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Correlation between the milling time and hydrogen-storage properties of nanostructured ZrFeNi ternary alloy

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ABSTRACT

Cubic (C15) Laves phase ZrFeNi alloy has been prepared by the arc melting method and then milled in an argon atmosphere to see the effect of milling on hydrogenation properties. Hydrogen absorption isotherms have been measured at pressures upto 60 bar and temperatures between 303 K and 373 K. The enthalpies of hydride formation, derived from temperature variation of equilibrium pressure show a decrease in hydride stability for a 1 h milled sample, while it again increased for longer milling times which may be due to the formation of some minor phases.

1. Introduction

Hydrogen-storage alloys are being used in various applications, e.g. hydrogen-fuelled transportation, hydrogen purification, secondary batteries, heat storage and heat pumps. A wide range of alloys has been investigated for their hydrogen-storage capacities, e.g. $LaNi_5$, FeTi, and Mg_2Ni. Zr-based Laves phase alloys are attractive due to their substantial hydrogen-storage capacities [1,2]. Zirconium forms a dihydride, ZrH_2, exothermically with a very high heat of formation $\Delta H = -39$ kCal (mol H)$^{-1}$. It forms AB-type binary compounds with Ni and Co with very high ΔH values for hydride formation [3,4]. The high stabilities of these hydrides make these alloys unsuitable for hydrogen-storage applications. Yet zirconium also combines with a wide range of transition metals such as Mn, Cr, V and Fe to form AB_2-type compounds with either the cubic C15 or hexagonal C14 Laves phase crystal structure. These have been studied in detail by many workers [5–8]. $ZrFe_2$ is also one of the important candidates among these AB_2-type alloys, but it has two disadvantages: (i) it forms a stable hydride and (ii) it requires many charge–discharge cycles for activation. Fortunately, the stabilities of this compound could be drastically reduced and the plateau pressure raised to a useful level by partial substitution of Fe by other elements. Ramaprabhu and co-workers [9–11] studied C14 Laves phase $ZrMnFe_{1-x}Co_x$ and $ZrMnFe_{1-x}Ni_x$ alloys and the effect of Co and Ni substitution on the hydrogen-storage properties, which were found to be changed drastically when Co or Ni with Fe were in the molar ratio of 1:1. Plateau pressures were found to be around 6.9 bar and 4.2 bar at 303 K for $ZrMnFe_{0.5}Co_{0.5}$ and $ZrMnFe_{0.5}Ni_{0.5}$ alloys [9,10]. In our earlier papers we have reported the effect of various substitutions at A and B sites of AB_2-type alloys [12–15]. It was found that Ni substitution at the Fe site in $ZrFe_2$ alloy makes these alloys less stable without reducing the hydrogen-storage properties markedly. We found the least stable hydride for $ZrFe_{1.2}Ni_{0.8}$, with a hydrogen capacity of about 3.08 H/f.u. at 50 bar and at 303 K [15]. Another problem of requirement of several activation cycles could be overcome by ball milling. Recently ball milling has been found to be an active tool for producing fresh surface for hydriding. Mechanical alloying led to marked improvements in activation, kinetics [16,17] and storage capacity [18].

In this work, we increased the Ni content up to a molar ratio of 1:1 with Fe in the alloy series $ZrFe_{2-x}Ni_x$ to reduce the stability of hydride formation. XRD and SEM were performed in order to study their crystallography and microstructures. *PCT* isotherms were measured in the temperature and pressure range 323–373 K and 0–60 bar, respectively. Then we synthesized the nanoparticles of these ternary alloys by milling in a high-energy ball mill and studied the effect of milling on the structural and hydrogenation properties of the prepared alloys.

2. Experimental

ZrFeNi alloy was prepared by arc melting on a water-cooled copper hearth under argon atmosphere and remelted four times to achieve better homogeneity. The ingot, pulverized into granules in air and powdered to 20–100 μm, was kept in a stainless steel bowl under argon atmosphere. Four steel balls were used with ball to powder ratio of 6:1. We made the milling runs in a sequence of 10 min milling and 10 min

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rest. The alloy was milled for different times i.e. 1 h, 2 h, and 3 h. The structures of the powders were characterized by XRD analysis using Cu Kα radiation (λ = 1.5418 Å). The morphologies and particle size of the powders were examined by scanning electron microscope (SEM). Hydrogen absorption behaviour of alloys was quantitatively characterized by the pressure–composition–temperature (*P–C–T*) curves, which were measured by using a Sievert-type apparatus. Prior to experiments, the whole system was evacuated to 10^{-5} Torr vacuum at 673 K for 2 h and the samples were introduced to hydrogen at 300 K for 12 h under 5 bar pressure. This process was repeated for 2–8 cycles to activate the samples and to get reproducible isotherms.

