentation depth at peak load) vs. T in annealed and deformed W polycrystals [42-43]. The evolution of h_r/h_{max} with temperature is considered to be due to different deformation mechanisms, and differences in the evolution of grain structure and dislocation sub-structure during deformation [41-43]. After testing at 950 °C microscopy shows that the surface retains the non-equiaxed granular structure typical of cold and warm deformation in W and Mo [43].

The loading history and analysis protocol, with longer hold at peak load, faster unload and restricting the fit range to 90-40%, was designed to mitigate possibility of time-dependent behaviour influencing the modulus measurements. Another approach is apply a viscoelastic compliance correction to the unloading data as has been suggested by Feng and Ngan [32]. These authors found that the correction term due to creep in the apparent contact compliance was equal to the ratio of the indenter displacement rate at the end of the hold to the unloading rate (Eqn. 2).

$$C = C_u + (dh/dt)/(dP/dt) \qquad \text{[Eqn 2.]}$$

where C = contact compliance, C_u = apparent contact compliance, dh/dt is the indenter displacement rate at the end of the hold at peak load and dP/dt is the unloading rate. The

Feng-Ngan correction has been previously used up to 400 ºC by Sawant and Tin in their 2008 study of the high temperature properties of Ni-based superalloys [24,25]. The uncorrected value of the elastic modulus of <001> oriented single crystal CMSX-4 was 140 GPa, reducing to 113 GPa after the viscoelastic compliance correction. After correction elastic modulus measurements for <110> and <001> oriented single crystals of CMSX-4 were in excellent agreement with literature values obtained by other techniques. For the high temperature tungsten results reported here the effect of the correction is quite small up to 800 ºC but above this temperature it significantly reduces the values of the elastic modulus, to within 5, 10 and 6% of literature values at 850, 900 and 950 ºC respectively. In contrast to its pronounced effect on elastic modulus, the viscoelastic compliance correction barely affects the measured hardness determination across the temperature range, with corrected hardness values being within 2% of the uncorrected values at 950 ºC. Alternatively, a possible refinement to the experiment design is to significantly increase the hold period at peak load, to allow the creep rate to reduce more before unloading. This strategy has previously been applied successfully in the high temperature nanoindentation of power generation steels by Davies [55] who reported that when testing P91 steel with a cBN indenter in argon at 675 ºC, the elastic moduli were ~20 GPa higher than expected from bulk determinations when using a 30 s hold at peak load. Increasing the time at peak load to 300 s was sufficient to reduce the measured elastic modulus so that data were in good agreement with the literature [55]. In a separate set of experiments on the tungsten sample, indentations at 945 ºC to 200 mN with longer (300 s) holds at peak load and at 90% unload also showed a significant reduction in modulus so that values were close to literature.

Another complicating factor is the presence of pile-up around the indentation which is not accounted for in the analysis (i.e. no correction to the contact area has been made). The standard unloading analysis of Oliver and Pharr [56,57], and the subsequent ISO14577 do not

take account of the possibility of pile-up altering the true contact area. However, tungsten is susceptible to pile-up when indented with diamond Berkovich indenters [58-60]. Bolshakov and Pharr used finite element analysis (FEA) to investigate the influence of pile-up on the accuracy with which hardness and elastic modulus could be measured by nanoindentation [61]. They determined that in non-work hardening materials the extent of pileup varied strongly with h_r/h_{max}. The value of h_r/h_{max} ~0.84 marked the transition from sinking-in behaviour below this to pile-up in non-work hardening materials when indented by a rigid cone with semi-vertical angle of 70.3º giving the same projected area to depth ratio as a Berkovich indenter. More recently Gale and Achuthan reported that pile-up is correlated with work hardening in cross-sections of copper subjected to surface mechanical attrition treatment with h_r/h_{max} = 0.9-0.95 [62]. For non-work hardening materials Bolshakov and Pharr found that the contact area computed with the contact area determined from the indenter shape could be under-estimated significantly so that the elastic modulus could be over-estimated by ~50 % when h_r/h_{max} approaches 1 (as pile-up is very large) [61].

