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The thermal stability of surface deformed zirconium

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Abstract

This study examined the microstructural and mechanical changes in shot-peened zirconium resulting from extended exposures to temperatures between 200 and 300°C. The peening hardens the surface region which extends to about 300 μm from the surface. It was discovered that the outermost (10–50 μm) shot-peened surface decreases in hardness from approximately 230 VHN (DPH) to about 220 VHN after 560 h at 200°C. The same drop in hardness was observed after about 5.5 h at 300°C. Further drops in hardness with time were observed at 300°C to a minimum surface hardness of 206 VHN after 560 h. Longer times at 200 and 300°C did not appear to significantly affect the hardness. These decreases in hardness were determined from hardness depth profiles before and after heat treating the zirconium to various times from 0.5 to 4458 h. The hardness between 150 and 300 μm (the less deformed region) was approximately unaffected by the thermal treatments. The grain dislocation structure of the shot-peened zirconium was examined in the as-peened as well as the annealed conditions using polarized light optical and transmission electron microscopy. These observations are consistent with an explanation of decreased hardness based on static recovery without any static recrystallization. © 1997 Elsevier Science B.V.

1. Introduction

Surface hardened shot-peened zirconium plates are being used for commercial applications where they are expected to experience moderate temperatures. One example of shot peening of the zirconium plates (impinging the surfaces with cast iron particles) under various intensifies and coverage specifications is described elsewhere [1]. There is concern that softening by recovery, recrystallization and grain growth may occur within the deformed, shot-peened, surface-region with prolonged exposure to temperatures as low as 200–300°C. It has been shown by McGeary and Lustman [2] that heavily cold-worked zirconium, by swaging (97% reduced bar) undergoes significant softening (decrease in hardness) after just 10 min at 300°C [2]. Several other authors [3–6] have also observed significant recovery in cold-worked zirconium at temperatures of approximately 400°C. No long term (> 200 h) softening studies appear to have been performed at temperatures as low as 200°C for cold-worked zirconium.

Desalvo and Zignani [4] observed a so-called 'stage I of recovery' over the temperature range of ambient temperature up to about 315°C in 80% cold-worked 99.5% pure zirconium plate using electrical resistivity measurements. This 'stage I recovery' was also reported at 30 to 35 K by Swanson et al. [7] for a study of 99.9% pure zirconium cold-worked in tension at 4 K and by Merle et al. [8] in a study of 82% cold-rolled Zircaloy-4 sheets at temperatures up to 100°C using electrical resistivity measurements. The authors proposed that 'stage I recovery' was due to interstitial atom migration [7] or short-distance dislocation rearrangement, which they claim was too small to be observed

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under the electron microscope [4]. Bostrom and Kulin [9] also observed restoration of resistivity at low temperatures. Hardness data were not reported in the above studies. The mechanism of recovery of the resistivity associated with 'stage I,' which is very sensitive to the purity of the zirconium, was not firmly established. In the present study, the term recovery describes a change in mechanical strength or hardness associated with a change in point (vacancy) or line defect (dislocation) density and/or arrangement.

The goal of this study is to determine if there is any mechanical softening in the shot-peened zirconium surface in the temperature range of 200–300°C. Recovery and/or recrystallization of the shot-peened surface layer would be manifested by structural change(s), perhaps detectable by changes in the micro-hardness and by optical and transmission electron microscopy (TEM). Although hardness testing has previously been regarded as an ambiguous measure of recovery [10,11], it has been utilized in this study. This is because of the variable amount of cold-work with depth associated with shot peening, which complicates the use of electrical resistivity measurements. Hardness testing was also chosen because the commercial community is often interested in changes in hardness of the surface of the shot-peened plates independent of any resistivity or microstructural changes.

2. Experimental procedure

The plate, that was eventually shot peened, was rolled to the final form of 15.0 cm × 21.6 cm × 0.86 cm thickness from a triple arc-melded ingot. The plate was then wet ground with a 220 grit silicon carbide belt to 0.65 cm thickness and then shot peened to 100% coverage and a 16 Aalmen intensity [12]. The nominal plate composition, measured using techniques described elsewhere [1], is listed in Table 1.

The zirconium was heat treated at 200 and 300°C for various times, increasing, in each instance, by a factor of ten or so, from an initial 0.5 h treatment. New hardness profiles were determined from the identical specimens after each heat treatment and compared to the initial (un-heat treated) profiles in order to eventually assess the softening or 'restoration' of the shot-peened zirconium. The grain and dislocation microstructure were examined using polarized light optical microscopy and TEM both before and after heat treatment to determine the source of any loss of strength (hardness) of the zirconium.

2.1. Sample preparation

Seven samples were removed from various locations in the 15.0 cm × 21.6 cm × 0.65 cm thickness test plate, using a water cooled silicon carbide abrasive cutoff saw. Specimens were cold mounted in Buehler epoxy resin (5–6 h cure), and a side that is transverse to the shot-peened surface was subsequently polished. Polishing proceeded in three steps: grinding, rough polishing, and final polishing. Samples were ground using wet silicon carbide grinding paper to 600 grit, removing about 10 μm at each grit level. Rough and final polishing utilized a combination of alumina slurry and acid on a polishing wheel. Samples were polished according to Table 2. The grinding and polishing techniques are described in greater detail elsewhere [1].