3. Results and discussions

The XRD pattern of as-cast ZrFeNi alloy before and after milling is shown in Fig. 1. The as-casted alloy shows the existence of a single cubic phase structure similar to that of $ZrFe_2$. Peaks confirm the presence of the C15 cubic structure and the lattice constant *a* was 6.9543 Å. One-hour milling results in peak broadening and simultaneous intensity decrease. The peak broadening reflects a decrease of the average crystallite size and an increase in the internal strain introduced by mechanical deformation. After 3 h milling, the XRD pattern shows the presence of mixed crystalline and amorphous material, which means that the alloy passes through the conversion process from a nanocrystalline to amorphous state.

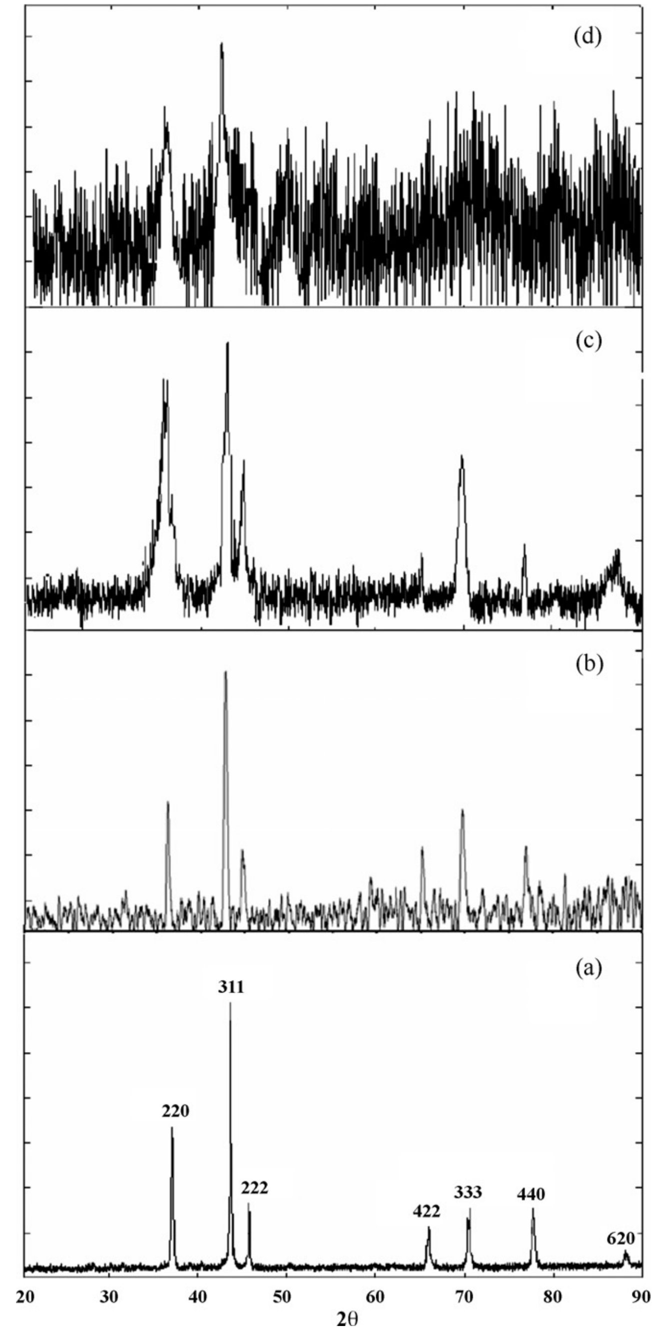

Fig. 1. XRD pattern of (a) as-cast, (b) 1 h milled, (c) 2 h milled and (d) 3 h milled ZrFeNi alloy.

Fig. 2 shows the SEM micrographs of as-cast alloys, indicating a single-phase homogeneous structure for all the alloys. Fig. 2 shows the SEM micrographs of as-cast and ball-milled ZrFeNi alloys. It was found that the microstructures of the 1 h milled sample consisted of very small particles (about 300–400 nm), while the size of the particles was reduced to 100–200 nm after 3 h milling. It is also clear from the figure that the particles are in the form of small bunches. These results show that nanostructures can be obtained easily by ball milling of pre-melted intermetallic compound.

