High temperature properties of hydrogenated Ti\textsubscript{50}Zr\textsubscript{25}Co\textsubscript{25} rapidly quenched alloy

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Abstract. The high temperature properties of hydrogenated Ti\textsubscript{50}Zr\textsubscript{25}Co\textsubscript{25} ribbons were investigated up to 380°C. As indicated by tensile tests at room temperature, hydrogen-induced strengthening occurred until ~21 at.% hydrogen. At this range of hydrogen concentration (H\textsubscript{conc}) varying from 0 to ~21 at.%, tensile tests conducted at high temperatures (300°C to 400°C; strain rate: 10^{-4}s\textsuperscript{-1}) showed that in addition to enhancement in strength, elongation larger than 20% was obtained. The temperature range at which such property improvements occurred depends on the hydrogen concentration. The change in the mechanical properties in this range of H\textsubscript{conc} and temperature is attributed to the corresponding changes in the thermal behaviour of the alloy, along with the inherent structural modifications induced by hydrogen addition.

1. Introduction
Hydrogen in amorphous alloys has been used as a probe to study the structural and chemical characteristics of the amorphous state [1,2]. Quite recently, amorphous alloys due to their unique structure, high hydrogen affinity (particularly those containing Zr and Ti) and high hydrogen solubility (without the formation of hydrides) are being suggested as alternative materials for hydrogen related applications [3,4]. While several studies on interaction between hydrogen and amorphous alloys indeed show potential for high solubility (upto 60 at.%), embrittlement was also reported at these hydrogen levels [2,5-7].

In a recent investigation on the hydrogenation behavior of the Ti\textsubscript{50}Zr\textsubscript{25}Co\textsubscript{25} alloy [8], we reported that the hydrogen destabilized the icosahedral short range order and increased the stability of the amorphous structure. Further, up to a H\textsubscript{conc} of ~ 21 at.%, hydrogen bending ductility was retained and the tensile strength was enhanced [8]. Noting such positive effects in that range of concentration, our current aim is to study the high temperature tensile properties of Ti\textsubscript{50}Zr\textsubscript{25}Co\textsubscript{25} alloy containing up to 21 at.% hydrogen. The present work highlights the variation in properties of hydrogenated Ti\textsubscript{50}Zr\textsubscript{25}Co\textsubscript{25} ribbons in the range 25°C to 380°C, brought forth by the structure-property relationship.

2. Experimental
Ti\textsubscript{50}Zr\textsubscript{25}Co\textsubscript{25} alloys of 5 mm width and 40 µm thickness, prepared using the single-roller melt-spinning technique by Amosense Ltd, Korea, were hydrogenated to various concentrations by electrolytic charging, at a constant current density of 25 mA/cm\textsuperscript{2} using a platinum anode in a 1N H\textsubscript{2}SO\textsubscript{4}
electrolyte. After measuring their hydrogen contents by a method explained elsewhere [8], their thermal and structural properties were determined using differential scanning calorimetry (DSC), and x-ray diffraction (XRD). Mechanical tests were performed in a 2.5 ton electro-mechanical universal tensile testing machine in air at room and elevated temperatures at a constant strain rate of 10^{-4}s^{-1}. Bone-shaped specimens with gauge length of 20 mm and width of 3 mm were used as test samples. Mechanical characteristics were obtained from the average values of 3 to 5 tests.

3. Results & Discussions

Figure 1a shows the DSC pattern of the as-received alloy that exhibits shallow peak before the main crystallization peak. The shallow peak (T_{x1}, inset in Figure 1a) was attributed to the i-phase formation, as demonstrated in Figure 1b, showing the variation of XRD traces taken at high temperatures, and indicating the formation of i-phase at temperatures > 400°C. Indeed, our earlier study demonstrated that although the Ti_{50}Zr_{25}Co_{25} as-spun ribbon exhibited an amorphous halo pattern, the HRTEM images revealed the presence of icosahedral quasicrystalline short-range order (i-SRO) dispersed in the amorphous matrix [8]. After introducing hydrogen, the HRTEM observations indicated a fully amorphous structure from H_{conc} ~ 21 at.%. Until ~ 40 at.%, hydrogen existed in solid solution, and H_{conc} ~ 60 at.% was required for the formation of hydrides [8]. At room temperature, the variation of tensile strength and bending fracture strain with hydrogen content showed that though embrittlement occurred at higher hydrogen contents, for H_{conc} ≤ 21 at.%, hydrogen addition induced an increase of the fracture strength and complete bending upto 180° was obtained without fracture [8].

### Table 1. Variation of material properties with hydrogen content

| H_{conc} (at.%) | T_{x1} (°C) | ΔH_{x1} (J/g) | Desorption Temperature, T_{onset} (°C) | Young’s Modulus at 25°C, GPa |
|----------------|------------|---------------|---------------------------------------|-------------------------------|
| 0              | 420        | 3.88          | -                                     | 55                            |
| 15             | 400        | 1.12          | 660                                   | 48.5                          |
| 21             | 340        | 0.73          | 640                                   | 46                            |

