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Modeling the α/ω thermal stability in shocked Zr: A coupling between dislocation removal and phase transformation

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ABSTRACT

Under high pressure, Zr undergoes a transformation from its ambient equilibrium hexagonal close packed α phase to a simple hexagonal ω phase. Subsequent unloading to ambient conditions does not see a full reversal to the α phase, but rather a retainment of significant ω. Previously, the thermal stability of the ω phase was investigated via in-situ synchrotron X-ray diffraction analysis of the isothermal annealing of Zr samples shocked to 8 and 10.5 GPa at temperatures 443, 463, 483, and 503 K [25]. The phase volume fractions were tracked quantitatively and the dislocation densities were tracked semi-quantitatively. Trends included a rapid initial (transient) transformation rate from $\omega \rightarrow \alpha$ followed by a plateau to a new metastable state with lesser retained ω (asymptotic). A significant reduction in dislocation densities in the ω phase was observed prior to initiation of an earnest reverse transformation, leading to the hypothesis that the $\omega \rightarrow \alpha$ transformation from is being hindered by defects in the ω phase. As a continuation of this work, we present a temperature dependent model that couples the removal of dislocations in the ω phase and the reverse transformation via a barrier energy that is associated with the free energy of remaining dislocations. The reduction of dislocations in the ω phase occurs as a sum of glide and climb controlled processes, both of which dictate the transient and asymptotic behavior of the annealing process respectively.

1. Introduction

At ambient conditions, the group IV transition metals (Zr, Ti, Hf) are thermodynamically stable as a hexagonal close packed (HCP) crystal ($P6_3/mmc$, $c/a = 1.593$), denoted as the α phase. At high pressure, the α phase in these metals undergoes a transformation to the ω phase, which has a simple hexagonal crystal structure ($P6/mmm$, $c/a = 0.623$). After shock loading [1] or severe plastic deformation by high-pressure torsion (HPT) [2,3], the ω phase displays a strong hysteresis; with a significant fraction remaining after pressure is released. In the case of ω material yielded from shock impact experiments, samples with retained ω fractions as high as 80% of ω phase have been observed [4–6]. The resulting two-phase microstructure is (meta)stable for years at standard temperature and pressure.

Over the past 60 years, there have been numerous studies on the $\alpha \rightarrow \omega$ forward transformation, with the majority focusing on the determination of the equilibrium temperature/pressure phase diagram, crystallography, mechanical properties, and electronic structure of the ω phase [7–10]. The significant disagreement amongst these studies attest to the influence of the transformation hysteresis on the determination of basic physical properties of group IV transition metals. As an example, the equilibrium transformation pressure for Zr has been reported to range from 2 to 7 GPa for the static pressure loading case [11–14]. However, even though the metastability of the ω phase is well documented, there is only a limited body of work on the stability of the α/ω dual phase microstructure.

The $\alpha \rightarrow \omega$ phase transformation in Zr has been shown to be achievable by several techniques, namely 1) hydrostatic pressure, 2) shock loading, and 3) high pressure torsion methods. It is not clear whether there is a single mechanism for the $\alpha \rightarrow \omega$ transformation or if multiple transformation pathways exist. Depending on the experimental conditions and loading mechanisms, multiple (α/ω) orientation relationships have been reported. The amount of retained ω, transformation pressures, and the apparent degree of ω

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stability vary significantly between experiments [15–19]. Hence there is a need for clear need for systematic studies of both the forward transformation and of the reverse $\omega \rightarrow \alpha$ reverse transformation. More specifically, models that link the evolution of the microstructure to thermodynamic state variables, coupled with in-situ experimental observation, are required to characterize the kinetics of the transformation under various conditions in order to provide evidence for or against proposed transformation or reverse-transformation mechanisms [20–22].

In this paper, emphasis is placed upon the *thermal stability of the ω phase generated from shock experiments*. The ω phase produced from shock impact is generally characterized by the $(0\,0\,0\,1)_\alpha \parallel (1\,0\,\bar{1}\,1)_\omega$ and $[1\,0\,\bar{1}\,0]_\alpha \parallel [1\,1\,\bar{2}\,\bar{3}]_\omega$ orientation relationship identified by Song & Gray [23]. Brown et al. first investigated the thermal stability of the ω phase by heating shocked samples under a constant temperature ramp from room temperature to 620 K at a rate of 0.05 K/s [24]. A subsequent study by Low et al. involved the isothermal annealing of shocked Zr samples over a similar temperature range [25]. Both experiments showed a significant decrease in dislocation content prior to the onset of the reverse transformation, leading to postulation that the metastability of the ω phase was highly correlated with the defect state of the microstructure. Furthermore, it was speculated that the dislocation population was somehow arresting the reverse transformation and that given sufficient thermal energy, the defects would gain mobility and annihilate through recovery mechanisms; allowing the reverse transformation to proceed. Here, we present a model based on this hypothesis and demonstrate that model predictions are consistent with the experimentally observed transformation kinetics. Section 2 reviews and summarizes the previously collected experimental data which informs the current work as well as a brief discussion of previous modeling efforts. This is followed by section 3 which provides detail into the model, after which section 4 provides the results from the model. Further discussion on the results and their implications are provided in section 5.

