Electron transport behaviour and soft magnetic properties of bulk amorphous Fe$_{72}$Si$_{4}$B$_{20}$Nb$_{4}$ alloy

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Abstract

The crystallization behaviour, electrical resistivity, magnetic and mechanical properties of as-quenched bulk amorphous Fe$_{72}$Si$_{4}$B$_{20}$Nb$_{4}$ alloy was investigated. The alloy, prepared in the form of rods by a copper mould casting technique, revealed an amorphous structure as observed from x-ray diffractometry. Differential scanning calorimetry and thermal variation of electrical resistivity measurements showed distinct glass transition temperature, $T_g$ occurring 50–60 K below the crystallization onset ($T_X$). Such a wide supercooled range was also attributed to the highly reduced glass transition temperature, $T_{rg}$ which was in the range of 0.56–0.58 found to be prevalent in good glass forming alloys. The alloy also showed a non-linear decrease in stability time at different temperatures between $T_g$ and $T_X$. The bulk amorphous alloy exhibited a drastic decrease in electrical resistivity around the glass transition temperature which was attributed to high electron propagation due to enhanced stress relaxation as result of a decrease in viscosity. The material exhibited superior soft magnetic properties with a coercivity value of 212 mOe, which is fairly low with respect to reported bulk amorphous alloys. The amorphous alloy also showed saturation induction of 12 kG and a moderate Curie temperature of 595 K. The as-quenched bulk amorphous alloy exhibited a high mechanical hardness of 1250 HV (Vickers). The superior soft magnetic properties coupled with high mechanical hardness opens up the scope for bulk amorphous Fe–Si–B systems with Nb incorporation.

1. Introduction

The interplay between different rapid solidification techniques and alloy compositions to achieve desired undercooling has been a subject of immense technological importance for the production of amorphous materials. The various processing routes include splat quenching, sputtering, gas atomization, vapour deposition and the much later developed melt spinning as well as in-water quenching techniques which provide a typical cooling rate of $10^5$–$10^6$ K s$^{-1}$. Besides the high cooling rate, the small dimensions of quenched materials in micron order ribbons, thin films or wires suffice for the requisite quenching to the amorphous state [1]. In these materials the high quench rate is facilitated by rapid heat dissipation due to the small geometrical shapes of prepared materials. The materials prepared using these techniques can be used only for small components in structural and magnetic applications. Besides their restricted applications, the materials typically in the form of ribbons have poor load bearing capacity.

To overcome the dimensional limitations, there has been continuing effort to achieve large-sized amorphous materials using conventional casting routes that are less sophisticated. Ultimately the thermodynamic barrier to this optimum dimensional constraint was solved with the
introduction of bulk amorphous systems [2]. This feasibility of getting bulk materials with dimensions \( \geq \) millimeter order arose from the paradigm shift in conventional alloy design. Latest reports suggest that the incorporation of thermally stable refractory elements stabilizes the amorphous phase during devitrification of amorphous materials [3]. These typically comprise of large sized elements like Nb, Ta etc, whose crystalline phases form at elevated temperatures. Owing to their large atomic volume these elements have low diffusivity and thereby have been found to stabilize the amorphous matrix in nanocrystalline alloys [4].

The present investigation addresses the crystallization, electron transport behaviour and soft magnetic properties of a bulk amorphous alloy where Nb is incorporated in a conventional FeSiB amorphous system.

2. Experimental

The samples used for the present study were prepared in the form of amorphous rods by the copper mould casting technique. A representative amorphous rod as shown in figure 1 is 2 mm in diameter and 60 mm in length with the nominal composition of Fe\(_{72}\)Si\(_4\)B\(_{20}\)Nb\(_4\). The structure of the as-cast material was examined using the x-ray diffraction technique (Siefert, PTS 3003) with Cu–K\(_\alpha\) target. The melting point of the alloy was measured using differential thermal analysis (DTA) (SDTQ 600). The melting point \( (T_m) \) of the alloy was found to be 1404 K. The crystallization behaviour was evaluated using differential scanning calorimetry (DSC) (Perkin Elmer DSC-7). Electron transport properties were determined from thermal variation of electrical resistivity (Sinku Riko, TER-2000) in argon atmosphere using a dc four-probe technique. The soft magnetic properties were determined from a computer controlled hysteresis loop measurement system by applying a quasi-dc field at 50 mHz. The Curie temperature of the bulk amorphous material was evaluated from the thermal variation of ac susceptibility measured at a frequency of 2 kHz and applied magnetic field of 5 mOe. The mechanical hardness was determined using a digital micro-hardness tester (Leitz Wetzler) at a load of 300 g.

