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Enhancement of Activation and Hydrogen Storage Kinetics of TiFe(Mn) Using High-Pressure Sliding (HPS) Process

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A titanium–iron intermetallic with minor addition of manganese (TiFe$_{0.7}$Mn$_{0.3}$) was processed by severe plastic deformation through high-pressure sliding (HPS). A rectangular strip sample was embedded in stainless steel and strained under a pressure of 4 GPa at room temperature. The hydrogen storage kinetics and activation of the HPS-processed sample were significantly enhanced in comparison with the as-received ingot without the HPS processing.   [doi:10.2320/matertrans.MT-MF2022059]

1. Introduction

It is well known that severe plastic deformation (SPD) through the process of high-pressure torsion (HPT)[1–3] is effective for significant grain refinement.[4,5] The HPT process is applicable to many metallic materials[2,6,7] including hard-to-deform materials such as intermetallics,[8–12] ceramics[13–17] and semiconductors.[18–29] This broad range of applications arises from the constraint of the sample under high pressure during straining. Alternatively, the high-pressure sliding (HPS) process is available,[30–33] where strain is imparted by reciprocation of the anvils with respect to the sample as illustrated in Fig. 1,[33] while the strain is induced by the rotation of the anvils in the HPT process. Because of the operation under high pressure as in the HPT process, the HPS process is also applicable to hard-to-deform materials. In fact, a Ni-based superalloy (Inconel 718) was processed by the HPS and nanograined refinement was successfully achieved to produce superplasticity when the processed sample was tested at elevated temperatures.[32,34]

In this study, the HPS process is applied, for the first time, to a titanium–iron (TiFe) intermetallic to improve its hydrogen storage kinetics and activation. This study is conducted as a follow-up of the earlier ones using the HPT process,[35–37] where the TiFe was well activated for hydrogenation kinetics. Because the HPS process utilizes a sample form not only of sheets[30–34] but also of rods[38–41] and pipes,[42] it is anticipated[43] that the practical application of the TiFe is promoted in comparison with the use of the HPT process where the sample form is rather restricted to disks.

Regarding the TiFe intermetallic, it is well known as a good candidate for hydrogen storage materials and its hydrogenation is possible at room temperature with good cycling capability.[44–49] Although its gravimetric storage capacity (∼1.9 wt.%) is rather low with respect to the
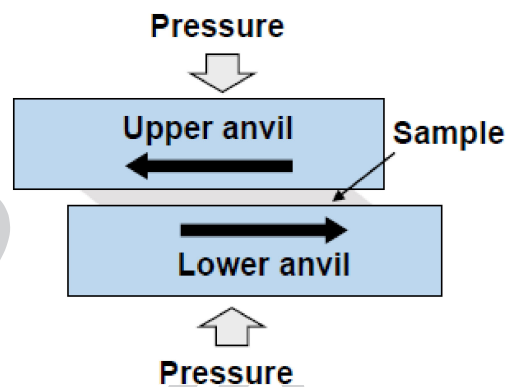

Fig. 1   Principle of high-pressure sliding (HPS).

mobile application target (5–7 wt.%), TiFe has a high volumetric storage capacity with reasonable price so that it is attractive for stationary hydrogen storage applications. Nevertheless, the practical use of the TiFe needs to overcome the difficulty of initial activation for the hydrogenation because it should be exposed to vacuum or a hydrogen atmosphere under a pressure of ∼3 MPa at temperatures higher than ∼400°C.[44–49] However, it was demonstrated that such a difficulty was solved when the sample is processed at room temperature by HPT.[35–37,50,51] Furthermore, once the sample is processed by HPT, activation of the sample is no longer required even after leaving it in the air for a prolonged period.[36,51] This was also demonstrated as an advantage over the activation under hydrogen atmosphere at elevated temperature because repeated activation is required once it is exposed to air. Thus, this study is initiated to confirm if the HPS process can activate TiFe for fast hydrogenation to promote the practical use.