2. Experimental methods and prior studies

2.1. Production of metastable ω through shock impact

The data used to develop and validate this model came from annealing studies of shocked Zr performed by Low et al. [25] and Brown et al. [24]. The shocked material for those studies came from gas gun experiments performed by Ceretta and collaborators [4,6,9,26,27]. Prior to shock loading, all Zr samples were prepared from a high-purity crystal bar Zr (< 100 ppm impurities) which was upset forged, clock rolled, and annealed, resulting in a plate with homogenous and fully recrystallized microstructure, with average grain size of 15–20 μm [28]. The plate exhibited a strong basal texture (> 8 times uniform random distribution) nearly aligned with the normal or through-thickness direction (TT) direction of the plate, with prism planes uniformly distributed about the in-plane directions of the plate (transversely isotropic). Shock loading by dynamic impact was performed utilizing a gas-driven 80-mm single stage launcher [26]. The impact direction was along the TT direction or parallel to the *c*-axis of the majority of grains in the sample. The targets were impacted by 2.5 mm thick Zr flyer plates accelerated to velocities of 640 or 835 m/s, resulting in peak compressive stresses of 8 or 10.5 GPa respectively on the Zr samples [6]. The total duration of the shock process (plasticity and transformation included) was approximately 0.5 μs [29]. The samples were soft-recovered and were further sectioned for X-ray and microscopy. The real-time process of the shock deformation was tracked via velocity interferometer system for any reflector (VISAR) measured wave profiles. The wave profiles and their interpretations are given in Fig. 1. The VISAR traces indicate that samples shocked to 10.5 GPa complete the $\alpha \rightarrow \omega$ transformation over a significantly shorter time duration than samples shocked to 8 GPa. It was also speculated that the ω phase in samples shocked to 10.5 GPa experienced additional plastic deformation, in addition to the higher pressure, resulting in a difference in defect population compared to the 8 GPa shocked samples. The resulting volume fractions of retained ω phase are $\sim$ 60% and $\sim$ 80% for samples shocked to 8 and 10.5 GPa respectively. Complete details of the shock experiments can be found in Refs. [4,6,9,26,27].

2.2. In-situ annealing experiments

The in-situ annealing experiments of the α/ω samples consist of work by Brown et al. [24] and Low et al. [25] and were performed via x-ray diffraction (XRD) characterization methods at the 1ID-C beam line at the Advanced Photon Source (APS), Argonne National Laboratory [30]. The experimental setup was typical for powder diffraction on a polycrystalline sample. A high energy monochromated incident beam (E = 86 keV) was used to illuminate the samples and the resulting diffraction images were collected on a two-dimensional detector placed at an appropriate distance to capture at least 5 diffraction rings from each phase [25]. The individual (α/ω) phase fractions were tracked quantitatively and the dislocation densities were tracked semi-quantitatively.

The experimental work by Brown et al. involved the heating of Zr samples shocked to 8 and 10.5 GPa from 300 to 620 K at a constant temperature ramp rate of 0.05 K/s. Significant $\omega \rightarrow \alpha$ transformation was observed within the temperature range of $475 < \theta < 550$ K [24]. Low et al. further investigated the transformation under isothermal conditions at temperatures of 443, 463, 483 and 503 K in samples similarly shocked to 8 and 10.5 GPa [25] and observed a rapid initial transformation rate. At all temperatures there was a continuous deceleration of the transformation, with the transformation rate approaching zero with significant ω phase remaining. This new metastable state appeared

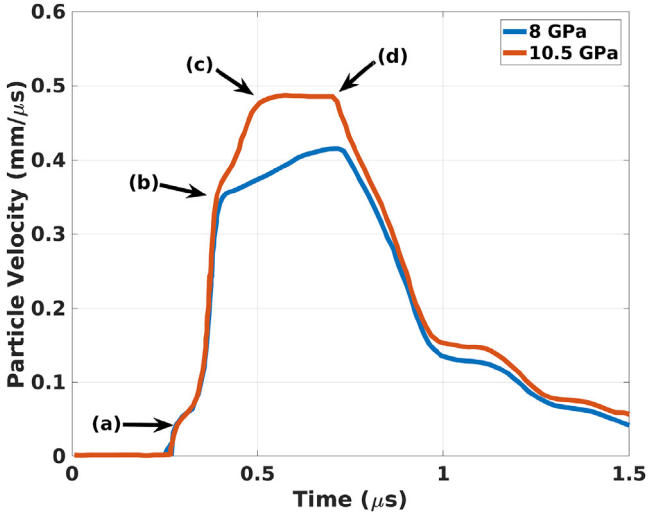

Fig. 1. Wave profiles of zirconium samples shocked to 8 and 10.5 GPa at room temperature. The arrows indicate significant events during the shock impact and are interpreted as (a) Hugoniot elastic limit and onset of twin and slip deformation, (b) onset of $\alpha \rightarrow \omega$ transformation, (c) flatlining indicating end of transformation and further deformation under peak pressure, and (d) end of shock process. Data sourced from Cerreta et al. [29].