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Superelastic load cycling of Gum Metal

V.A. Vorontsov,[a,*] N.G. Jones,[b] K.M. Rahman[a] and D. Dye[a]

[a]*Department of Materials, Royal School of Mines, Imperial College, Prince Consort Road, South Kensington, London SW7 2BP, UK*
[b]*Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, UK*

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Abstract—The superelastic beta titanium alloy, Gum Metal, has been found to accumulate plastic strain during tensile load cycling in the superelastic regime. This is evident from the positive drift of the macroscopic stress vs. strain hysteresis curve parallel to the strain axis and the change in its geometry subsequent to every load–unload cycle. In addition, there is a progressive reduction in the hysteresis loop width and in the stress at which the superelastic transition occurs. *In situ* synchrotron X-ray diffraction has shown that the lattice strain exhibited the same behaviour as that observed in macroscopic measurements and identified further evidence of plastic strain accumulation. The mechanisms responsible for the observed behaviour have been evaluated using transmission electron microscopy, which revealed a range of different defects that formed during load cycling. The formation of these defects is consistent with the classical mathematical theory for the *bcc* to orthorhombic martensitic transformation. It is the accumulation of these defects over time that alters its superelastic behaviour.

Keywords: Gum Metal; Beta titanium alloys; Martensitic transformation; Synchrotron X-ray scattering; Transmission electron microscopy

1. Introduction

In 2003, Saito et al. [1] presented their findings on a novel metastable β-titanium alloy (Ti–36Nb–2Ta–3Zr–0.3O wt.%), Gum Metal, that exhibited a unique combination of attractive mechanical properties. These included a high tensile strength in excess of 1 GPa, a low elastic modulus of $\approx$70 GPa in the hot worked condition ($\approx$55 GPa after cold rolling) as well as superelastic and superplastic behaviour. These 'super' properties were attained by selecting a composition that simultaneously satisfied three theoretically predicted electronic parameters: electron per atom ratio ($e/a = 4.24$), bond order ($Bo = 2.87$) and d electron orbital energy level (Md = 2.45 eV).

The authors noted that the material exhibited very little hardening even after substantial cold work. Based on this and their microstructural observations, it was stipulated that the material underwent plastic deformation *via* a dislocation free mechanism. They claimed that no martensitic transformation took place during cold work. Instead, the unstable β lattice readily formed giant faults by ideal shear and thus accommodated the plastic strain. However, the *in situ* synchrotron X-ray work of Talling et al. [2,3], has conclusively proven that a reversible stress induced martensitic transformation, whereby the body-centred cubic (*bcc*) β phase transforms to the orthorhombic α'', is responsible for the superelastic behaviour.

Despite this, the mechanisms responsible for the peculiar mechanical behaviour of Gum Metal are complex and remain a subject of ongoing work. Morris et al. [4] have shown that the propensity of Gum Metal for undergoing the martensitic transformation is orientation and texture dependent. Furthermore, structures commonly referred to as "giant faults", nanodisturbances, twinning, dislocations and α'' are typically observed in the β phase after cold working of Gum Metal as well as other superelastic alloys like Ti-2448 and Ti-12Mo. Their exact role in the deformation processes remains to be determined, while there has been no evidence to date that their origin is assisted by dislocation glide [1,5]. Furthermore, cold work results in the formation of large number of fine stress-induced ω phase precipitates [6–9]. These have a hexagonal crystal structure that results from the systematic collapse of the $\{111\}$ planes in the β phase. Since cold working increases the tensile strength of Gum Metal, it is likely that the formation of the ω phase plays an important role. Lastly, plasticity that is mediated by dislocation glide has also been reported in derivative alloys [10,11,5].

Due to its low elastic modulus and the low toxicity of niobium as a β stabilising element [12], Gum Metal is receiving significant attention from the biomedical community as a candidate material for orthopaedic implants. In addition, the low modulus and the possibility of hysteretic superelastic behaviour make the alloy interesting to engineers for energy absorbing applications. Therefore, it is important to understand fully the mechanical behaviour of Gum Metal during superelastic load cycling.

* Corresponding author.

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In this work we examine the superelastic behaviour of Gum Metal under cyclic tensile loading using synchrotron X-ray diffraction and high-resolution electron microscopy. We show that the $\beta \rightarrow \alpha''$ martensitic transformation introduces a variety of permanent lattice defects. This leads to accumulation of plastic strain and changes the shape of superelastic hysteresis with every load–unload cycle. Finally, we provide an explanation for this accumulation of defects by employing classical mathematical theory to evaluate the martensitic transformation in Gum Metal.

2. Experimental method

2.1. Material preparation

The Gum Metal employed in this study was produced using ingot metallurgy. An elemental powder compact was melted in a high purity argon atmosphere using a helium plasma torch. The initial ingot was then triple remelted with inversions. A billet 60 mm in diameter was machined from the button-shaped ingot. It was then subjected to a 60 min solution heat treatment at 850 °C. Deltaglaze™ 3418 (Acheson, MI, USA) glass lubricant, was subsequently applied to the surface of the billet and it was extruded into 12 mm rod after a 105 min heat treatment at 975 °C. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to verify the chemical composition of the final product: Ti–36.2Nb–1.96Ta–3.16Zr–0.26O wt.%. (LECO analysers were used to measure the oxygen and hydrogen content.)