Table 1
Nominal composition of zirconium 702 [13]

Zr	99.17%	Hf	0.276%
Al	120 ppm	Ti	84 ppm
Nb	50 ppm	Cu	25 ppm
Sn	1800 ppm	Mo	< 10 ppm
C	142 ppm	P	10 ppm
H	30 ppm	V	< 25 ppm
Ni	98 ppm	Fe	1547 ppm
Ta	< 100 ppm	N	55 ppm
Cr	1022 ppm	Si	58 ppm
O	1320 ppm	W	< 25 ppm

2.2. Hardness testing

A Leco M400A microhardness testing machine was utilized for all hardness measurements. A 300 g load was used to develop a hardness profile from the shot-peened surface to a depth of about 800 μm. The first hardness measurement was taken about 35 to 50 μm from the shot-peened surface. Any measurements closer than about 35 μm gave artificially low results because the free surface results in diminished resistance to the plastic flow of material. The samples were photographed under polarized light at, typically, 100 × magnification following hardness measurements, to determine the average grain size and the depth to which mechanical twinning (known deformation) is observed. The latter helped ensure that the hardness profile extended beyond the minimum plastic deformation depth.

A best fit curve (third-order polynomial) was formulated for the initial, or non-heat treated, zirconium plate hardness profile. This was compared to profiles after 200 and 300°C thermal treatments for various times. Hardness profiles for the shot-peened surface were developed for six samples in the initial, or pre-heat treated, condition. Three of these samples were then used for 200°C testing and the remaining three for 300°C testing. Hardness profiles were established after each heat treatment and were compared to the initial profile to determine if any changes in the hardness profile occurred.

The hardness of zirconium varies substantially with composition. This was shown by Bailey [14] who measured the effect of oxygen and nitrogen on the hardness of commercial grade zirconium and zirconium single crystals. The hardness of commercial grade zirconium with about

Table 2
Polishing solution compositions

Step description	Duration	Composition
Rough polishing	3–4 min	250 ml H_2O, 22 ml HNO_3 (70%), 3 ml HF (48%), slurry (300 ml H_2O, 20 g of 1 μm alumina powder)
Final polishing	4 min	200 ml H_2O, 30 ml HNO_3, 20 ml H_2O_2 (70%), 8–10 drops HF, slurry (200 ml H_2O, 3 g of 0.05 μm alumina powder)
Etching	6–8 s	18 ml H_2O, 18 ml HNO_3, 4 ml HF

0.1 wt% of oxygen and nitrogen was 185 ± 5 VHN while higher purity (0.03 wt% oxygen and nitrogen) had a much lower hardness of 100 ± 3 VHN. This would indicate that direct comparisons between hardness (associated with plastic deformation) investigations where small changes in composition (often not reported) can exist, may be less useful than the relative changes in hardness with deformation observed in zirconium of a given composition.

The hardness profiles in this study were well defined and reproducible with a sufficient number of tests. The variation of hardness values in a region may vary by, typically, about ±5%. The accuracy of the profile is, however, improved with an increasing number of tests within a region. This is shown in Fig. 1.

2.3. Heat treatment

A cylindrical furnace was built by Zircar Corporation specifically for low temperature (200–300°C) annealing studies. The furnace used zirconia insulation with a Sigma MDC4E temperature controller and was capable of maintaining a temperature within less than 1°C at either 200 or 300°C for periods of over several months. The first heat treatment for the three samples was 0.5 h at 200°C. Following grinding, polishing, and hardness profiling to determine the effect of the annealing, the same samples were treated at 200°C for 5, 50, 504, 1684, and 2214 hours (cumulative time of 4458 h). Three different samples were similarly treated at 300°C for 0.5, 5, 50, 502, and 2233 hours (cumulative time of 2790 h).

2.4. Oxygen effects

As mentioned previously, the oxygen concentration can dramatically affect the hardness. The difference in hardness as a function of oxygen content was also investigated by Sauby and Lee [15] for Zircaloy-2. Also, the solubility of oxygen in zirconium is about 30 at% at the temperatures used in this study. If a significant amount of oxygen diffused into the samples during air annealing, the softening due to recovery could be countered by an increase in hardness due to the absorbed oxygen. Although the effects of oxygen could have been minimized by vacuum annealing, annealing in ambient air was still performed since this is the 'service condition' that the shot-peened plates would often experience. Some companion vacuum annealing was performed in this study to determine the effect of air annealing (oxygen absorption) on the hardness.

