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Solid-state foaming of titanium by hydrogen-induced internal-stress superplasticity

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Abstract

Titanium foam was produced by expansion of pressurized argon-filled pores within titanium at 860 °C. Alternating atmospheres of pure Ar and Ar/4% H_2 resulted in cyclical hydrogen alloying/de-alloying. The associated internal-stress plasticity enhanced pore expansion, volume fraction and size, as compared to foams expanding by creep without composition change.
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1. Introduction

Solid-state expansion of gas within metals is a novel technique for fabricating metallic foams, which has been demonstrated for Ti–6Al–4V [1–6] and unalloyed Ti [7,8]. The first step of this foaming process consists of hot isostatic pressing (HIPing) metallic powder in the presence of argon gas. The resulting compacted material exhibits low fractions (typically <1%) of entrapped argon-filled pores, which are small in size (<25 μm) and have a high internal pressure. On annealing at ambient pressure and elevated temperatures, the pressurized pores expand by creep of the surrounding metal: Kearns et al. [1,2,9] reported porosities of up to ~40% after heat treatments at very high temperatures (1250 °C) for long durations (several days).

Recently, we demonstrated that the slow creep deformation of the matrix surrounding the high-pressure argon pores could be enhanced by inducing transformation superplasticity in the metal [7,8]. This deformation mechanism is active in polymorphic materials, (e.g., titanium, Ti–6Al–4V, and many other polymorphic metals, alloys and composites, as reviewed in Refs. [10–12]), and relies on internal mismatch strains produced by the density difference between the two allotropic phases coexisting during the phase transformation. This mismatch is accommodated by the development of creep strains, which can be biased in the direction of an externally applied stress, resulting in rapid Newtonian flow in the biasing direction. At the end of the phase transformation, the material

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has acquired an increment of permanent strain in the biasing direction. By repeatedly triggering the phase transformation, these strain increments can be accumulated to tensile elongations well in excess of 100% without fracture or cavitation.

In our recent work on solid-state foaming of titanium [8], we used thermal cycling to repeatedly induce the phase transformation, and pressurized Ar inside the pores provided the biasing stress; under these superplastic conditions we reported faster foaming rates and higher maximal porosities than under isothermal, creep conditions [8]. In addition, in uniaxial tension we have recently reported that transformation superplasticity can occur isothermally during chemical cycling, e.g., by alloying and de-alloying hydrogen into solid specimens of titanium or Ti–6Al–4V [13–15]. Since chemical cycling produces both transformation and chemical swelling mismatch strains [13–15], the deformation mechanism during this process is best referred to as *internal-stress superplasticity*. In the present paper, we investigate foaming of CP-Ti under internal-stress superplasticity conditions, using chemical cycling with hydrogen at constant temperature to induce transformation and swelling mismatch, and the internal gas pressure of the pores as the biasing stress. We compare final porosities and foaming rates with those obtained for thermally induced transformation superplastic foaming of hydrogen-free titanium, reported in Refs. [7,8].

2. Experimental procedures

Spherical CP-Ti powders (from Starmet, Concord, MA) were used, with median size of ~130 μm and the following impurities (wt.%): 0.14% O, 0.14% Fe, 0.01% N, 0.01% C, and <0.01% H. The powders were packed to approximately 70% density by applying uniaxial pressure in a steel can, which was subsequently evacuated, back-filled with 0.33 MPa of Ar and sealed. The sealed can was densified by HIPing at 890 °C and 100 MPa for 125 min at UltraClad (Andover, MA).