In general practice, the alloy powders are covered with an oxide film that prevents hydrogen to enter into the powder. It needs an activation treatment for the formation of fresh surface so that hydrogen can be absorbed. Yet by ball milling, a large difference in the morphology of particles was observed, resulting in a large reduction in particle size during milling such that a large amount of fresh surface is generated for hydrogenation. Although all the milling was carried out in argon atmosphere, it was found that activation was still required. This may be due to slight oxide formation during the transfer of sample from glove box to sample holder.

Fig. 3 shows the hydrogen absorption characteristics of ZrFeNi for a temperature and pressure range $303\,K \le T \le 373\,K$ and $0.5\,bar \le P \le 60\,bar$, respectively, for as-melted alloy. The *PCT* diagrams for all other alloys of $ZrFe_{2-x}Ni_x$ ($x = 0.2, 0.4, 0.6, 0.8$) are reported in our previous paper [15]. The maximum hydrogen-storage capacity for ZrFeNi alloy is 3.19 H/f.u. at 50 bar and 303 K, which is more than for $ZrFe_{1.2}Ni_{0.8}$. This may be attributed to the increase in the atomic order of the alloy due to the presence of Fe and Ni in the molar ratio 1:1 [10]. Fig. 4 shows the *PCT* diagrams for the as-melted and milled ZrFeNi alloys at 303 K. It is found that the hydrogen absorption pressure of the ball-milled alloys is lower than that of the as-melted alloy. The lower plateau pressure means easier hydrogenation of the milled alloy in comparison to that of the as-melted one. This easier hydrogenation may be due to the ball milling, which creates many defects on the surface and in the interior of the powder particles, and due to the production of a nanocrystalline structure. The ball milling of pre-melted alloy caused a shift of the *P–C* isotherm towards lower pressure, but it reduced the width of the plateau region. After milling for 2 h and 3 h, the storage capacity was found to be decreased, which may be due to some other minor phases formed during milling. These minor phases could not be indexed by XRD as the percentage of these phases is very low, although the plateau behaviour is also giving a indication that there is a distribution of sites associated with an amorphous phase. Probably these phases stopped hydrogen to enter into the material. On comparing the *PC* isotherm of the 3 h milled sample, it was found that the hydrogen-storage capacity is reduced drastically compared to that of other alloys, which may be due to the formation of an amorphous phase. The *PC* isotherm of the 3 h milled sample shows the continuous increase in the hydrogen-storage capacity in the β-phase region, which also reflects the amorphous nature of the sample. As a result of ball milling, it may be possible that a chemical disordering takes place by mechanical deformation, creating some new phase.

The thermodynamics of metal hydrides have been discussed in detail by some workers [19,20]. The enthalpy, ΔH and entropy, ΔS of hydride formation have been derived by utilizing the Van't Hoff plot of $\ln P_{eq}$ vs $1/T$, according to the equation

