

# Communications

## Hydrogen-Induced Internal-Stress Plasticity in Titanium

DAVID C. DUNAND and PETER ZWIGL

Internal-stress plasticity is a deformation mechanism resulting from the biasing of internal mismatch stresses by an external stress.<sup>[1]</sup> These internal stresses can be produced by a temperature change in materials with grains (or phases) exhibiting different thermal expansion coefficient<sup>[2]</sup> or different density during a phase transformation<sup>[3]</sup>; alternate sources of internal stresses include compressibility mismatch during pressure changes<sup>[4]</sup> and swelling mismatch during irradiation.<sup>[5]</sup> The most common type of mismatch generation is thermal, as it easily lends itself to cycling during which tensile strains well in excess of 100 pct can be accumulated; this phenomenon is known as internal-stress superplasticity.<sup>[1]</sup>

The purpose of the present article is to report, for the first time, internal-stress plasticity where internal stresses are induced by a reversible change of chemical composition (at constant temperature and pressure) rather than a change of temperature or pressure (at constant composition), as illustrated in Figure 1. We use the Ti-H system to demonstrate this effect, because hydrogen diffuses rapidly in and out of titanium where it produces mismatch strains both directly (by lattice swelling in the presence of concentration gradients) and indirectly (by inducing the hcp ( $\alpha$ -Ti) to bcc ( $\beta$ -Ti) transformation), as demonstrated in a recent study of hydrogen-induced ratchetting.<sup>[6]</sup> We note that this chemically induced internal-stress plasticity is fundamentally different from thermochemical processing of titanium<sup>[7]</sup> where hydrogen alloying is used to produce a weaker, more easily workable  $\beta$ -Ti phase, and where internal stresses are unimportant.

Titanium plates (99.7 pct pure, from Alpha Aesar, MA) were machined into dog-bone specimens with a gage 28 to 52 mm in length, 5.4 to 6.0 mm in width, and 2 mm in thickness. Specimens were tested in a low-stress creep apparatus described earlier,<sup>[8]</sup> modified to allow for a gas atmosphere flowing at a rate of 1.22 L/min, which could be changed from Ar (99.999 pct pure) to an Ar/4 vol pct H<sub>2</sub> mixture. This 4.1 kPa hydrogen partial pressure corresponds to an equilibrium hydrogen concentration in titanium well within the  $\beta$ -Ti field (Figure 1). The specimen strain was continuously measured at the cold end of the load train and the temperature was maintained at a constant value of 805 °C  $\pm$  2 °C or 860 °C  $\pm$  2 °C by a thermocouple contacting the gage section or the pull head.

Figure 2 shows the creep rate as a function of the applied stress for hydrogen-free  $\alpha$ -Ti and for fully hydrogenated  $\beta$ -Ti at temperatures of 805 °C and 860 °C. The stress exponents

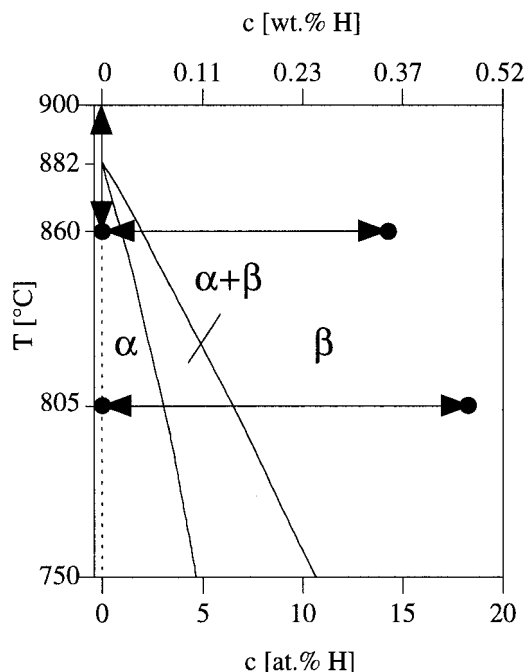


Fig. 1—Titanium-hydrogen phase diagram<sup>[14]</sup> showing chemical cycles used in the present study of chemically induced internal-stress plasticity at 805 or 860 °C ( $p_{H_2} = 0 \leftrightarrow 4.1$  kPa) as well as typical thermal cycles used in the literature for thermally induced internal-stress plasticity in hydrogen-free Ti ( $T = 860 \leftrightarrow 900$  °C).

