The deformation of “Gum Metal” in nanoindentation

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Received 19 February 2007; received in revised form 3 July 2007; accepted 20 July 2007

Abstract

“Gum Metal” describes a newly developed set of alloys with nominal composition Ti–24(Nb + V + Ta)–(Zr,Hf)–O. In the cold-worked condition these alloys have exceptional elastic elongation and high-strength; the available evidence suggests that they do not yield until the applied stress approaches the ideal strength of the alloy, and then deform by mechanisms that do not involve conventional crystal dislocations. The present paper reports research on the nanoindentation of this material in both the cold-worked and annealed conditions. Nanoindentation tests were conducted in situ in a transmission electron microscope (TEM) stage that allows the deformation process to be observed in real time, and ex situ in a Hysitron nanoindenter, with samples subsequently extracted for high-resolution TEM study. The results reveal unusual deformation patterns beneath the nanoindenter that are, to our knowledge, unique to this material. In the cold-worked alloy deformation is confined to the immediate neighborhood of the indentation, with no evidence of dislocation, twin or fault propagation into the bulk. The deformed volume is highly inhomogeneous; the deformation is accomplished by a series of incremental rotations that are ordinarily resolved into discrete nanodomains. The annealed material deforms in a similar way within the nanoindentation pit, but dislocations emanate from the pit boundary. These are pinned by microstructural barriers only a few nanometers apart, a condition that recent theory suggests is necessary for the material to achieve ideal strength.

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Keywords: Gum Metal; Nanoindentation

1. Introduction

The term “Gum Metal” (a trademark of Toyota Central R&D Laboratories) describes a newly developed class of Ti-rich alloys which can be processed to have a remarkable combination of strength and ductility [1,2]. A typical alloy composition (and the alloy that is the subject of this paper) is Ti–35.9Nb–2Ta–2.7Zr–0.3O (mass%). This alloy has the bcc structure, but, with an electron–atom ratio, e/a ∼4.24, is almost unstable with respect to transformation to hcp. The stress–strain behavior of the alloy is illustrated in Fig. 1. The alloy has high strength and elongation in the annealed condition, but develops exceptional properties after severe cold work (90%). The elastic modulus softens and the strength increases with the consequence that the alloy has an elastic elongation of nearly 3% before yielding at a strength near 1.2 GPa. It then stretches plastically to a total elongation that exceeds 12%.

The deformation mechanisms of Gum Metal are at least as interesting as its properties. The elastic limit of the cold-worked material is reached at an applied shear stress, τ ∼ τ m ∼0.11G ⟨111⟩, where G ⟨111⟩ is the modulus that governs shear in the ⟨111⟩{112} system, and τ m is the “ideal shear strength” of a bcc crystal, the stress at which the lattice becomes elastically unstable and must necessarily deform [3,4]. The mode of deformation is consistent with this result. While dislocations are found in the annealed microstructure [2], severely cold-worked Gum Metal is deformed by well-defined shear bands with no apparent dislocation activity [1,2,5]. Cold-worked Gum Metal is the first documented example of a material that yields in shear at its ideal strength.

In order for a material to fail in shear at its ideal strength when it is tested in tension, two conditions must hold. First, the ideal shear strength must be less than the critical resolved shear stress for dislocation glide, otherwise dislocation plas-
ticity would intrude before failure in shear. Second, the ideal strength in shear must lie sufficiently far below the ideal strength in tension that shear failure predominates, otherwise the material would cleave before plastic deformation could relieve the applied stress.

Recent work done as part of this research program suggests how both of these criteria may be satisfied in Gum Metal [6]. First, Nb [7] and V [6] are unusual among bcc metals in that they fail in shear rather than cleavage when pulled to ideal strength in tension. Model calculations of the elastic constants of Ti–Nb [8] and Ti–V alloys [6] suggest that this preference for shear failure is preserved over a wide range of Ti concentrations. Second, Ti–Nb and Ti–V alloys become very resistant to dislocation glide when the electron/atom ratio decreases toward 4.2 with increasing Ti content. When this happens, the impending instability of the bcc structure is forecast by a rapid decrease in the shear modulus, (C_{11}−C_{12}). This causes an increase in the effective line tension of potentially active dislocations in bcc, and, hence, a dramatic increase in the critical resolved shear stress for dislocation penetration through fields of microstructural obstacles [6]. If the microstructural obstacles are strong and dense, as they plausibly are in Gum Metal doped with Zr and O and severely cold worked, then the critical resolved shear stress for dislocation glide may exceed the ideal shear strength, leading to the bulk mechanical behavior that is observed.