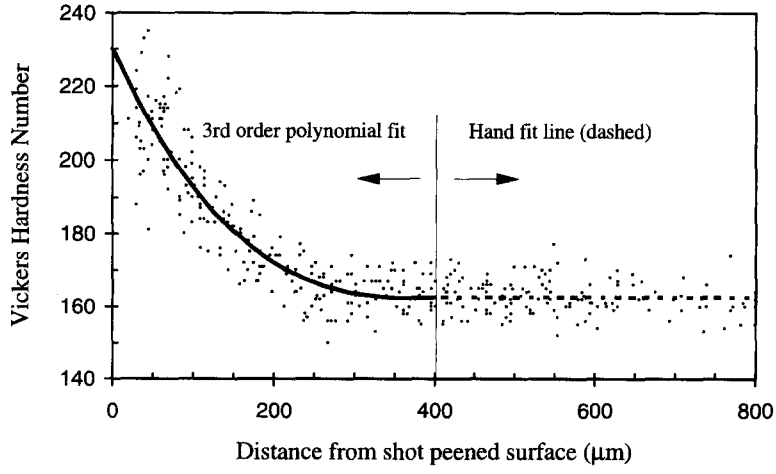

Fig. 1. Initial hardness profile of shot-peened zirconium in this study.

2.5. Vacuum annealing

A zirconium sample was removed from the shot-peened test plate and annealed in a vacuum furnace in order to determine how annealing in air leads to the absorption of oxygen that would independently increase the hardness. Samples were wrapped in about 15 layers of zirconium foil that acted as a 'getter' for residual oxygen. The sample was annealed at 300°C for 1.5 h under a vacuum of about 25 mTorr. This time produces, as will be shown subsequently, substantial softening for the conditions used in this study.

The annealing performed in the vacuum furnace appeared to effectively minimize oxidation of the surface of the zirconium specimen. The sample surface was only very slightly yellow in appearance which indicated that a slight oxide (much less than would be present in an air anneal) was developed. Oxidation of zirconium proceeds through various colors, gold being the first or thinnest oxide. The thickness of the oxide is not easily determined without an analysis of the refractive index of the material and measuring the phase change occurring in reflections from the surface. Douglass and Van Landuyt [16], however, attempted to measure a range of oxide thickness for various colors associated with oxidation in air at 250 to 450°C. The thickness estimated corresponding to the initial gold color was 10 nm. The maximum thickness that could be examined under TEM by Douglass et al. was estimated to be about 400 mn and corresponded to a gray purple surface color. This indicates that very little oxidation on the order of just 10 nm occurred on the sample vacuum annealed in this study.

2.6. Quantification of cold-work induced by shot peening

Previous studies on the effect of thermal heat treatment on deformed zirconium were only relevant to uniformly cold-worked zirconium. The equivalent amount of cold-work with various depths from the shot-peened surface needed to be quantified. This would allow comparisons to be made with other studies, that utilized uniformly cold-worked zirconium, to determine if shot-peened specimens responded consistently to thermal exposure. Characterizing the amount of cold-work induced by the shot-peening would also provide thermal stability results over a much broader range of cold-work than is currently available in the literature, especially for low temperatures.

A 'baseline' hardness corresponding to 0% cold-work was determined after annealing the shot-peened plate and a non-shot-peened plate for 1 h at 790°C. The annealed (non-peened) zirconium plate (702) was cold-rolled from approximately 3 to 57% (larger values were not possible due to tearing). One surface of the undeformed and each of the cold-rolled specimens was etched in a 45 ml H_2O, 45 ml HNO_3, and 10 ml HF solution until approximately 0.5 to 1.0 mm of material was removed from the surface. Hardness tests were then performed on each sample. The non-shot-peened plate had an average grain size of about 3–4 times larger than that of the shot-peened plate. This had no substantial effect (Hall-Petch) on the hardness, as the shot-peened (peened surface removed) and non-peened specimens both had an average hardness of 164.

A parabolic function was used to relate the hardness to the cold-work. Percentages of cold-work could then be reasonably assigned to the hardnesses of the profile of the shot-peened specimens. From these values, a new curve was developed of cold-work versus distance from the (initial or pre-heat treatment) shot-peened surface. The fit allows extrapolation to the depth associated with 99% cold-work. As might be expected, the predicted hardness at 99% cold-work was within 5% of the value at the surface of the shot-peened specimens as determined from extrapolation of the polynomial describing the initial hardness profile.

2.7. Transmission electron microscopy

Transmission electron microscopy (TEM) was utilized in order to examine the dislocation microstructure of the heavily deformed surface region of the shot-peened zirconium and to observe any changes in the dislocation microstructure after annealing. Several foils, at various depths from the surface, were examined in the non-heat-treated shot-peened and the annealed shot-peened zirconium plates.

Each disk was electropolished to perforation using a Fischione twin jet electropolishing unit with a solution of 5% perchloric acid, 5% methanol, and 35% butoxy ethynol (butocelusol), at 34 V, 25 mA and a medium jet speed setting at -25°C. The depth of the perforation from the shot-peened surface was determined using an optical microscope, with an accuracy of about ± 5 μm. A JEOL 200CX transmission electron microscope (TEM) at the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory (LBNL) was utilized.

