Hydrogen storage properties of TiFe + x wt.% $ZrMn_2$ (x = 2, 4, 8, 12) alloys by arc melting

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Abstract

We present the effects of $ZrMn_2$ on hydrogen storage properties of TiFe+x wt.%$ZrMn_2$ alloys prepared by arc melting. Each alloy is made of two phases: a primary phase with small amount of zirconium and manganese, and a secondary phase which has a higher proportion of zirconium and manganese. We found that when x increases, the first hydrogenation is much faster and the alloy is getting more stable. Moreover, for x = 12, air exposure had a minimal impact on hydrogen sorption behavior.

Introduction

TiFe alloy is a promising candidate for solid state hydrogen storage. However, the practical applications are limited due to the slow first hydrogenation, which needs high pressure and temperature[1]. In a previous investigation, we found that activation of TiFe alloy could be improved by adding Zr[2] and Mn[3].

Experiment

Alloys were prepared by arc melting.
Morphology was measured by scanning electron microscopy.
Structure was done by X-ray diffraction.
Hydrogen storage properties were measured by Sieverts-type apparatus.

First hydrogenation

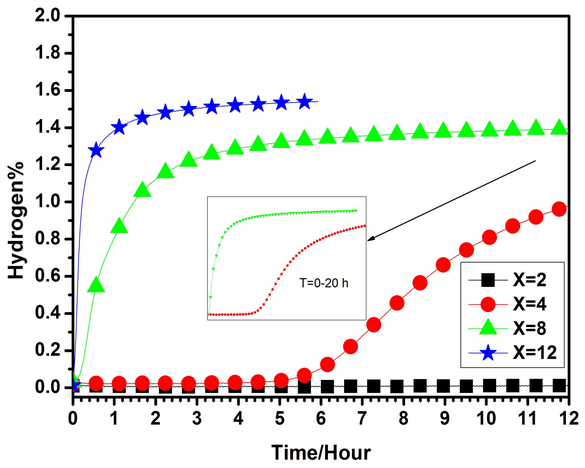


Fig.1–First hydrogenation of TiFe+x wt.%$ZrMn_2$ (x=2, 4, 8, 12) alloys at room temperature under 3 MPa hydrogen pressure.

This figure shows that x=2 does not absorb hydrogen even after 12 h. With increasing x the first hydrogenation becomes much faster, especially for x=12.

Morphology

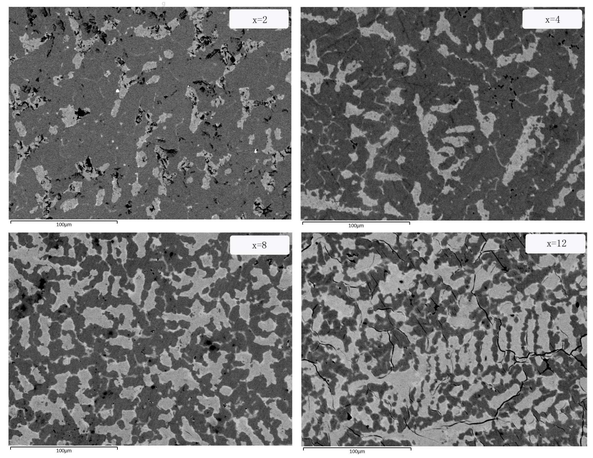


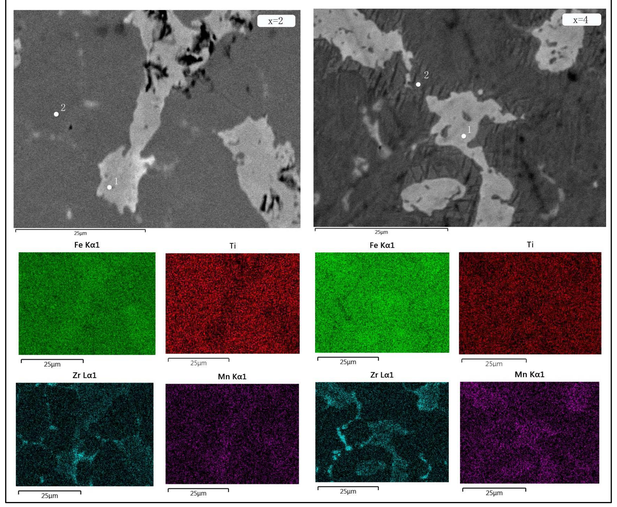
Fig.2–Backscatter micrographs of TiFe+x wt.%$ZrMn_2$ (x=2, 4, 8, 12) alloys prepared by arc melting

This figure shows that these samples have similar microstructure which includes bright and dark phases. Table 1 shows that the bright phase increase with x.

Table 1-The percentage of bright and dark phases are analysed by image J software

Phase	x=2	x=4	x=8	x=12
Bright (%)	18.2	21.3	38.2	47.6
Dark (%)	81.8	78.7	61.8	52.4

Fig.3 shows that for all composition the dark phase has titanium, iron and manganese with a very small amount of zirconium. The bright phase is zirconium and managanese rich. Actually zirconium is mainly located in the bright phase and not in the dark phase.