2.2. In situ synchrotron X-ray scattering

The *in situ* loading experiment was performed at the I12 beamline of the Diamond Light Source synchrotron X-ray facility in Didcot, Oxfordshire, UK. Fig. 1 shows a schematic representation of the experimental set-up. A ‘dog bone’ tensile test specimen, with gauge dimensions of 1.5 × 1.5 × 19 mm was electric discharge machined (EDM) from the extruded Gum Metal bar, with the tensile axis aligned parallel to the extrusion direction. It was subjected to sub-yield cyclic tensile loading between 15 and 700 MPa on a purpose built 5 kN frame using a loading rate of 4 MPa s^{-1}. The maximum stress does not exceed the yield strength of Gum Metal as can be seen from the full stress vs. strain curve in Fig. 2. A total of 20 load–unload cycles were carried out. The macroscopic strain was recorded using a 10 mm contact extensometer.

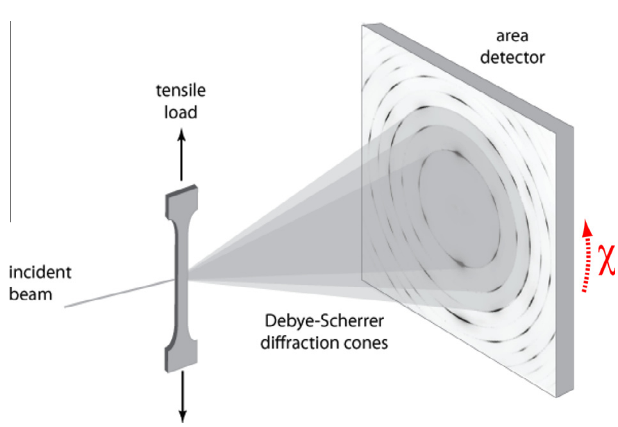

Fig. 1. Schematic representation of the experimental arrangement used to make the *in situ* synchrotron measurements. The data are binned over an azimuthal angle, χ, to produce intensity vs. 2θ spectra. Adapted from [30].

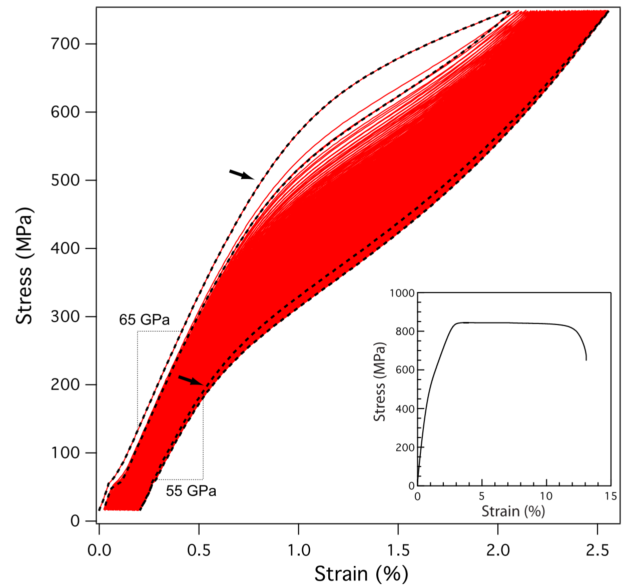

Fig. 2. Evolution of the stress vs. strain hysteresis over 200 load–unload cycles between 15 and 750 MPa. The loops corresponding to the first (left) and last (right) load cycles are highlighted by the black dashed lines. Arrows show approximate positions of superelastic transition stress upon loading. The full stress vs. strain curve for Gum Metal is shown in the bottom left corner.

The Debye–Scherrer diffraction rings formed by the monochromated incident X-ray beam (0.5 × 0.5 mm, 80 keV ($\lambda = 0.15498$ Å)) were imaged using a Thales Pixium RF4343 2880 × 2880 pixel 2D area detector positioned 1320.725 mm from the specimen. The images were acquired using 2 s exposures, while the detector's write time was a further 0.5 s per image.

The diffraction ring images were processed using the FIT2D [13] analysis software to obtain the intensity vs. 2θ (scattering angle) spectra. The data are taken from a 10° azimuthal bin around 90°, i.e. aligned to the tensile axis. The instrument parameters necessary for the analysis were determined using a powder standard. The Wavemetrics IGOR Pro software package was then used to perform fitting of a Gaussian function to the individual lattice peaks observed in the integrated spectra.

2.3. Post-mortem electron microscopy

Screw-threaded fatigue specimens with a round cross section, a gauge diameter of 5 mm and gauge length of 19 mm were prepared using EDM. In order to help isolate the effects of various deformation related phenomena the specimens were subjected to sub-yield cyclic loading in both the superelastic regime 15–750 MPa, as well as below the superelastic transition stress between 15 and 300 MPa. Furthermore, different numbers of load–unload cycles were investigated: 1, 2, 20 and 200 cycles at a loading rate of 4 MPa s^{-1}. A 100 kN Instron servo-hydraulic thermo-mechanical fatigue (TMF) frame was used to carry out the mechanical tests with a contact extensometer to record the macroscopic strain.