2. Experimental

This study used a TiFe intermetallic with a minor addition

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Fig. 2   TiFe(Mn) sample embedded in stainless steel sheet.

of Mn ($TiFe_{1-x}Mn_x$ with $x = 0.3$), of which hydrogenation behaviour was examined earlier[37] before and after processing by HPT. Although the addition of Mn to TiFe reduces the hydrogenation pressure and temperature for activation,[52–54] the content of $x = 0.3$ is usually insufficient for the activation at room temperature as reported in the earlier experiment.[37]

For HPS processing, strips with dimensions of 5 mm width, 30 mm length and 2 mm thickness were cut from an ingot by an electrical discharge machine (EDM). A strip was then embedded at the center portion in a 304 stainless steel sheet with dimensions of 10 mm width, 100 mm length and 4 mm thickness as illustrated in Fig. 2. For embedding, a transverse slit was cut by the EDM and a strip sample was inserted while the space left on both sides of the strip was closed by stainless steel pieces. The HPS processing was conducted at room temperature ($\sim$300 K) under a pressure of 4 GPa for the sliding distance of 15 mm with a sliding speed of 1 mm/s.

Hydrogenation kinetics was examined using a Sieverts-type gas absorption apparatus at 293 K. Crushed fragments with a total weight of $\sim$0.5 g were prepared for the examination from the as-received ingot and the HPS-processed strip. The fragments were exposed to a hydrogen atmosphere under 2 MPa at 293 K following evacuation by a rotary pump for 2 h and replacement by the compressed hydrogen gas.

3.   Results

Figure 3 shows the hydrogenation kinetic curves of the HPS-processed strip and the as-received ingot. For both samples, the curves were delineated as a function of time after exposure to hydrogen atmosphere at 2 MPa. The exposure was made for up to $\sim$200 min or up to when the hydrogenation ceases (i.e., the amount of hydrogen in the sample reached saturation with respect to the exposure time). In this study, the measurement for hydrogenation was repeated twice. For comparison, the hydrogenation curves are also included from an earlier study using HPT processing.[37] The following points arise from Fig. 3.

(1) The hydrogenation occurred quickly in the sample processed by HPS, while no appreciable hydrogenation proceeded in the as-received ingot without the HPS process at least for the period exposed to the hydrogen atmosphere, which was 200 min in this study.

(2) Incubation was required for $\sim$60 min after the first exposure but the hydrogenation started immediately after the second exposure in the HPS-processed sample.

(3) The fast hydrogenation for the second exposure without incubation is similar to the one observed in the HPT-processed sample in the earlier report.[37] It should be noted that the hydrogenation for the HPT-processed sample was made after the third measurement of the
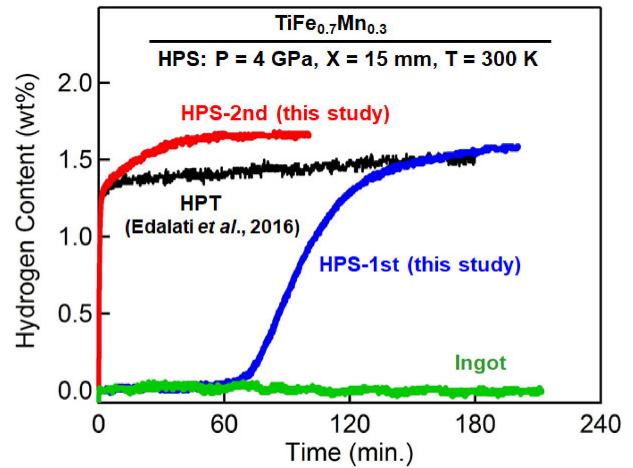

Fig. 3   Variation of hydrogen content against hydrogenation time after 1st and 2nd exposures at 273 K under hydrogen pressure of 2 MPa for sample processed by HPS at $\sim$300 K including as-received ingot. Result by Edalati *et al.* using HPT process[37] is included for comparison.

pressure-composition isotherms (PCT) so that the hydrogenation curve reproduced in Fig. 3 corresponds to the behavior after the fourth exposure to the hydrogen atmosphere.

(4) Figure 3 thus demonstrates that the HPS processing is effective for the enhancement of hydrogenation as the HPT processing.

4.   Discussion

The advantage of the HPS processing is that it is applicable to rectangular sheets with the same principle as the HPT processing where a disk form of samples is used. Thus, as discussed earlier,[43] HPS processing provides a better potential to enlarge the processed area in comparison with HPT processing. It is expected that a combination of the HPS process with a sample feeding process, called incremental feeding HPS (IF-HPS), further increases the SPD-processed area and thus the IF-HPS process should be more practical.[55,56]

In this study, a rectangular strip was embedded in stainless steel. This is to protect the anvils from wearing because the hardness of the TiFe intermetallic is as high as $\sim$1000 HV as reported earlier,[35] which is higher than the hardness of tool steel used in this study. The embedding technique was also adopted for groove rolling where a rectangular rod was encapsulated in stainless steel.[50] Powders may be put in a tube so that subsequent rolling or drawing enables the straining. Although rolling and drawing are processing techniques to introduce strain in the sample, the HPS processing as well as the HPT processing can be more efficient for the introduction of strain because the sample shape remains essentially unchanged during straining.