$$RT \ln P_{eq} = 2(\Delta H - T\Delta S)$$

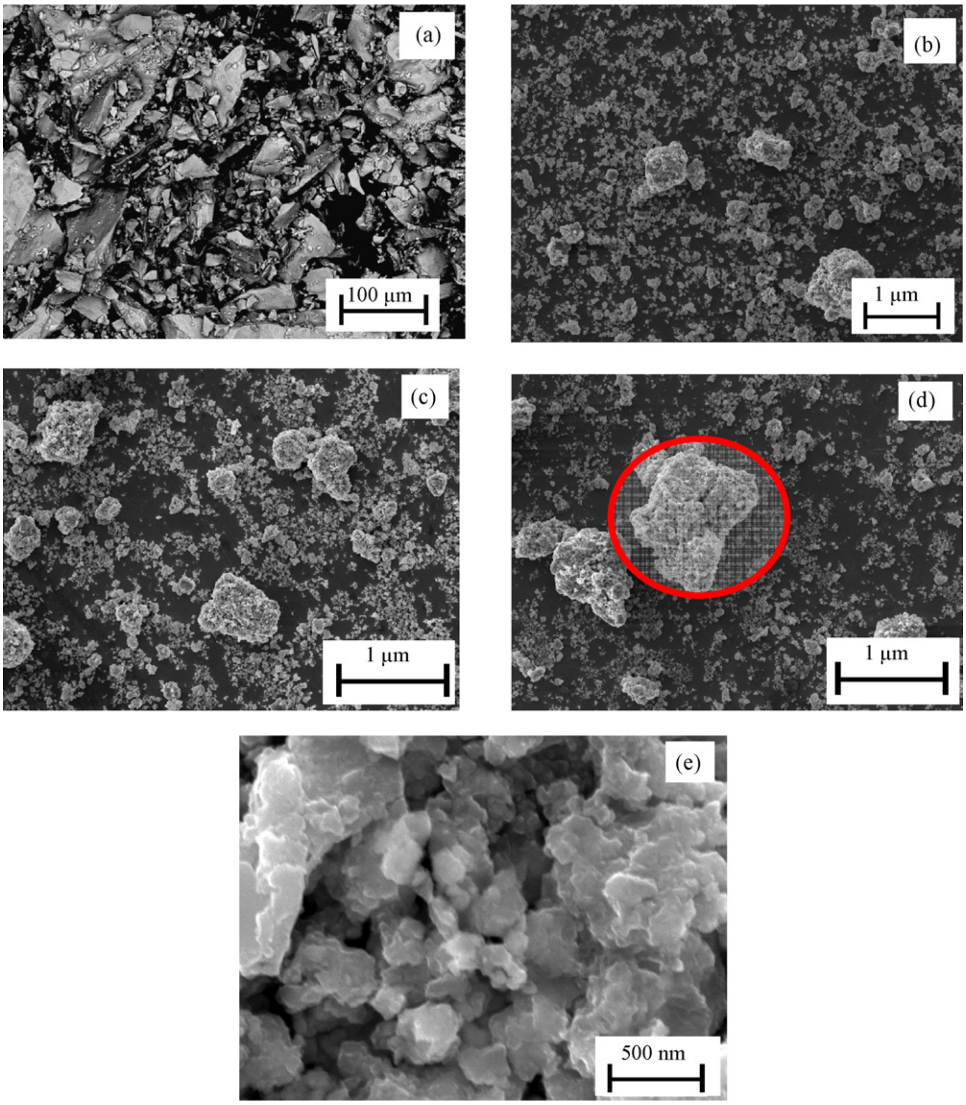

Fig. 2. SEM images of (a) as-cast, (b) 1 h milled, (c) 2 h milled, (d) 3 h milled ZrFeNi alloy and (e) circled area at high magnification.

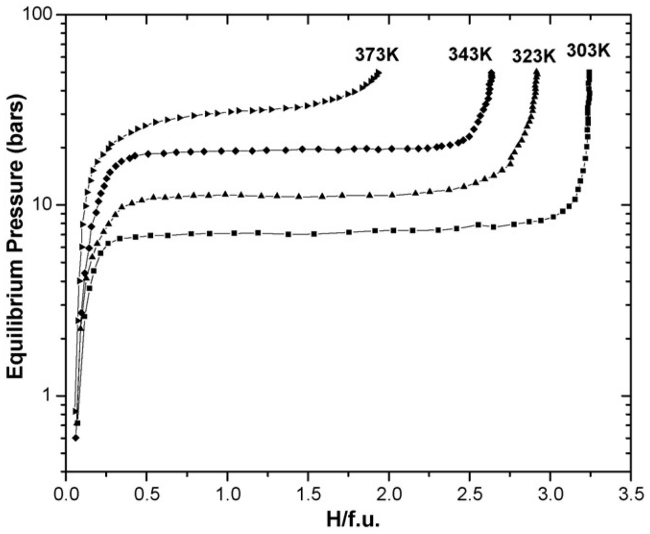

Fig. 3. *PCT* isotherms of as-cast ZrFeNi alloy for temperature range 303 K ≤ *T* ≤ 373 K.

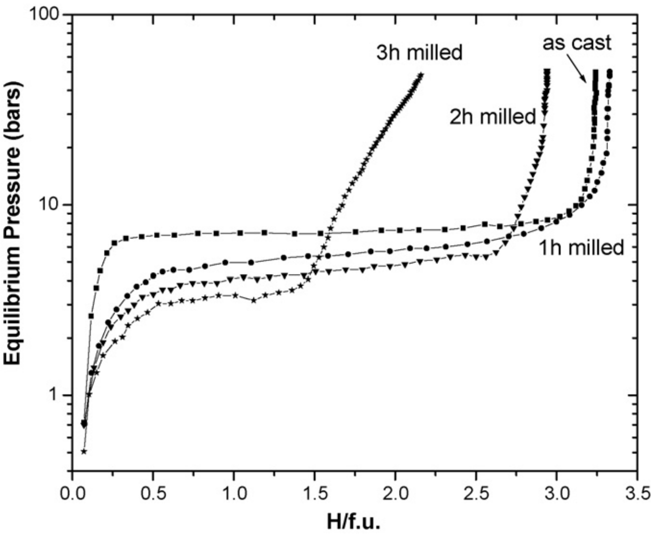

Fig. 4. *PCT* isotherms of as-cast and ball-milled ZrFeNi alloy for *T* = 303 K.