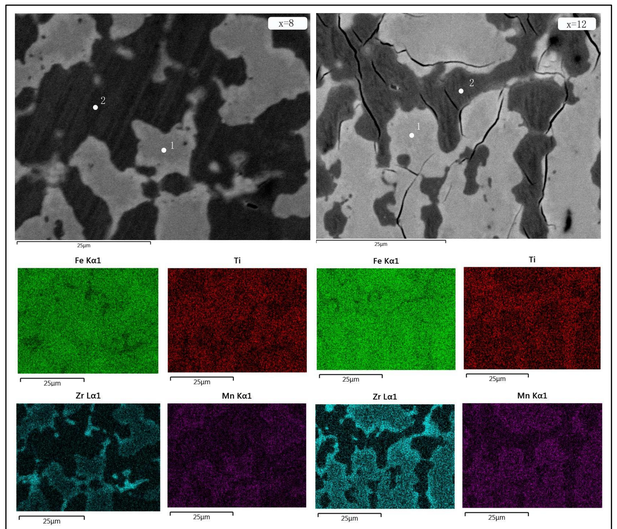
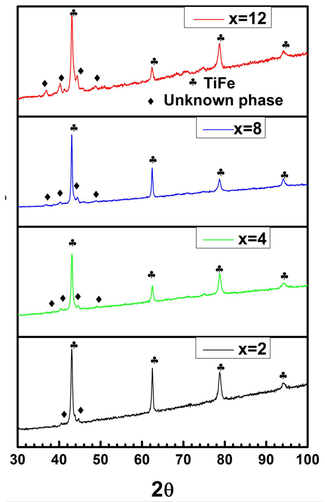


Fig.3–Elements mapping of TiFe+x wt.%$ZrMn_2$ alloys with EDX

Structural characterization



This figure shows that all alloys prepared have TiFe phase, but the secondary phase are very weak and difficult to identify. As XRD was from a copper target the fluorescence from iron is strong and has an important background which makes the detection of a secondary phase more difficult. Later we will use the neutron diffraction to identify the phase.

Fig.4–XRD of TiFe+x wt.%$ZrMn_2$ (x=2, 4, 8, 12) alloys

Pressure-composition isotherms

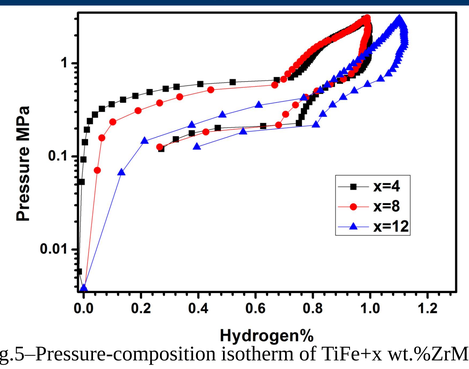
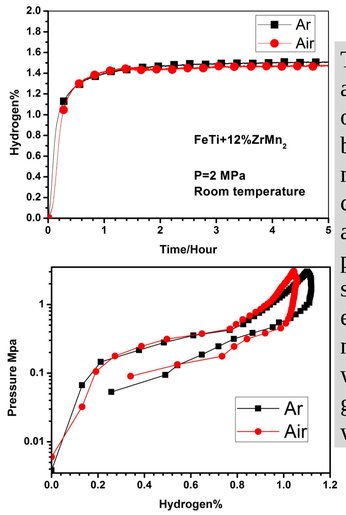


Fig.5–Pressure-composition isotherm of TiFe+x wt.%$ZrMn_2$ (x= 4, 8, 12) alloys at room temperature

Fig.5 shows that the absorption and desorption plateau pressure all decrease from x=4 to x=12. We also can see that the reversible capacity rises with incraesing x.

Air exposure



These figures show that air exposure has no effect on the first hydrogenation but slightly reduce the maximum capacity. It also can be found that the absorption and desorption plateau pressure were similar for samples where expose to air or Ar. This means TiFe+12 wt.%$ZrMn_2$ alloy is a good potential material to work in air.

Fig.6–The first hydrogenation and pressure-composition isotherms of TiFe+12 wt.%$ZrMn_2$ alloys in air and Ar at room temperature

Conclusion

1.The first hydrogen absorption capacity and kinetic of TiFe+x wt.%$ZrMn_2$ (x=2, 4, 8, 12) alloys increases with the amount of $ZrMn_2$.
2.All samples have similar microstructure which includes bright and dark phases, but the bright phase surface increases with the amount of $ZrMn_2$.
3. The air exposure has an small effect on the first hydrogenation of TiFe+12 wt.%$ZrMn_2$ alloy. But exposing to the air can result in decreasing the reversible capacity.

Reference

[1] J. Reilly, R. Wiswall Jr, Inorganic Chemistry, 13 (1974) 218-222.
[2] C. Gosselin, J. Huot, Materials, 8 (2015) 7864-7872.
[3] H.I. Miller, J. Murray, et. al, J. Alloys Comp, 231 (1995) 670-674.

Acknowledgment

Peng Lv is thankful to Fonds de rechetrche du Quebec-Nature et technologies (FRQNT) for fellowship. We would also thanks Mrs. A. Lejeune for SEM analysis, C. Gosselin and ZH. Zhang for help in experiment.