3. Results

3.1. Thermal stability study

The initial hardness profile (before annealing) decreased from about 230 VHN at the surface to about 165 VHN at the metal interior, about 300 μm from the surface. The initial profile developed for the pre-heat treated shot-peened zirconium is illustrated in Fig. 1 with a third-order polynomial curve to fit the data.

The third-order polynomial curve fits from the hardness profiles developed at 200°C after 0.5, 5, and 50 hours did not show a significant decrease in hardness from the initial profile shown in Figs. 1 and 2. The third-order polynomial best fit curves from these plots appear in Fig. 2(a). The

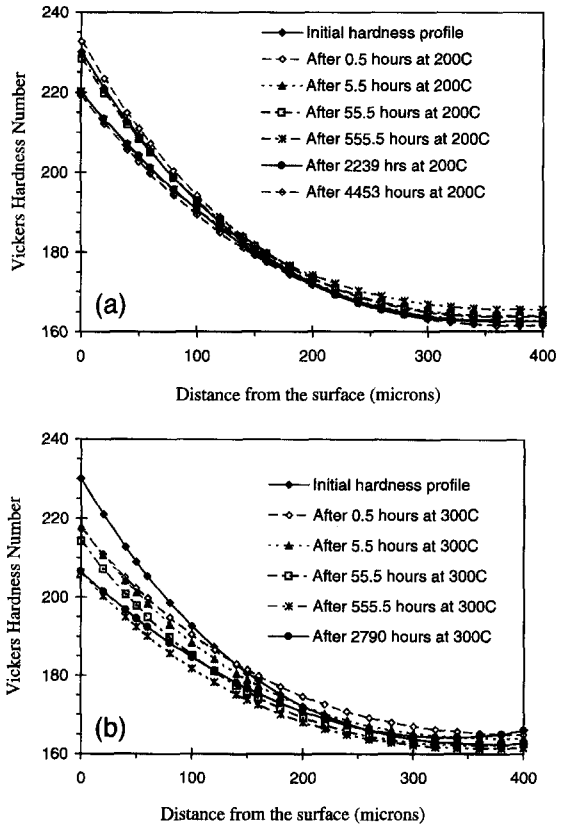

Fig. 2. The hardness profile of the shot-peened zirconium after exposure for various times at (a) 200°C and (b) 300°C.

hardness near the surface noticeably decreased after 500 h. The deformed metal to the nearest 100 μm of the surface seemed to decrease while the remainder remained unchanged. The surface hardness predicted by the computer curve decreased from 230 VHN to 220 VHN. The surface hardness decreased from 230 VHN to 217 VHN after 0.5 h at 300°C. These results, and yet larger decreases in hardness at the surface after longer times, and the decrease in hardness that occurred at larger distances from the surface are plotted in Fig. 2(b). The effects of thermal softening can be alternatively illustrated by plotting the decrease in hardness as a function of time for a *fixed depth*. This is illustrated in Fig. 3. Thus, it appears that some restoration of the surface hardness (0–50 μm) due to shot peening occurs at both 200 and 300°C, the former requiring longer times. Intermediate depth layers (100–150 μm) undergo small or negligible softening, while deeper (to maximum damage depth of about 300 μm) appear to undergo no apparent softening over the time range studied.

3.2. Vacuum annealing

The hardness profile of a shot-peened specimen was determined after 1.5 h of annealing at 300°C, in vacuum. The third-order polynomial curve from the resulting profile is plotted in Fig. 4 along with the profiles from 0.5 and 5 hours at 300°C in air that were previously illustrated in Fig. 2(b). Fig. 5 plots the data from the vacuum annealed hardness profile with the 300°C air anneal data for hardness as a function of time for fixed distances from the