Table 1 shows the thermal properties of the alloys in the range of hydrogen concentration wherein improvement in strength was obtained at room temperature [8]. It can be observed that the stability of the shallow peak (i-phase) diminishes, as seen from the reduction in enthalpy of formation (ΔH_{x1}), and T_{x1} shifted towards lower temperatures. To further the study on the effect of hydrogen on properties, high temperature tensile tests were conducted on alloys with H_{conc} = 0, 15 and 21 at.%. It is worth noticing that in that concentration range, the hydrogen desorption occurs at temperatures as high as 650°C (Table 1) and hence would not be desorbed in the temperature range investigated (300°-370°C).
Figure 2(a-c) shows the high temperature tensile properties of Ti$_{50}$Zr$_{25}$Co$_{25}$ ribbon for H$_{\text{conc}}$ ≤ 21 at.%. At room temperature, the alloys show an almost linear increase in strength with the H$_{\text{conc}}$ and do not exhibit plastic deformation [8], a characteristic of the inhomogeneous deformation behavior of amorphous alloys due to the formation of shear bands [9]. At high temperatures (300°C to 370°C), not only does plastic deformation occur, the extent of such deformation depends on H$_{\text{conc}}$. In the lower temperature range, the hydrogenated alloys show increased strength and/or large deformation with elongations up to ~20%; however, the as-spun alloy exhibits better behavior beyond 370°C.

It can be observed that with initial increase in temperature, along with appreciable plastic deformation, there is also a significant improvement in strength, particularly for the as-spun alloy. Such an increase can be attributed to the existence of the icosahedral phase; the onset of its formation is in the near vicinity of the test temperature. With respect to the variation in properties with the H$_{\text{conc}}$, the alloy with ~15 at.% shows superior properties, in terms of both strength and ductility, which are comparable or higher than the as-spun alloy, especially at lower temperatures (< 350°C). However, at higher temperatures, the reverse is observed. From Table 1, it can be observed that with increase in H$_{\text{conc}}$, the ΔH$_{x1}$ and T$_{x1}$ of the i-phase decreases, implying the formation of low volume fraction i-phase at temperatures lower than that of the as-spun alloy. As observed in Figure 2d, the formation of the i-phase readily occurs on isothermal annealing at 330°C, the temperatures being much lower than the T$_{x1}$ shown in Table 1. In such a case, further increase of the test temperature would lead to an excessive growth of the existing short range order, resulting in the reduction of strength as well as ductility, as observed for H$_{\text{conc}}$ < 15 at.% at 370°C. For H$_{\text{conc}}$ ~ 21 at.%, the property improvement over either of the variants is pronounced only at lower temperatures, as temperatures greater than 330°C would facilitate the growth of the i-SRO. Hence for ~21 at.%, tests conducted at T > T$_{x1}$ results in a brittle failure, characterized by lowering of both strength and ductility.

In order to understand the high temperature behavior of alloy, it is important to consider the site occupancy of hydrogen. At low H$_{\text{conc}}$ (≤ 15 at.%), hydrogen would occupy the tetrahedral sites of low
energy in the free volume (stable sites) \cite{8,10}. With increase in $H_{\text{conc}}$ (~21 at.%), hydrogen atoms would tend to sufficiently fill the sites of the free volume, forming a dense-packed structure. As reported earlier \cite{8}, at much higher contents (~21 at.%), due to reduction in the available free volume, hydrogen would occupy the high energy unstable sites by local structural rearrangement, resulting in decohesion between the transition metal atoms, causing embrittlement \cite{5,8}.

As mentioned earlier (Table 1), for the range of concentration used in the present study ($H_{\text{conc}} \leq 21$ at.%), the test temperatures would not result in hydrogen desorption, as the desorption temperatures are quite high. Also, while the process of desorption is temperature dependent but stress independent, atomic diffusion is dependent on both the loading condition and temperature \cite{9,11}. It is hence expected that during high temperature tensile loading for $H_{\text{conc}} \leq 15$ at.% (containing a few i-SRO \cite{8}), the hydrogen atoms would possess a higher degree of freedom for motion, thus enabling an increased atomic mobility for the neighboring metal atoms, consequently aiding plastic deformation. However at $H_{\text{conc}} \sim 21$ at.%, due to attaining a near-complete occupation of free volume sites of low energy (stable sites) and a dense-packed amorphous structure \cite{8}, the atomic movement would presumably be restrained on the application of stress/temperature. This would further explain the high strength of alloy with $H_{\text{conc}} \sim 21$ at.% at room temperature. Further, due to the shifting of $T_{x1}$ peak to lower temperatures on hydrogen addition, tests performed beyond $T_{x1}$ result in brittle failure.

4. Conclusions
Positive effects of hydrogen, the first of its kind, have been identified on the room and high temperature tensile properties of Ti$_{50}$Zr$_{25}$Co$_{25}$ ribbons charged electrolytically with ~15 and ~21 at.% hydrogen. Following are the main highlights:
(i) Hydrogen addition improves the high temperature tensile properties, and the temperatures at which such improvements occur was found to depend on the hydrogen content. Hydrogen indeed reduced the temperature at which the plastic deformation occurs.
(ii) Hydrogen-induced strengthening and ductility is attributed to the inherent structural changes during hydrogen charging and the simultaneous occupation of free volume, which facilitate local atomic motion (i.e., flow) during deformation in the investigated temperature range.
(iii) Ti$_{50}$Zr$_{25}$Co$_{25}$ alloy with $H_{\text{conc}} \sim 15$ at.% has the best properties, in terms of strength and deformation, since significant plastic deformation as high as ~20% was obtained at 350°C, while the as-received alloy could be deformed only up to 8%.

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