Figure 4 shows strain distributions calculated earlier by a finite element method (FEM) after processing by HPS for the samples with thicknesses of 3 and 5.5 mm after a sliding distance of 20 mm. Details for the FEM calculation were described earlier.[32] It should be noted that the calculation was made for a Ni-based superalloy (Inconel 718) of which mechanical properties are similar to the 304 stainless steel.
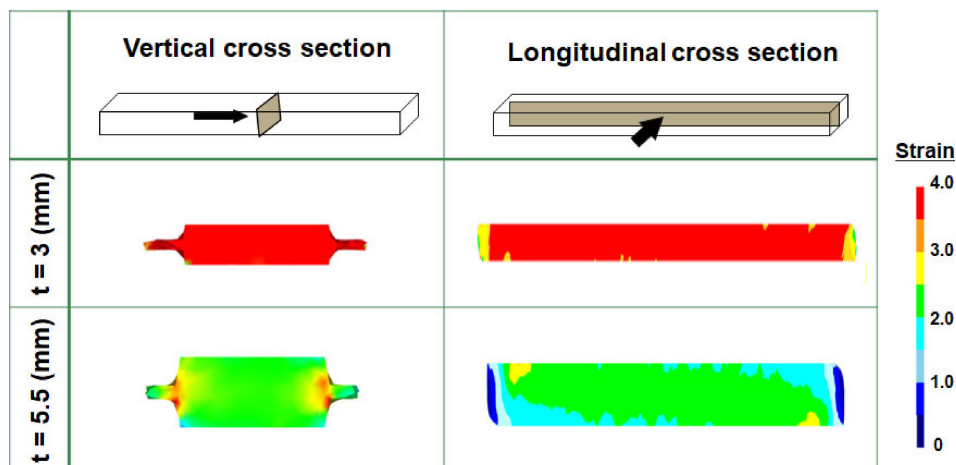
Fig. 4 Strain distributions calculated by FEM for Inconel 718 with thicknesses of 3 and 5.5 mm after processing by HPS for sliding distance of 20 mm. Vertical cross section (left) and longitudinal cross section (right). Calculation was carried out along with study reported earlier.[32] Vertical scale is enlarged with respect to the longitudinal length so that thickness is same as vertical cross section.

Although the amount of strain generation is reduced as the thickness is larger, it is clear that the strain distribution is almost homogeneous across the thickness and throughout the longitudinal direction except at the longitudinal edges of the samples and near the points where the upper and lower anvils are met each other. It is reasonable that the strip samples embedded at the center parts of the stainless steel plates equally received intense shear strain under the constraining condition.

Finally, as discussed earlier,[36,51] the enhanced hydrogenation kinetics is due to the formation of high density lattice defects introduced by HPS processing. Earlier studies also reported that large fractions of grain boundaries and dislocations were formed in many different materials after processing by HPT.[2,57,58] Grain boundaries provide pathways for fast hydrogen diffusion and improve both hydrogenation activation and kinetics while dislocations may be trapping sites for hydrogen.[36,51] Lattice defects would not only accelerate diffusion but also facilitate the phase transition from the intermetallic phase to the hydride phase.[49] It is concluded that the formation of lattice defects by HPS processing could result not only in reducing the effective temperature for metal-to-hydride phase transformations,[59] but also in decreasing the activation temperature for hydrogenation.[60]

5. Summary and Conclusions

(1) The HPS process was successfully applied to a TiFe intermetallic with a minor addition of Mn to improve its hydrogenation kinetics.

(2) The HPS-processed sample was activated quickly after exposure to a hydrogen atmosphere of 2 MPa at room temperature.

(3) Although incubation was required after the 1st exposure to the hydrogen atmosphere, hydrogenation occurred immediately for the 2nd exposure.

(4) This study suggests that HPS processing is promising for practical applications because it has the advantage that the sample size can be enlarged.

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