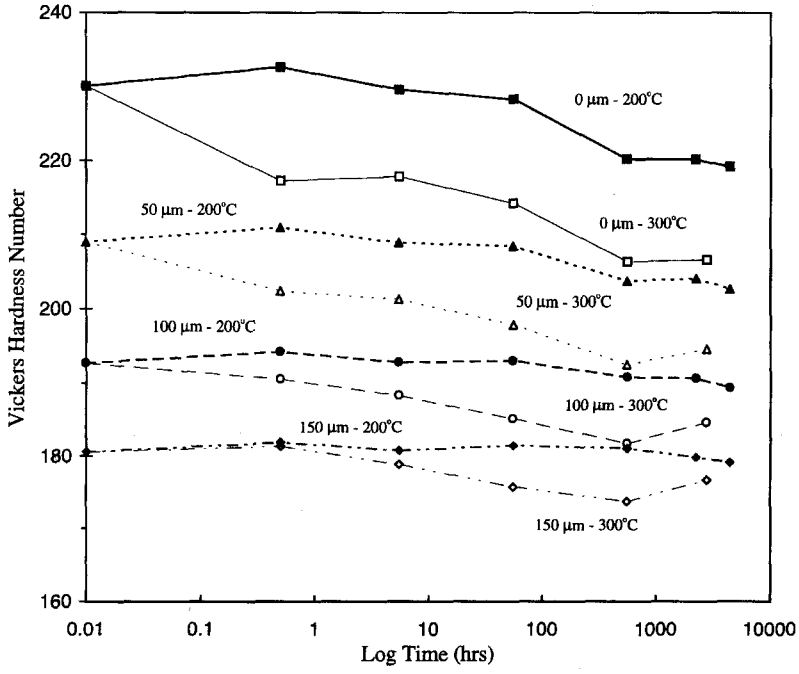

Fig. 3. Decrease in hardness as a function of time and temperature, for various depths from the shot-peened surface, at 200°C and 300°C.

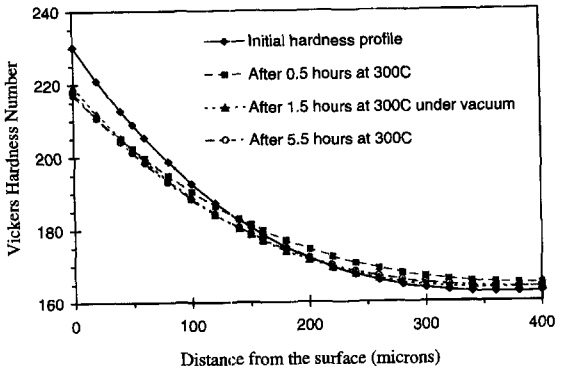

Fig. 4. Hardness profiles after 1.5 h at 300°C under vacuum compared to annealing in air for 0.5 and 5.5 h at 300°C.

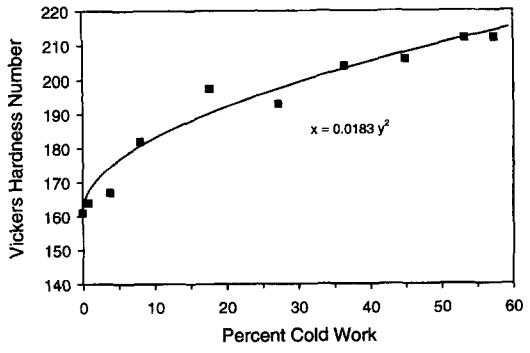

Fig. 6. Cold-work versus hardness for the cold-rolled plate.

shot-peened surface. The vacuum data coincide fairly well with the 300°C air anneal data; no increases in the surface hardness or change in the hardness profile were observed, as might be expected if oxygen had diffused to a significant distance from the surface. This indicates that the hardness profiles of this study are not affected by oxygen diffusion from the surface, since it is expected that any small increase in oxygen content would have a significant effect on hardness [14,15].

3.3. Hardness / cold-work study

The shape of the hardness versus cold-work (cold-rolled annealed zirconium plate) curve is shown in Fig. 6 and is consistent with data reported by Gray [5] for cold-rolled zirconium. A curve was fit to the data using a parabolic of the form $x = Cy^2$, where x is the percent cold-work, C is a constant, and y is the difference between the baseline hardness (fully annealed) and the hardness at a given percent of cold-work. As mentioned earlier, a value of about 230 VHN is predicted by the equation near 99% cold-work. The highest (not average) hardness values observed in the shot-peened zirconium were about 230 VHN at 40 μm from the shot-peened surface (see Fig. 1). The cold-rolled versus hardness data is also consistent with the 230 VHN value predicted by extrapolating the best fit third-order polynomial curve (of the hardness versus depth from the surface of the shot-peened zirconium) to the top surface. Thus, the surface of the shot-peened specimens was deformed to a level comparable to cold-working to nearly 100% as might be expected. The hardness values from a typical pre-heat treated shot-peened specimen were converted to percent cold-work and the cold-work versus depth-from-surface profile appears in Fig. 7.

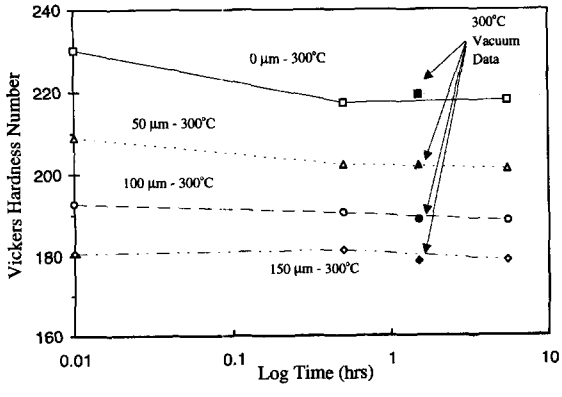

Fig. 5. Decrease in hardness as a function of time for various depths from the shot-peened surface with annealing at 300°C in both air and vacuum.