Table 1
The hydrogen-storage capacities and thermodynamical parameters of as-cast and ball-milled ZrFeNi.

Alloy hydride ZrFeNi	Equilibrium pressure* 303 K, 323 K	H/f.u.**	Enthalpy ($-\Delta H$) (kJ (mol H)$^{-1}$)	Entropy ($-\Delta S$) (J K^{-1} (mol H)$^{-1}$)	Gibb's Free Energy ($\Delta\mu$) (kJ/mol H)
As-cast	7.02, 11.01	3.24	10.61	43.12	2.455, 3.318
1 h milled	5.40, 9.83	3.32	10.24	41.11	2.216, 3.038
2 h milled	4.53, 7.86	2.94	12.66	48.01	1.887, 2.847
3 h milled	4.82, 6.82	2.11	14.34	53.43	1.849, 2.918

* At H/f.u. = 1.5.
** At 303 K, 40 bar.

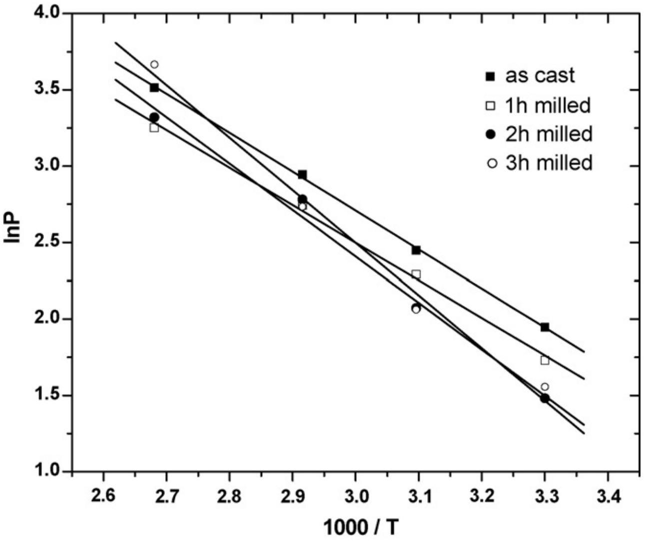

Fig. 5. Van't Hoff plots for H/M = 1.5 for as-cast and ball-milled ZrFeNi.

The Van't Hoff plots for H/f.u. = 1.5 for ZrFeNi is shown in Fig. 5. The parameters, entropy and enthalpy, were obtained using the least square technique from the slope and Y intercept of the Van't Hoff plot shown in Fig. 5 for equilibrium pressure. The practical significance of ΔH is that it is an index of thermochemical stability of the metal hydride. The higher value of ΔH shows a high degree of stability of hydride, low dissociation pressure and the requirement of moderately higher temperature to decompose it or to liberate the hydrogen than hydride formation temperature [21]. The hydrogen-storage capacities and thermodynamical parameters of all as-cast and ball-milled $ZrFe_{2-x}Ni_x$ alloys are summarized in Table 1. If we compare the enthalpy we find that the ΔH value decreases for 1 h milled sample in comparison to that of as-cast alloy, but it increases again with the increase in milling time. It is really a very interesting result. The local amorphous structure could be considered for the explanation of this behaviour. Although the H bonding is stronger on average, but the number of these strong sites decreases on average compared to the more crystalline structure.

4. Conclusions

Hydrogen absorption isotherms of as-cast and ball-milled ZrFeNi alloys have been investigated in the ranges 303 K $\leq T \leq$ 373 K and 0.5 bar $\leq P \leq$ 60 bar. This study revealed that substitution of Ni at the Fe site in the molar ratio of 1 : 1 increases the storage capacity while decreasing the plateau pressure of absorption in comparison to other $ZrFe_{2-x}Ni_x$ alloys, which is due to the increase in the atomic order of the alloy. The enthalpy of the hydride formation of this alloy was less than for other $ZrFe_{2-x}Ni_x$ alloys with $x < 1$. The enthalpy was even smaller for the 1 h milled ZrFeNi sample before increasing again for 2 h and 3 h milled samples. This means that the 1 h milled ZrFeNi alloy results in the least stable hydride, which is good for practical applications.

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