3. Results

3.1. Crystallization behaviour and thermal electrical resistivity

Figure 2 shows the x-ray diffracrogram of the as-cast Fe\(_{72}\)Si\(_4\)B\(_{20}\)Nb\(_4\) alloy. The broad halo indicated the absence of long range ordering and hence, the amorphous nature of the as-quenched alloy. Scanning from the room temperature, the DSC plot (figure 3) showed the thermal response of the alloy obtained at a heating rate of 10 K min\(^{-1}\). It is interesting to find the present bulk amorphous alloy revealing a gradual change in the thermal profile with an endothermic transition at \( T_g \). This is the glass transition temperature, \( T_g \) occurring around 810 K. Further heating showed two exothermic transformations with primary and secondary crystallization onsets \( T_{X1} \) and \( T_{X2} \) at 860 K and 938 K, respectively. The activation energy of the first crystallization stage was obtained using Kissinger’s modified equation [5] written as

\[
\ln\left(\frac{T_p^2}{S}\right) = \frac{E_{\text{act}}}{RT_p} + \ln\left(\frac{E_{\text{act}}}{Rk_0}\right),
\]

where \( S \) = rate of thermal scanning, \( E_{\text{act}} \) is the effective activation energy for the process associated with the peak, \( T_p \) is the peak temperature of process completion, \( R \) is the gas constant and \( k_0 \) is the pre-exponential factor in the Arrhenius equation for the rate constant \( k \). From the slope of the Kissinger plot shown in figure 4(a), activation energy was found to be 88 kcal mol\(^{-1}\). The time constant for the primary crystallization process was also determined from Kissinger analysis [4] and shown in figure 4(b). A good linear fit with a correlation factor \( (R) = 0.99 \) was obtained with the following
expression:

\[ \ln \tau = 44.51 \times 10^3 \times \frac{1}{T} - 45.84. \]  

The stability of the amorphous phase at any desired temperature could be obtained using equation (2).

Besides thermodynamic behaviour measured through DSC, electron transport properties were also observed from thermal variation of electrical resistivity (TER). The TER plot of the as-cast bulk amorphous alloy from room temperature to 1000 K obtained at a heating rate of 10 K min\(^{-1}\) is shown in figure 5. Thermal scanning initially showed a continuous increase in electrical resistivity with a gradual slope change at \(T_s\) that was identified to be the softening temperature which is also shown in a magnified scale in figure 6. Beyond 750 K shown in figure 5, the as-quenched alloy indicated distinct changes in the profile of resistivity. The first one was observed at the glass transition temperature \(T_g\) where a drastic lowering of electrical resistivity took place. Subsequently, the first and the second crystallization temperatures showed resistivity drops at 845 K and 1005 K, respectively. The thermal variation of resistivity for the sample annealed at 825 K and 875 K that were above its \(T_g\) and \(T_{X1}\) were also obtained and shown in figure 5. Both the crystallization temperatures increased with the increase in annealing temperatures. However, such drop in resistivity at \(T_g\) was not shown by these annealed samples.

3.2. Curie temperature and soft magnetic properties

The Curie temperature of the as-quenched bulk amorphous alloy was measured from thermal variation of ac susceptibility. The susceptibility values were normalized with respect to room temperature and the plot is shown in figure 7. The sharp drop in the plot indicated ferromagnetic to paramagnetic transition of the as-quenched material. The Curie temperature value

Figure 4. Plots of (a) Kissinger’s and (b) time constant obtained for bulk amorphous Fe\(_{72}\)Si\(_4\)B\(_{20}\)Nb\(_4\) alloy.

Figure 5. Thermal variation of electrical resistivity plot of bulk amorphous Fe\(_{72}\)Si\(_4\)B\(_{20}\)Nb\(_4\) alloy in as-cast state and after annealing at 825 and 875 K.

Figure 6. Thermal variation of electrical resistivity plot of bulk amorphous Fe\(_{72}\)Si\(_4\)B\(_{20}\)Nb\(_4\) alloy in as-cast state and after annealing at 775 and 795 K.

Figure 7. Thermal variation of ac susceptibility plot of bulk amorphous Fe\(_{72}\)Si\(_4\)B\(_{20}\)Nb\(_4\) alloy.
Bulk amorphous Fe<sub>72</sub>Si<sub>4</sub>B<sub>20</sub>Nb<sub>4</sub> alloy. The coercivity value estimated from the derivative of the ac susceptibility plot was found to be 595 K.