The extrapolated hardness values near the surface of the shot-peened specimens were used to compare the results of this investigation to those of the McGeary and Lustman [2] study on the softening of 97% cold-worked zirconium. After each heat treatment, a hardness value was estimated for an equivalent 97% cold-work level. The changes in these hardness values were compared to the changes observed over the 80 h duration of the McGeary et al. study. These comparisons are illustrated in Fig. 8, a plot of the relative change in VHN, as a percent, versus time. The relative change in VHN was calculated by dividing any change in hardness experienced after annealing at the given temperatures by the total change in hardness between the cold-worked (to 97%) zirconium and the annealed zirconium for each study. Normalizing the data in this manner allowed a direct comparison with the data reported by McGeary et al., since differences in composition, grain size, and texture between the studies all affect the (baseline) hardness. As illustrated in Fig. 8, the observed softening in the current study at 200 and 300°C is fairly consistent with the results obtained by McGeary and Lustman [2], who observed softening apparently by recovery rather than recrystallization.

It should be mentioned that the deformation mechanisms involved in the cold-rolling may not be identical to that of shot peening. The surface layer of the shot-peened zirconium exhibited substantial mechanical twinning. The

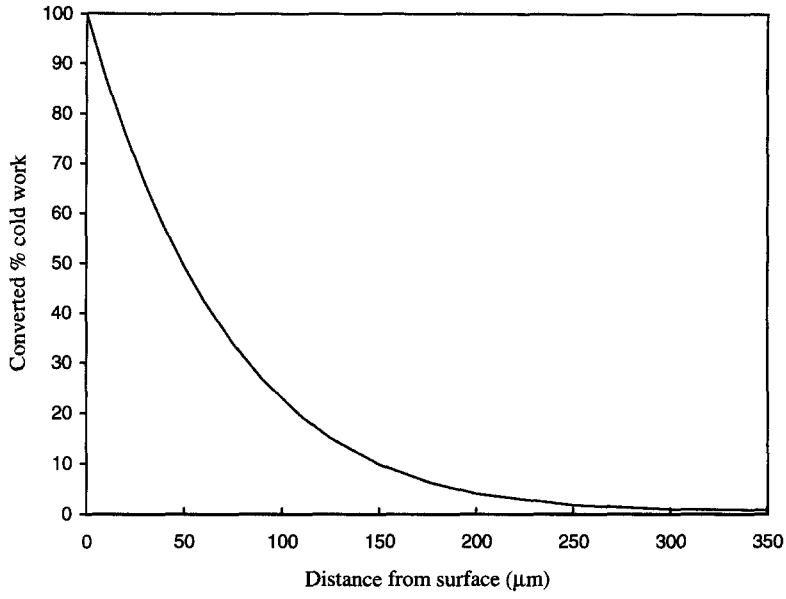

Fig. 7. Plot of cold-work versus distance from the shot-peened surface.

grains throughout the cold-rolled zirconium exhibited much less twinning. There were also differences in the grain morphology as evidenced by greater grain elongation with rolling than with shot peening. Deformation is generally 'unidirectional' with rolling, whereas some of the hardening associated with shot peening may involve different or

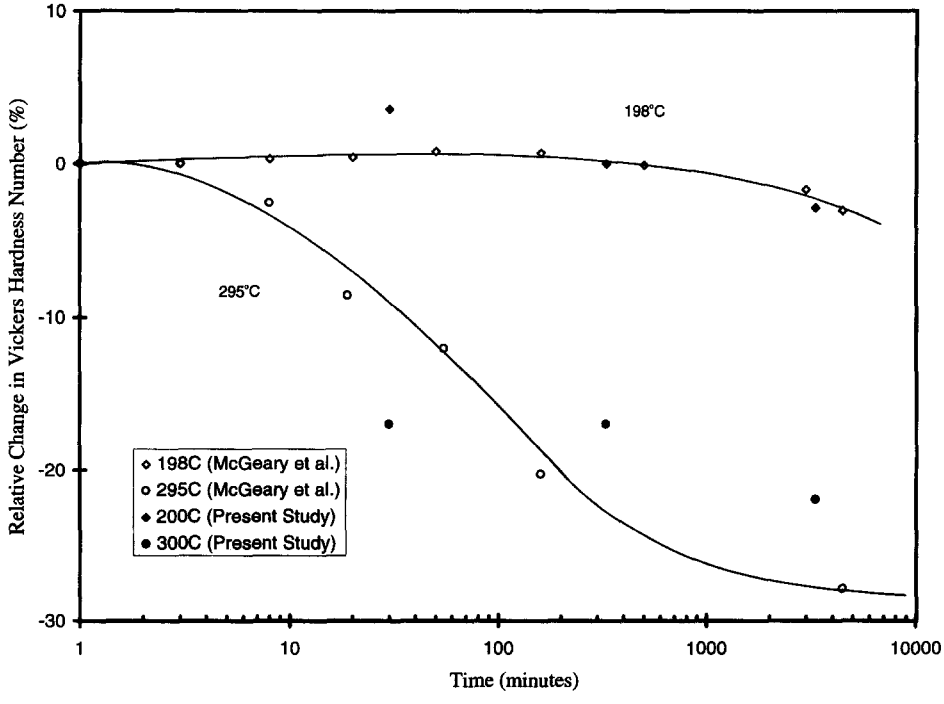

Fig. 8. Comparison of the recovery of the 97% cold-worked 'level' in the shot-peened specimens of the current study to the 97% cold-worked study by McGeary and Lustman [2].