Given this background, nanoindentation is a particularly attractive tool for studying the behavior of Gum Metal. Nanoindentation is uniquely suited for studying failure at the ideal strength in shear. The maximum shear developed under the indenter is within the bulk of the material, away from free surfaces, in a region of hydrostatic compression free from cleavage, and applied to a nanosized volume that is likely free of any pre-existing defects [9]. Therefore, it should be possible to achieve failure at the ideal strength by nanoindentation of even the annealed Gum Metal. The very sharp strain gradients around the nanoindent should reveal and help to clarify the detailed deformation mechanisms. For this reason, we performed nanoindentation tests on annealed and cold-worked Gum Metal using high-resolution transmission electron microscopy to monitor and clarify the mechanisms involved.

2. Experimental procedure

The experimental materials used for this work were processed bars of Gum Metal provided by the Toyota Central R&D Laboratories, Nagoya, Japan. The composition of the specimens was Ti–35.9Nb–2Ta–2.7Zr–0.3O (mass%). One bar was annealed after cold-working, the other was received as-cold-worked by 90%. Experiments were performed on discs cut from the bars.

Two kinds of nanoindentation experiments were performed. In the first, the nanoindentation was done ex situ in a Hysitron Triboindenter© fitted with a triangular, Berkovich indenter. The indented samples were thin discs, ∼3 mm in diameter, cut from the processed Gum Metal bars. Five hundred indents were done on each sample in a 50 × 10 array with 10 rows, spaced 50 μm apart, each contained 50 indents, spaced 10 μm apart. The load–deflection curves for the successive indents almost superimposed, as illustrated in Fig. 2 for the annealed specimens. There is no evidence of "pop-ins" as small as our resolution limit, ∼5 nm, on the loading curve for either type of specimen.

Following testing, the discs were thinned from the back side to make electron-transparent transmission electron microscopy (TEM) specimens that contained a few of the indents in the transparent area. To prepare the samples the indented surfaces of the discs were protected. The discs were mechanically polished to ∼80 μm thickness in two steps, then dimpled and ion milled to create a transparent area. The final sample is illustrated in Fig. 3, which shows how the thinned area of the sample presents a group of neighboring indentations for observation. The samples were studied in microscopes at the National Center for Electron Microscopy (NCEM) at the Lawrence Berkeley National Laboratory (LBNL).

The second set of samples were annealed specimens prepared for in situ nanoindentation in an in situ nanoindentation stage at NCEM [10,11]. In this test a disc sample was machined.
Fig. 3. Schematic diagram of a plan-view indentation sample after thinning.

Fig. 4. Schematic diagram representing the geometry of an in situ indentation specimen along with a scanning electron micrograph of an electron-transparent window in a Gum Metal specimen.

by focused-ion beam (FIB) milling to create a sample with the geometry shown in Fig. 4 [12]. The machined “wall” on the sample is thin enough to be transparent near its tip, while being thick enough to support a nanoindenter mounted on a stage in the microscope that permits an indentation experiment to be monitored in real time. The in situ indentation tests reported here were done with an older, qualitative indentation stage that measures displacement, but not load. A fully quantitative in situ stage has recently become available [13], and will be used for future work.

3. Results

The most interesting results were obtained from indentation experiments on the annealed Gum Metal specimens, so we shall discuss these first.

3.1. Tests and observations on annealed Gum Metal

3.1.1. Ex situ indentation

The ex situ indentation tests on the annealed Gum Metal samples produced the results shown in Fig. 2. The indentations were consistent, and gave hardnesses with a mean of 3.25 GPa, with a standard deviation of 0.33 GPa.

A number of indentation pits were transparent after thinning. All had the same characteristic appearance, which is illustrated in the TEM image shown in Fig. 5. The bottom of the pit is perforated by thinning. The flanks of the pit are clear, with some evidence of a cellular structure. The periphery of the pit is deformed by a thick array of dislocations.

The dislocation field in the periphery of the pit shown in Fig. 5 is examined in more detail in Fig. 6. There is a dense array of dislocations emanating from the edge of the pit. These are, primarily, dipole loops that consist of long, straight segments parallel to \(<111>\) joined by short, irregular segments in a roughly perpendicular orientation. The straight segments are, apparently, screw dislocations with \(<111>\) Burgers vectors. The short segments that join them are in an overall edge orientation. These dislocations are severely bowed between microstructural obstacles, whose nature is not well resolved at the magnification used here. As shown in the magnified, dark-field view, Fig. 6b,
the pinning obstacles are only a few nanometers apart, and are apparently present in a very dense distribution.