One specimen with ca. $6.7\times3\times2.8$ mm dimensions and two specimens with ca. $6.7\times2.8\times1.8$ mm dimensions were cut by electro-discharge machining from the HIPed billets and were subsequently polished to remove any surface damage due to the machining process. One specimen of each size was then foamed by chemical cycling at 860 °C in a custom-built furnace described in Ref. [16]. The atmosphere consisted of flowing 99.999% pure Ar gas with or without 3.66 vol% H_2 at ambient pressure, corresponding to equilibrium hydrogen compositions of 0 or 13.7 at.% in titanium [17], the latter concentration being well within the β-Ti phase field. Each chemical alloying and de-alloying half-cycle step was 15 min in duration to ensure complete saturation and degassing of the specimen, respectively. One control specimen was annealed at 860 °C under a flowing atmosphere of Ar/3.66 vol% H_2, i.e., in the fully alloyed condition (13.7 at.% H). All experiments were interrupted by excursions to room temperature at 7.5 h intervals (corresponding to 15 alloying/de-alloying cycles for cyclical experiments), to determine their density by the Archimedes method in distilled water. For these measurements the surface of each specimen was sealed with a thin layer of vacuum grease to prevent water infiltration of open porosity, thus yielding direct measurement of the total porosity (consisting of open and closed porosity) with an estimated error of ±0.1% (±0.0038 g/cm^3). At the end of the foaming experiments, the two smaller specimens (foamed under chemical cycling conditions and under Ar, respectively) were exposed to 25–30 keV X-rays with 1200–1400 ms exposure times at the Advanced Photon Source (Argonne National Laboratory), using a synchrotron X-ray beam. Images from the phosphorescent screen were collected using a 1300×1300 bit CCD camera while each specimen was rotated 180°. A three-dimensional (3-D) image was created using custom reconstruction software.

3. Results

As illustrated in Fig. 1, initial pores in the HIPed billets were located at the interface between powder particles in the original preform and were non-spherical, as also reported in Refs. [1,2,9] for Ti–6Al–4V consolidated under somewhat different conditions. Initial average pore size was roughly

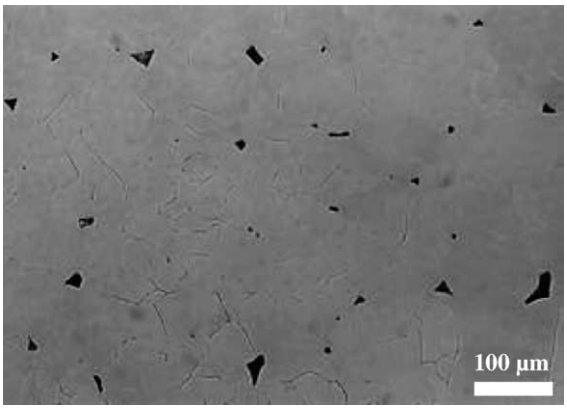

Fig. 1. Optical micrographs of as-HIPed CP-Ti showing irregularly shaped Ar-filled pores at interstices of (non-visible) prior powder particles.

25 μm and the initial porosity was 0.65%. Matrix grain size was approximately 50 μm, much larger than the critical value of 10 μm below which structural superplasticity is active [11].

The average specimen porosity as a function of annealing time is shown in Fig. 2 under constant composition (isochemical conditions at 13.7 at.% H) and under chemical-cycling conditions (0–13.7 at.% H). This figure demonstrates that chemical cycling results in a faster foaming rate and a higher

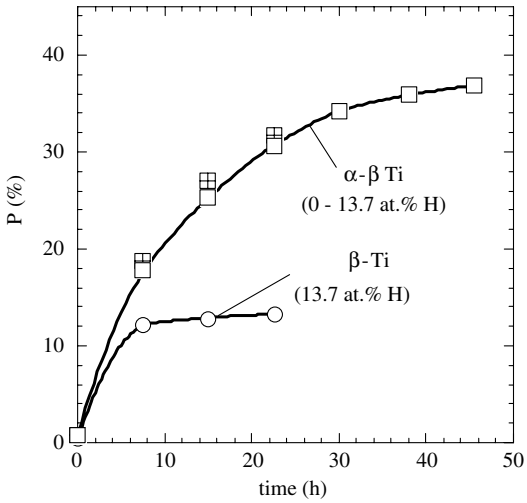

Fig. 2. Porosity as a function of time at 860 °C for isochemical and chemically cycled experiments. Crossed (larger specimen) and blanks squares (smaller specimen) distinguish between two distinct chemically cycled specimens.

terminal porosity (38% vs. 12%) as compared to isochemical foaming. Pore growth is exhausted earlier for the isochemical than for chemical cycling foaming (ca. 8 vs. 45 h).