even reversals of the direction of plasticity. This may explain less grain elongation with shot peening. Twinning may be activated at high strain rates, while a 'conventional' dislocation slip mechanism may predominate at lower strain rates. It is possible then that the relatively high deformation rates associated with shot peening ($\sim 10^4$ s^{-1}) activated a twinning mechanism, while the more modest deformation rate experienced in rolling did not. Still, in order to compare the results from this study to those from previous studies, the hardness profile resulting from shot peening must be converted to percentages of cold-work. The previously outlined procedure appeared to be the most reliable method.

3.4. Microscopy

TEM micrographs taken in the initial (pre-heat treated) shot-peened condition at the surface (within 10 μm), in the un-peened region (over 300 μm from the surface), after 0.5 h at 300°C and 2790 h at 300°C both at the surface (within 10 μm), are all shown in Fig. 9. These micrographs illustrate that the decreases in hardness with depth in the un-heat-treated shot-peened specimen and with time at 300°C are all associated with a decrease in the dislocation density. The dislocation density at the surface of the shot-peened layer was estimated as about 1.05×10^{11} cm/cm^3. It decreased to about 1.56×10^{10} cm/cm^3 after 0.5 h at 300°C and 1.2×10^{10} cm/cm^3 after 2790 h at 300°C. The density towards the interior (over 300 μm from the surface) is about 3.2×10^9 cm/cm^3. Microtwins were not shown, since differences in the dislocation density were emphasized.

No changes in grain size or morphology were observed after elevated temperature exposures using polarized light optical metallography. This indicates that the hardness changes that occurred were a result of classic recovery and not recrystallization or grain growth. Fig. 10 shows micrographs of the shot-peened surface region using polarized

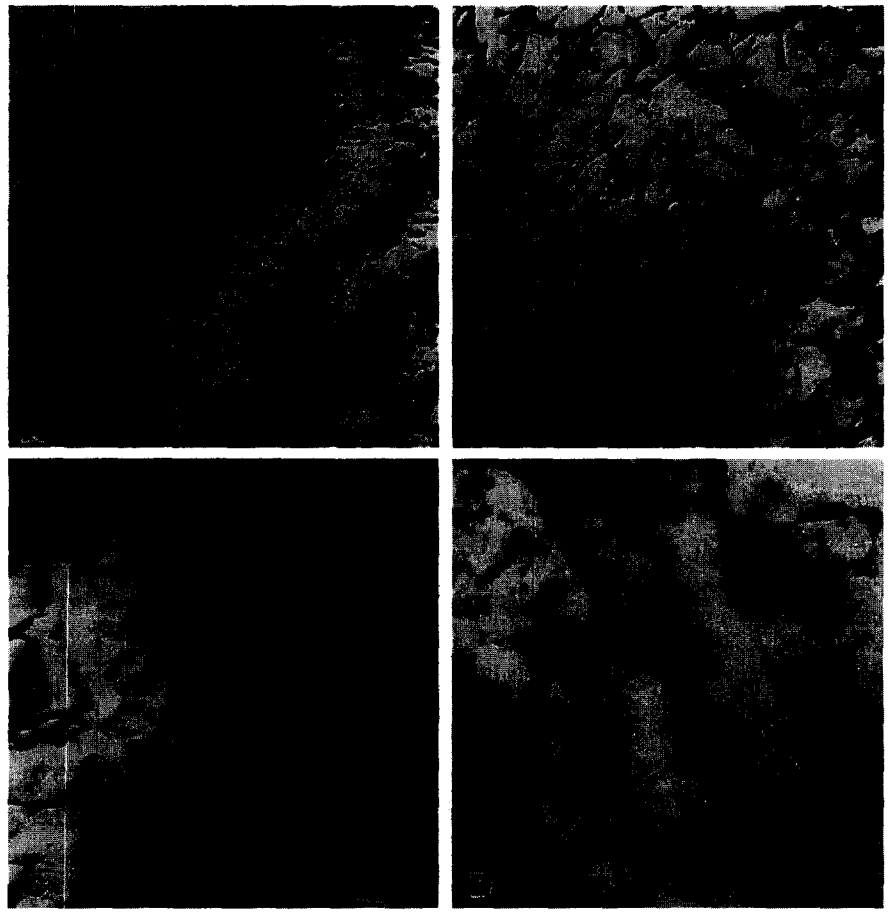

Fig. 9. TEM micrographs of (a) the initial shot-peened condition at the surface, (b) surface (within 10 μm) after 0.5 h at 300°C, (c) surface after 2790 h at 300°C, and (d) in the interior, unaffected by deformation.