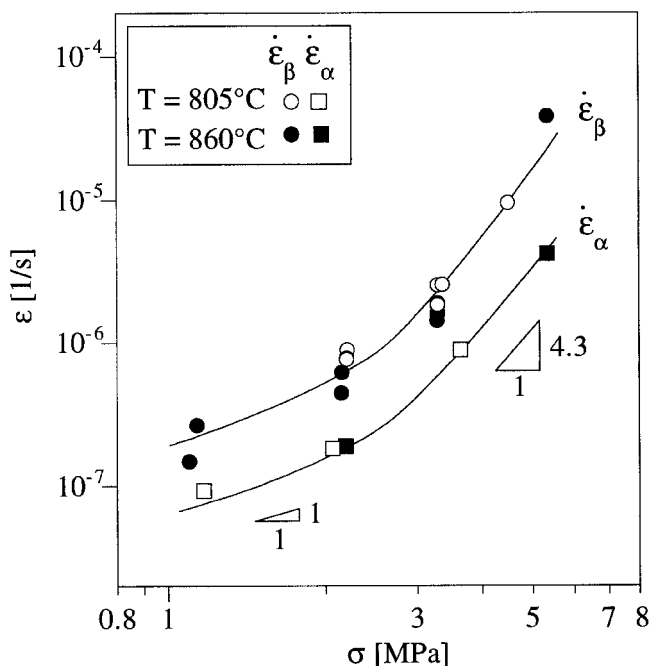


Fig. 2—Isothermal creep rate at 805 °C and 860 °C for hydrogen-free  $\alpha$ -Ti and fully hydrogenated  $\beta$ -Ti.

DAVID C. DUNAND, Associate Professor, is with the Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208. PETER ZWIGL, formerly Graduate Research Assistant, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, is Sr. Quality Engineer with Intel Corp, Folsom, CA 95630.

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in Figure 2 tend toward values of  $n \approx 1$  at low stresses and  $n \approx 4.3$  at high stresses, in good agreement with the reported stress exponents of pure titanium in the diffusional and dislocation creep regimes.<sup>[9]</sup> The transition between these mechanisms is in the range of 1.5 to 3.5 MPa, in rough agreement with the calculated value of about 1 MPa for a 20  $\mu$ m grain

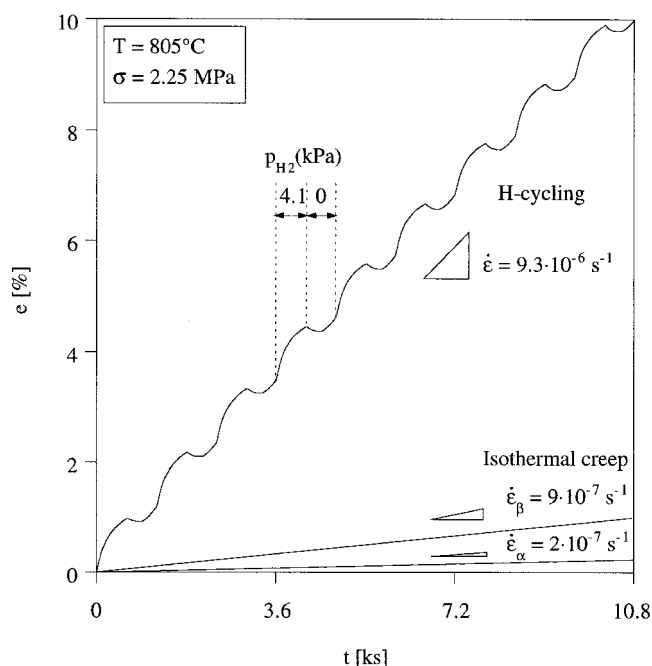


Fig. 3—Strain history at constant stress (2.25 MPa) and temperature (805 °C) recorded for titanium subjected to nine chemical cycles ( $\alpha/\beta$  cycling,  $p_{\text{H}_2} = 0 \leftrightarrow 4.1$  kPa, and  $v = 3 \text{ h}^{-1}$ ) and calculated from Fig. 2 for uncycled, hydrogenated  $\beta$ -Ti ( $p_{\text{H}_2} = 4.1$  kPa) and uncycled, hydrogen-free  $\alpha$ -Ti ( $p_{\text{H}_2} = 0$  kPa). The two hydrogen charging and discharging segments are shown in the fourth chemical cycle.

size.<sup>[9]</sup> A doubling in creep rate from 805 °C to 860 °C is expected from the bulk diffusion activation energy<sup>[9]</sup> but is not clearly visible in Figure 2, possibly because of minor differences in grain size or dislocation densities between specimens. However, as expected from the low creep resistance of hydrogen-free bcc  $\beta$ -Ti above 882 °C,<sup>[9]</sup> hydrogenated bcc  $\beta$ -Ti crept 3 to 5 times faster than hydrogen-free hcp  $\alpha$ -Ti tested at the same temperature.