Figure 8(a) shows the hysteresis loop of the as-quenched bulk amorphous Fe<sub>72</sub>Si<sub>4</sub>B<sub>20</sub>Nb<sub>4</sub> alloy. The coercivity value measured from its saturating value with a magnetizing field (inset of figure 8(a)) was found to be 212 mOe, revealing the superior soft magnetic nature of the bulk amorphous alloy. The alloy also exhibited fairly high saturation induction ~12 kG as seen from the high field magnetization curve shown in figure 8(b).

4. Discussion

4.1. The supercooled region and undercooling

Bulk metallic glasses can be produced by casting at low cooling rates from the amorphous state for such alloy systems having a wide supercooled liquid region. In this process the melt is undercooled from the melting temperature whereby the quench rate appreciably suppresses crystallization to maintain the random atomic ordering up to glass transition temperature and even lower. Such a critical aspect of maintaining the glassy structure to obtain bulk metallic glasses can be addressed in terms of two significant thermodynamic parameters, (i) the supercooled region associated with glass transition below crystallization and (ii) the reduced glass transition temperature correlated to glass transition with respect to the low-lying eutectics.

The present as-quenched Fe<sub>72</sub>Si<sub>4</sub>B<sub>20</sub>Nb<sub>4</sub> alloy exhibited a distinct glass transition temperature, \( T_g \) before the onset of crystallization, \( T_X \) as observed from DSC (figure 3) and thermal electrical resistivity (TER) plots (figure 5). Their characteristic temperatures calculated from DSC and TER measurements are summarized in Table 1. The reduced glass transition temperatures calculated through these techniques with respect to the melting point (\( T_M \)) of the alloy is also indicated in the table.

Using both techniques it is found that the amorphous alloy exhibited a fairly wide supercooled region \( \Delta T_X \) between the first crystallization onset \( T_{X1} \) and glass transition \( T_g \) [6]. The values of the super cooled region \( \Delta T_X \) were 50 and 60 K as determined from DSC and TER profiles, respectively. This may be attributed to the selection of an optimum concentration of B equal to 20 at% in the present alloy in view of same concentration of boron providing the highest supercooling range in Fe<sub>91</sub>xZr<sub>9</sub>B<sub>x</sub> (x = 0 to 30 at%) alloys [7, 8]. Such high order of \( \Delta T_X \) has also been observed recently in other magnetic bulk amorphous alloys [9–11]. This large value of supercooled region is helpful in enhancing the stability against crystallization and thus high glass forming ability (GFA). Such stability of the bulk amorphous alloy at different temperatures between \( T_g \) and \( T_X \) has been derived from the equation of time constant (equation 2) and shown in figure 9. From TER data (table 1), annealing at \( T_g \) and 10 K above it reduced the stability against crystallization from 868 min to 425 min (figure 9(a)), respectively. Above 810 K both TER and DSC (figure 9(b)) revealed a nonlinear reduction in stability time with temperature which is an important parameter for the use of the bulk amorphous alloy at different thermal environments.

Alloys with high GFA have low nucleation tendency for subsequent crystallization. Another significant thermodynamic parameter that determines the nucleation tendency in glass forming alloys is their reduced glass transition temperature, \( T_{rg} \) [12]. The reduced glass transition temperature, \( T_{rg} \) is given by the ratio of the glass transition temperature, \( T_g \) to the melting temperature, \( T_M \). The melting temperature of the present alloy as obtained from DTA was 1404 K. Using the \( T_g \) values obtained from DSC and TER measurements, the corresponding reduced glass transition temperatures \( T_{rg} \) were calculated and shown in Table 1. Both the techniques validate highly

<table>
<thead>
<tr>
<th>Characteristic temperatures (K)</th>
<th>Characteristic temperatures of as-quenched alloy calculated from DSC and TER measurements.</th>
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</thead>
<tbody>
<tr>
<td>( T_g )</td>
<td>810 \quad 785</td>
</tr>
<tr>
<td>( T_{X1} )</td>
<td>860 \quad 845</td>
</tr>
<tr>
<td>( T_{X2} )</td>
<td>938 \quad 1005</td>
</tr>
<tr>
<td>( \Delta T_X (T_{X1} - T_g) )</td>
<td>50 \quad 60</td>
</tr>
<tr>
<td>( T_{rg} ) (= ( T_g/T_M ))</td>
<td>0.58 \quad 0.56</td>
</tr>
</tbody>
</table>