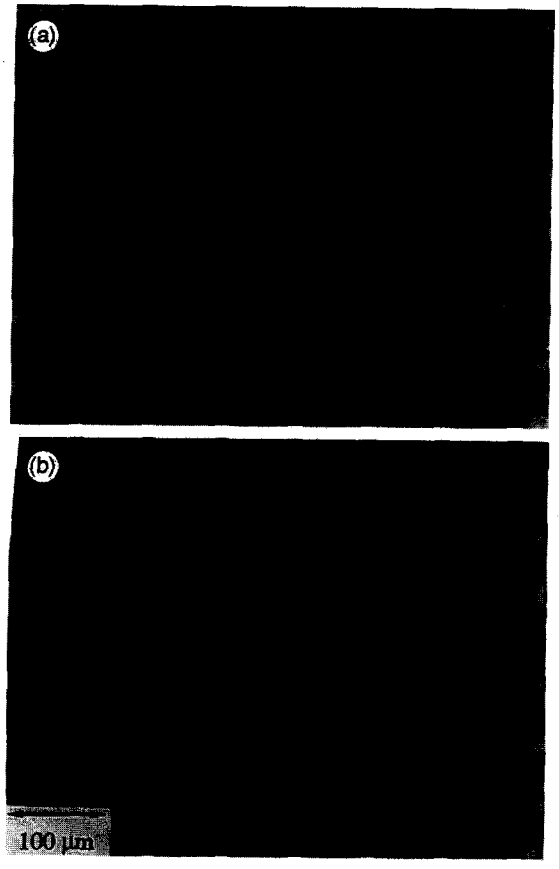

Fig. 10. Optical micrographs of shot-peened surface region in (a) the initial condition and (b) after 2790 h at 300°C.

light in the initial (pre-annealed) condition and after 2790 h at 300°C.

4. Discussion

4.1. Thermal stability study

Softening may occur principally by two restoration mechanisms: recrystallization and recovery. Recrystallization is the nucleation and growth of new grains involving motion of grain boundaries, leading to decreased dislocation densities. Recovery, which we observed in this study, may consist of several mechanisms. First, the highly dense dislocations can change their configuration from a tangled state to a polygonized condition. Polygonization in deformed single crystal zirconium has been observed by Dedo et al. [3] at temperatures as low as 300°C. Second, there may be some recovery of point defects, and third, some annihilation of dislocations may occur, decreasing the total dislocation density.

Our observations that recovery occurred about two orders of magnitude more quickly at 300°C than at 200°C is consistent with the results of McGeary and Lustman [2] (see Fig. 8). In the McGeary et al. study, the same reduction in hardness occurred after 8 min at 295°C as was experienced after about 4500 min at 198°C. They concluded a recovery-type mechanism at these temperatures for this level of cold-work.

For the same amount of recovery (same reduction in hardness) at two different temperatures,

$$t_1 M e^{-Q/kT_1} = t_2 M e^{-Q/kT_2}, \tag{1}$$

where t is the time required to recover a given fraction of the hardness, M is a constant, and Q is the activation energy for recovery of zirconium. M is associated with a fixed amount of softening and, therefore,

$$\frac{t_1}{t_2} = e^{-Q/k((1/T_2)-(1/T_1))}. \tag{2}$$

Solving for the activation energy,

$$Q = \frac{k}{(1/T_1)-(1/T_2)} \ln \frac{t_1}{t_2} \tag{3}$$

yields a value of 104 kJ/mol. The activation energies for the lattice self-diffusion in zirconium have been reported between 92 and 310 kJ/mol [17–22] for temperatures ranging from 506 to 860°C (no self-diffusion data below 506°C have been located). Although the reason for the variability is not clear, it has been suggested that the lower values (e.g., 92–110 kJ/mol) may actually reflect short circuit diffusion along dislocation lines, even in annealed zirconium [23–26]. The activation energy for self-diffusion in the shot-peened zirconium at 200 to 300°C may be that of dislocation pipe diffusion, as the activation energy of about 100 kJ/mol calculated in this study is in good agreement with the lower activation energies of 92 kJ/mol [17,18] and 110 kJ/mol [19] reported for self-diffusion. Thus, a diffusion controlled process such as dislocation climb (necessary for recovery processes such as edge dislocation annihilation and polygonization) may be associated with the observed softening or recovery in this study. The activation energy in the present study may also be decreased by the very fine grain size (about 30 μm) and an increase or supersaturation of vacancies (above the equilibrium concentration) with the substantial cold-work associated with shot-peening.

5. Conclusion

(1) Significant softening of the surface of the shot-peened zirconium was observed after annealing at both 200 and 300°C.

(2) Transmission electron microscopy indicated that the decrease in hardness with time at 300°C is associated with a decrease in dislocation density, without a change in grain size or morphology. The apparent activation energy for the

softening correlated with the activation energy that would be expected for short-circuit self-diffusion.

(3) Thus, the softening appears to be due to static recovery, consistent with some earlier studies of cold-rolled zirconium.

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