In our measurements (see figure 3) h_r/h_{max} approaches 1 as the temperature increases. Optical microscopy confirmed the presence of extensive pile-up in the high temperature indentations. Milman reported a non-linear temperature dependence of h_r/h_{max} when deformed tungsten was indented by diamond [42]. There was a sharp rise from 0.90 at room temperature up to 0.955 at the characteristic temperature of ~450 ºC, with a much more gradual increase above this to 0.97 at 1000 ºC. The plasticity index (plastic work/total work) is very strongly correlated with h_r/h_{max} (Eqn. 1) [48,49]. Experimentally, we have shown that the agreement between the two measures of plasticity is to ~1% for metallic materials, but less good for glasses with lower h_r/h_{max} [63], and Milman has stated that they practically coincide provided that $h_r/h_{max} \geq 0.5$ [42]. Plasticity is generally higher for fcc metals than those with bcc or hcp lattices [42,43]. The plasticity index (figure 5) increases with temperature from 0.85 at 25 ºC

to 0.95 at 900 and 950 ºC. Both the plasticity index and h_r/h_{max} are not fundamental material properties as they are influenced (albeit very slightly) by the stiffness of the indenter material, being lower when indented with lower modulus indenters. For tungsten at room temperature the plasticity index with a sapphire Berkovich indenter is ~0.83, cBN Berkovich indenter is ~0.85 and with a diamond Berkovich it is ~0.89. Equation 1 also shows that plasticity index is correlated with the H/E_r ratio of the material being tested. Plasticity index data from 25-950 ºC exhibited an approximately linear relationship (R^2 = 0.996) with H/E_r over the interval from H/E_r = 0.006-0.021, with a value of x = 7.4 determined from the slope. When x was determined from the individual data at a given temperature slightly higher values of 7.4-8.0 were found at elevated temperature than the 7.2 found at 25 ºC. For loads and penetration depths where the geometry of the Berkovich indenter is self-similar and substrate influence is small, results on 3-4 μm diamond-like carbon (DLC) coatings on steel have shown that the relationship between H/E_r and plasticity is robust and the apparent proportionality constant x varies very little across a wide load range [64]. Rounding of the indenter influences this relationship at lower depth where lower plasticity and higher values of x are found. In the current study x tended to be slightly higher for the indentations at 90 mN than at higher loads, presumably reflecting the non-ideal nature of the cBN Berkovich used in this work. FEA has predicted x ~5 [48,49] whilst for bulk materials experimental evidence suggests that x ~ 5 for glasses and x ~6-7 for metals [63,65], and for coatings at a sufficiently shallow depth so that substrate influence is minimal, 5-6 for DLC [64] and ~6 for nitride coatings [63]. Choi et al 65] have suggested the higher values found for metals are due to pile-up. The increase in plasticity and in the apparent proportionality constant x at higher temperature would suggest progressively greater pile-up is occurring at elevated temperature which is not being accounted for in the standard unloading analysis. Slightly increased pile-up at elevated temperature has been recently reported in high temperature macro-scale indentation of steels

over the temperature range 25-600 ºC [66]. Although time-dependency is the much more significant influence on elastic modulus it is considered that the small differences that remain at 850-950 ºC are due to slightly increased pile-up at these temperatures.

5. Conclusions

The capability for high temperature measurements to 950 ºC in high vacuum has been demonstrated on polycrystalline tungsten. It was possible to produce measurements with minimal thermal drift (typically ~0.05 nm/s at 750-950 ºC) and no visible oxidative damage. Hardness measurements are consistent with previous determinations. Above 800 ºC the hardness changes relatively little but more pronounced time-dependent deformation and plasticity are observed. Plasticity index, indentation creep and creep recovery increase with temperature. Elastic modulus measurements determined from elastic analysis of the unloading curves are in reasonable agreement with bulk measurements up to 800 ºC but show an upward deviation at higher temperatures. This is thought to be due to the dual influence of increased time-dependency and pile-up at these temperatures which are not being accounted for in the elastic unloading analysis. Application of a viscoelastic compliance correction brings the elastic modulus data at 850-950 ºC to within 5-10 % of literature values.

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Figure captions

1. (a) internal view of the vacuum nanoindenter (b) external view of the vacuum nanoindenter (c) side-view at 950 ºC

2. (a) Load-displacement curves at 900 ºC (b) indentation creep curves at 900 ºC (c) indentation creep strain at 900 ºC.

3. Nanoindentation curves to 160 mN at 25 ºC (open diamonds); 750 ºC (open squares); 850 ºC (open circles) and 950 ºC (closed circles).

4. Indentation creep strain vs. temperature.

5. Plasticity index vs. temperature

6. Displacement vs. time during the hold at 90 % unload. (a) 230 mN at 850-950 ºC (b) 160-300 mN at 850 and 900 ºC. The underlying thermal drift was assessed from the last 60% of the 60 s hold period.

7. (a) Hardness vs. temperature for polycrystalline, work hardened and single crystal tungsten (b) normalised hardness (H at temperature/H at 25ºC) vs. temperature. Key: NI = nanoindentation; MI = non-depth sensing microindentation; squares = data from ref. 42; open circles and open triangles = data from ref. 23. diamonds = data from ref. 37; closed circles = current study.