Figure 3 shows the creep curve of a specimen subjected to nine consecutive hydrogen cycles ( $p_{\text{H}_2} = 0 \leftrightarrow 4.1$  kPa) at constant applied stress (2.25 MPa) and temperature (805 °C). The cyclic oscillations in the creep curve correspond to reversible lattice strains from hydrogen dissolution and titanium transformation. A reproducible plastic strain increment of 1.1 pct was recorded after each cycle, corresponding to an average strain rate of  $9.3 \cdot 10^{-6} \text{ s}^{-1}$  for the experimental cycle frequency of  $3.0 \text{ h}^{-1}$ . Also illustrated in Figure 3 are the creep curves for hydrogen-free  $\alpha$ -Ti and hydrogenated  $\beta$ -Ti at 805 °C and 2.25 MPa constructed from creep data in Figure 2. It appears from Figure 3 that hydrogen cycling leads to an average deformation rate that is 10 times higher than creep in the weak, hydrogenated  $\beta$ -Ti phase, even though the cycled specimen was in the slower creeping  $\alpha$ -Ti phase during part of the cycles. The most likely explanation for this result is that internal-stress plasticity is activated during chemical cycling, as observed in titanium subjected to temperature cycling.<sup>[3,10]</sup> Two other possible explanations for the enhancement shown in Figure 3 cannot be retained upon further analysis. First, temperature fluctuations due to hydrogen dissolution and phase transformation could increase the average strain rate; reproducible temperature changes of  $\pm 3$  K were indeed recorded after each change

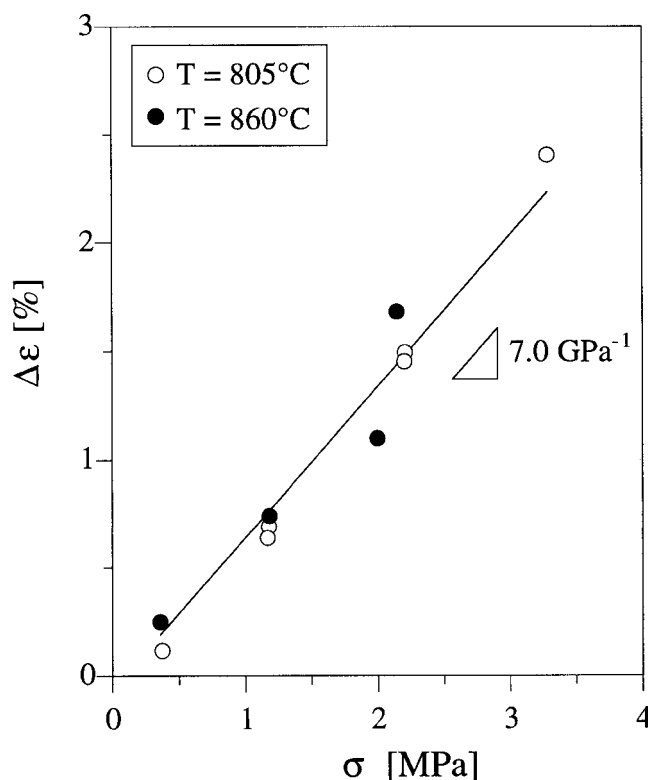


Fig. 4—Stress dependence of creep-corrected strain increments accumulated after a full chemical cycle ( $p_{\text{H}_2} = 0 \leftrightarrow 4.1$  kPa, and  $v \leq 1.35 \text{ h}^{-1}$ ) at 805 °C and 860 °C.

of atmosphere, but their magnitude is too small to have any measurable effect on the deformation rate. Second, hydrogen-induced transformation may result in finer grains and/or lower dislocation densities and thus a higher deformation rate in the diffusional and dislocation creep regimes; grain growth and dislocation multiplication, however, are expected to be rapid in  $\beta$ -Ti, so this “primary creep” effect would be short lived and unlikely to contribute significantly to the strain difference of 9 pct between cycled and uncycled specimens observed in Figure 3.

Figure 4 shows the stress dependence of the strain increment accumulated during chemical cycling. Long cycle times ( $v \leq 1.35 \text{ h}^{-1}$ ) were used to ensure that complete hydrogen alloying or dealloying had occurred (cylinders 3.2 mm in diameter were found to be fully hydrogenated at 860 °C in Ar-4 vol pct  $\text{H}_2$  after only 600 seconds, *i.e.*,  $v = 3 \text{ h}^{-1}$ <sup>[6]</sup>). A creep correction was applied to the data in Figure 4, by subtracting from the experimental strain increment after each half-cycle (with and without hydrogen) a creep contribution taken as the creep rate (measured at the end of the half-cycle) multiplied by the half-cycle time. The resulting strain increments are then, to a good approximation, only due to internal-stress plasticity. The fact that these strain increments are non-zero and can be well fitted by a straight line (leading to an average stress exponent  $n = 1$  under steady-state cycling conditions shown in Figure 3) confirms that internal-stress plasticity is the dominant deformation mechanism. Indeed, all theoretical models for internal stress plasticity induced by thermal-expansion mismatch or by allotropic mismatch (*e.g.*, References 3, 11, and 12) predict