Fig. 3(a) and (b) show the pore structure as obtained by X-ray microtomography at the end of foaming experiments (48 h of chemical cycling in Fig. 3(a) and 22.5 h of isochemical foaming in Fig. 3(b)). In both cases, pores are equiaxed and rounded. However, the pore size for the specimen subjected to cyclic hydrogen alloying/de-alloying (up to 250 μm, Fig. 3(a)) is much larger than for the isochemically foamed samples (ca. 100 μm, Fig. 3(b)).

4. Discussion

For uniaxial experiments on dense specimens (performed at 860 °C under a stress of 1.36 MPa), creep of β-Ti (with 13.7 at.% H) has been reported to be slower by a factor 15 than under chemical cycling conditions (0–13.7 at.% H, 10 min cycles) [13]. This is in qualitative agreement with Fig. 2, showing that the overall foaming rate is significantly higher under chemical cycling conditions than under constant composition conditions. Furthermore, cycled specimens also exhibit much higher maximal porosity, which is controlled either by pore wall rupture and escape of the argon out of the foam, or by the drop in Ar pressure associated with pore expansion. The pores shown in Fig. 3(a) and (b) are much larger for the chemically cycled case than under isochemical conditions. This is consistent with earlier work on CP-Ti [7,8] and Ti–6Al–4V [7], which showed that for thermally induced transformation superplasticity, pore walls can be deformed to larger strains before pore-wall fracture occurs, as compared to foaming under creeping conditions. Even when comparing chemical cycling experiments to β-Ti isothermal experiments at a much higher temperature of 960 °C (with 0 at.% H) [8], as shown in Fig. 4(a), the terminal porosity is higher for the chemically cycled specimens, as expected if internal-stress plasticity is operational.

Fig. 4(a) and (b) compare foaming kinetics for specimens from the same HIPed billet produced by

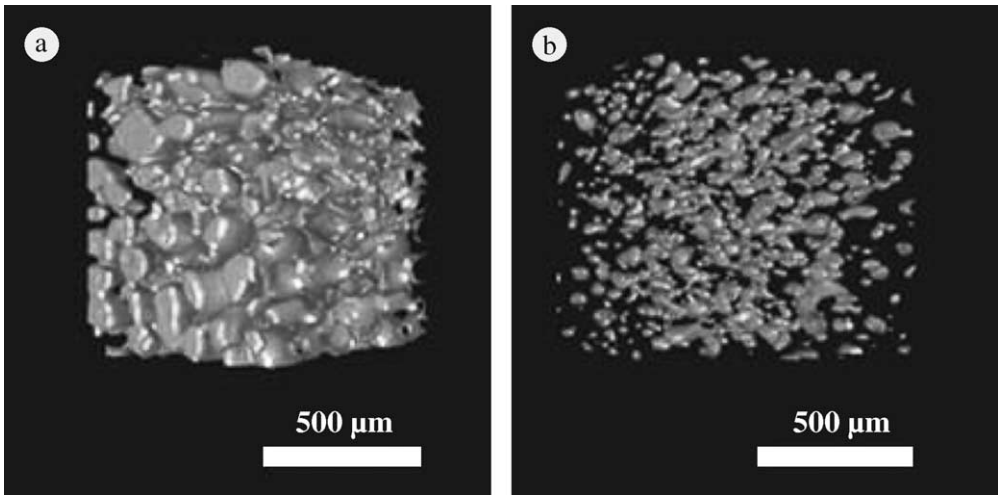

Fig. 3. 3-D tomographs of CP-Ti foamed (a) by chemical cycling between 0 and 13.7 at.% H for 45 h with 38% porosity and (b) isochemically at 860 °C for 22.5 h with 12% porosity. Gray represents the surface of the pores and the metal is not shown.

thermal cycling [7,8] and by chemical cycling (present study). Fig. 4(a) shows clearly that foaming is much slower in the latter case, as expected from the longer duration of the chemical cycle (30 min) as compared to that of the temperature cycle (4 min). However, if these data are re-plotted as a function of the number of cycles as in Fig. 4(b), then very similar foaming kinetics are found for chemical and thermal cycling, illustrating that in both cases pore expansion is controlled by internal-stress plasticity, not by creep. For fully dense specimens deformed uniaxially, Dunand and Zwigl [15] found that chemical cycling produced a larger per-cycle strain (by a factor of ~3) than thermal cycling for a given uniaxial stress. The data shown in Fig. 4(b) however show that the