The deformed region along the flank of the indentation pit is shown in Fig. 7. It is, apparently, free of dislocations, but does show evidence of diffuse cell-like structures in its interior (these are more pronounced in other micrographs that are not included). A close examination reveals continuous deformation along the flank of the pit. The succession of microdiffraction patterns taken from the periphery of the pit to the edge of the perforation shows a sharp rotation of the zone axis from \([\bar{1}12]\) through \([\bar{3}35]\) to \([\bar{1}11]\), a rotation of \(\sim20^\circ\) about the \([1\bar{1}0]\) axis in a distance of about 500 nm. Examinations of the flanks of other indentation pits show similar features: dislocation-free regions with evidence of diffuse cells and lattice rotations of up to \(35^\circ\) from the periphery of the pit down to the core.

To identify the defects that maintain these lattice rotations, atomic resolution microscopic studies are needed, and are underway. Preliminary results suggest that the flanks of the nanoindentation pits are dense with local nanoscale lattice distortions of the type that have been previously identified in Gum
Metal and have been termed “nanodisturbances” [1,2,5]. The nature of these defects is not yet clear.

3.1.2. In situ indentation

The annealed material was also used for in situ nanoindentation experiments that follow indentation in real time. The results of these experiments are recorded in motion pictures. These show the gradual development of a structure like that shown in Fig. 8, which is essentially the same as that observed in the ex situ indentation case. The region immediately beneath the indenter is broken up into nanocells that are slightly rotated with respect to one another. No dislocations are imaged in this region. It is not yet clear whether dislocations are formed and retained in the periphery of the pit, as in the ex situ case.

3.2. Tests and observations on cold-worked Gum Metal

To date only ex situ nanoindentation tests have been done on the severely cold-worked material. The indentation curves resemble those shown in Fig. 2, and are reproducible load-deformation traces with no evident “pop-in” or other discontinuities. The measured hardnesses have a mean of 5.05 GPa with a standard deviation of 0.58 GPa, which is significantly higher than that of the annealed material.

The nanoindentation pits revealed by thinning are, again, very similar to one another. An example is shown in Fig. 9. No dislocations are found either in the peripheries of the pits or in their flanks. Instead, the deformed material is broken up into nanocells that are slightly rotated from one another. The cells seem somewhat more sharply defined than in the annealed case, but are otherwise similar in structure. The nature of the cell boundaries is not yet clear. The preliminary evidence suggests that adjacent cells have no simple crystallographic correspondence. In particular, they are not twin-related to one another.

4. Discussion and conclusion

Perhaps the most interesting and important result of this work concerns the dislocations found in the periphery of the nanoindentations in the annealed material. The theoretical analysis that was recently done as part of this work [6] shows that for Gum Metal to reach ideal strength before failure it is necessary for dislocations to be severely restricted by microstructural obstacles. Somewhat disturbingly, these obstacles were required to have separations of no more than a few nanometers. As the present work shows, in fact, the dislocations in the periphery of nanoindentation pits are pinned by obstacles with separations in the nanometer range. If cold work accomplishes a slightly further decrease in the effective separations of these barriers, the theory suggests that ideal strength can be achieved.

That ideal strength is, apparently, achieved during the nanoindentation of the annealed material seems consistent with prior work [9]. The maximum shear beneath the nanoindenter comes in the bulk of the material, beneath the surface, and is applied over a volume so small that pre-existing defects are unlikely.

Fig. 8. Displaced-aperture dark-field TEM image showing domains in divot of an in situ indent in the solution-treated sample. The letters on the diffraction pattern indicate the diffraction spot used to produce the respective image.
The dislocations in the periphery of the pit are presumably formed at the free surface as indentation proceeds. The lower nanohardness of the annealed material, ~3.25 GPa versus ~5.05 GPa for the worked material, is a likely consequence of the dislocation plasticity that intrudes as the nanoindentation pit develops in the annealed material. It may be possible to extract the maximum shear stress developed during nanoindentation from the load–deflection curve using techniques like those developed in Ref. [9], and that investigation is underway.

The nanodomain structure of the severely deformed Gum Metal is puzzling; the structure of the domain boundaries is particularly mysterious since these do not appear to result from any plausible dislocation structure. Computer modeling and high-resolution microscopic studies of this structure are underway, and we shall refrain from speculating here. However, it does seem pertinent to note that shear deformation at the limit of strength is, in effect, a mechanical melting of the material [3]. It may be useful to visualize the final structure we see not as a conventional defect structure, but rather as the product of re-solidification after mechanical melting. Since this is a low-temperature re-solidification, perhaps complex structures should be expected.

Acknowledgements

The authors gratefully acknowledge support from Toyota Motor Corporation under a grant to the University of California, Berkeley and from the National Science Foundation under grant DMR 0304629 and a Graduate Research Fellowship. Research by AMM and the facilities of the National Center for Electron Microscopy that were used in this work are supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, US Department of Energy under contract DE-AC03-76SF0098.
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