an average stress exponent of unity at low stresses. On the other hand, creep at constant composition occurs by both diffusional and dislocation mechanisms in the range 2 to 3 MPa with an average stress exponent  $n \approx 2$  (Figure 2), which clearly does not fit the data in Figure 4. Finally, the lack of difference for transformation-plasticity strains at 805 °C and 860 °C in Figure 4 may indicate that internal mismatch stresses due to lattice swelling and phase transformation are similar at both temperatures. The contributions of these mismatch-producing mechanisms in the Ti-H system will be modeled in future publications.

In conclusion, we have demonstrated, for the first time, that internal-stress plasticity can be induced by a reversible change in composition which produces internal mismatch by lattice swelling and phase transformation at constant temperature. For externally stressed titanium subjected to cyclic alloying/dealloying with hydrogen at 805 °C, uniaxial strains per cycle as high as 2.3 pct were measured. This phenomenon could be exploited as a superplastic forming process (*e.g.*, for metals such as Ti, Zr, Nb, and Pd, which show high hydrogen swelling and/or hydrogen-induced allotropic transformation or hydride precipitation<sup>[13]</sup>), but may be undesirable in some other cases (*e.g.*, in hydrogen-storage materials subjected to multiple absorption-desorption cycles).

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## Preparation of Ti-Al Intermetallic Compounds by Spark Plasma Sintering

BINGCHU MEI and Y. MIYAMOTO

Titanium aluminides based on  $\text{Ti}_3\text{Al}(\alpha_2)$  and  $\text{TiAl}(\gamma)$  stoichiometries have excellent potential to become some of the most important aerospace materials because of their high refractory nature, low densities, high specific strength, high melting temperature, and environmental resistance at elevated temperature.<sup>[1,2,3]</sup> There are three main phases ( $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$ , and  $\text{TiAl}_3$ ) in the Ti-Al binary system.<sup>[2]</sup> While various  $\alpha_2$  alloys based on  $\text{Ti}_3\text{Al}$  possess reasonable room-temperature ductility, their high-temperature applications are limited due to loss of strength, excessive oxidation, and susceptibility to hydrogen permeation. Increasing the aluminum content to produce  $\gamma$ -TiAl alloys can improve all of these properties but with the attendant penalty of reducing room-temperature ductility and toughness,<sup>[2]</sup> that is, the contents of  $\alpha_2$ - $\text{Ti}_3\text{Al}$  relative to  $\gamma$ -TiAl are important as regards the properties of Ti-Al intermetallic compounds. Therefore, through microstructure control, some of their properties can be improved.

The conventional melting or casting route of fabrication of titanium aluminides is unfavorable to improving their properties owing to segregation, resulting in many alternative techniques for producing these intermetallics being sought. One alternative method is spark plasma sintering (SPS), which is receiving increased attention.<sup>[4,5]</sup> The process diagram of this method is schematically shown in Figure 1. This method makes possible sintering and sinter bonding at a low temperature for a short period by charging the intervals

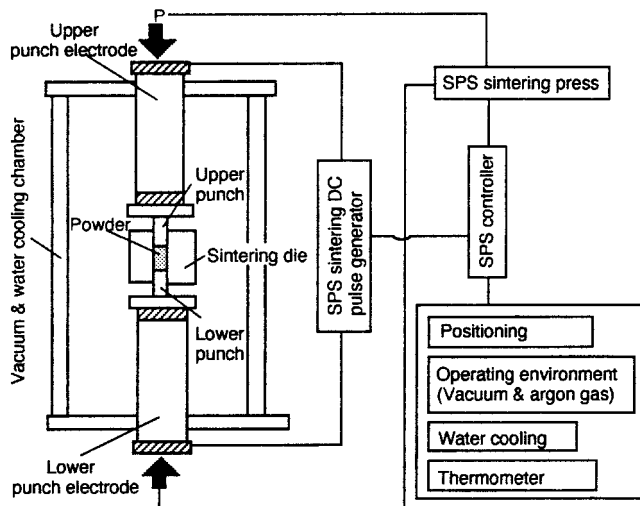


Fig. 1—Schematic diagram of the SPS sintering system.

BINGCHU MEI, Professor, is with the State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, People's Republic of China. Y. MIYAMOTO, Professor, is with the Joining and Welding Research Institute, Osaka University, Osaka 567, Japan.

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