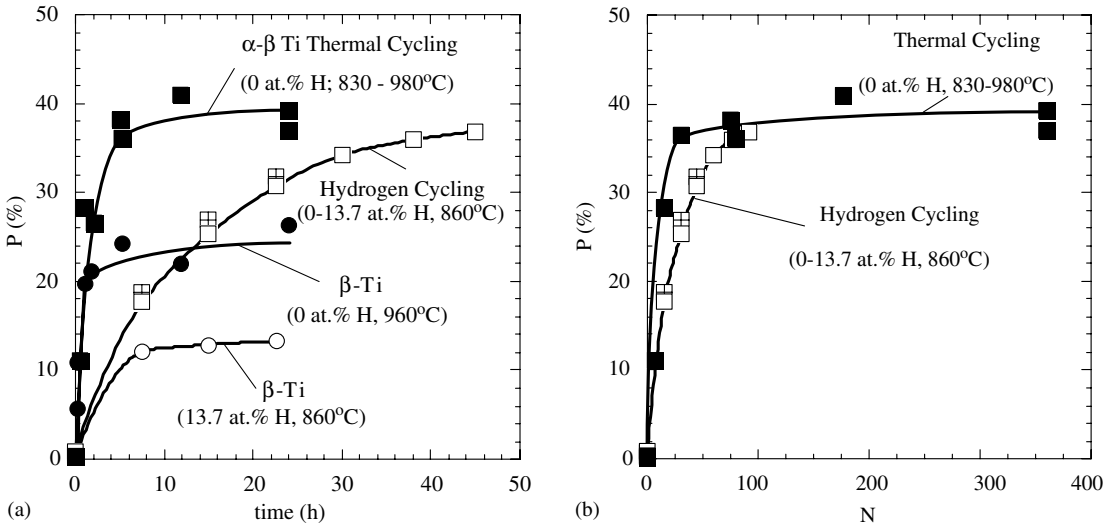

Fig. 4. Porosity as a function of (a) time, for chemical cycling, thermal cycling, and isothermal and isochemical experiments (b) cycle number, for chemical cycling and thermal cycling experiments. Data for thermal cycling is taken from Ref. [8].

porosity gain per cycle is somewhat higher for thermal cycling. However, direct comparison between uniaxial testing of non-porous specimens and foaming of porous specimens is impossible, due to the complicating effect of the pores, which affect the overall transport of hydrogen in and out of the specimen; depending on the ease of hydrogen absorption/desorption at internal pore surfaces, pores may enhance hydrogen transport by vapor-phase transport within them, or act as obstacles for the solid-state hydrogen diffusion process. Furthermore, during foaming, the stress state is multiaxial and varies both with position (within the porous material) and time (as pores expand). Additionally, we cannot exclude the possibility of slight differences in original porosity between specimens from the same billet, due to powder settling prior to and during HIPing, which have been shown to affect foaming kinetics and terminal porosities [8].

5. Conclusions

The solid-state foaming of titanium by the expansion of high-pressure argon bubbles using transformation superplasticity was studied. The phase transformation of titanium was induced by chemical cycling (through cyclic alloying and dealloying with hydrogen), inducing internal mismatch strains in the matrix, which were biased by the pore pressure. It was found that:

1. Chemical cycling improves foaming by increasing both the foaming kinetics and terminal porosity, when compared to isochemical foaming of β-Ti at 860 °C.
2. Isothermal foaming of β-Ti at 860 °C (with hydrogen) or 960 °C (without hydrogen) leads to lower terminal porosities than α/β-Ti chemical cycling at 860 °C.
3. Foaming by chemical cycling was slower than by thermal cycling because of lower cycling frequency. However, similar foaming kinetics are observed when foaming is considered on a per-cycle basis. Additionally, similar terminal porosities are found for either chemical or thermal cycling foaming.

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