![Figure 8](image-url)
reduced glass transition temperature values of 0.56–0.58 which is around the critical value of 0.60 required for the formation of bulk glassy alloys [13]. The values of the supercooled region, \( \Delta T_X = 50–60 \) K and the reduced glass transition temperature, \( T_{rg} = 0.56–0.58 \) obtained in the present Fe\(_{72}\)Si\(_4\)B\(_{20}\)Nb\(_4\) bulk amorphous alloy are in conformity with their empirical relation obtained for the other glass forming alloys [6, 14]. These high \( \Delta T_X \) and \( T_{rg} \) values from our findings correspond to the critical low cooling rate of \( 10^2–10^3 \) K s\(^{-1}\) reported for a range of bulk amorphous systems [15]. Such low cooling rates, feasible even through the copper mould casting technique as in the present case, open the scope of developing bulk amorphous materials from the well-known FeSiB systems with due incorporation of elements like Nb.

4.2. Electron transport properties

In bulk amorphous alloys the various significant phenomena like glass transition temperature, \( T_g \) and crystallization temperature, \( T_X \) have been more often investigated through thermodynamic functions involving inflection in specific heat during transformation. Few reports address the effect of electron transport phenomena around these characteristic temperatures as in the case of some Pd-based metallic glasses [16, 17]. In an effort to investigate such phenomena in the present bulk amorphous Fe\(_{72}\)Si\(_4\)B\(_{20}\)Nb\(_4\) alloy, the profile of electrical resistivity variation in as-quenched material in figure 5 was analysed and the temperature coefficients around the characteristic temperatures are shown in table 2. It was observed that scanning from room temperature, the electrical resistivity increased rapidly. The Curie temperature, \( T_C \), determined from ac susceptibility shown in the plot did not present any change in the electrical resistivity variation.

However, a slope change in the profile beyond \( T_g \) equal to 710 K was noticed in the as-quenched amorphous alloy (figure 6) whereby there was a reduction in the temperature coefficient of electrical resistivity from \( \alpha_1 \) to \( \alpha_2 \). The decrease in resistivity beyond \( T_g \) is attributed to the onset of mechanical softening [18] and consequent thermal expansion [19]. This was due to the fact that the x-ray diffractogram shown in figure 10 revealed a broad halo, a characteristic of amorphous structure of the sample annealed at 775 K. As an outcome of this mechanical softening, there was an onset of the structural relaxation process above \( T_g \) which led to increased electrical conductivity and lowering of resistivity. However, such change in resistivity (figure 6) was not observed in the samples annealed at \( T_{a1} = 775 \) K and \( T_{a2} = 795 \) K which were just below and above \( T_g = 785 \) K. This confirms the fact that in these samples, the structural relaxation effect that was very pronounced close to the glass transition temperature could not be noticed due to release of stresses when annealed around \( T_g \).

Beyond the glass transition temperature, \( T_g \), the change in electron transport behavior became very significant. The electrical resistivity exhibited a drastic decrease above \( T_g \) shown by a negative temperature coefficient \( \alpha_3 \). At this subsequent higher temperature above \( T_g \) there was an enhanced effect of mechanical softening as the viscosity of the material decreased very rapidly. This decrease in viscosity led to a greater stress relieving process marked by an increase in the conductivity of electrons leading to a sharp decrease in thermal electrical resistivity at glass transition \( T_g \). Such a decrease in resistivity around \( T_g \) has also been reported by others [19, 20]. This suggests that glass transition is an intrinsic property exhibiting a continuous and significant change in electron transport before amorphous to crystalline transformation occurs. In the present case the transition from a completely supercooled liquid state to a glassy state [21] exhibited a pronounced effect of resistivity decrease in sharp contrast to nucleation of a large volume fraction of nanoparticles that would have offset this decrease by increasing the resistivity due to electron scattering [22]. However, some
incipient nucleation in the nanoscale that cannot be entirely ruled out as observed from the x-ray diffractogram of 790 K annealed alloy (figure 10) indicated narrowing of the broad maximum.

Above 845 K the electrical resistivity once again decreased rapidly in the as-cast sample at the crystallization temperature $T_X$ shown by the DSC onset at 860 K. This decrease in resistivity was due to the disorder to ordering transition [23, 24] arising out of the formation of α-FeSi phase as observed from the x-ray diffractogram of sample annealed at 875 K (figure 10). However, it is noticed that the negative temperature coefficient in the case of crystallization-induced resistivity $\alpha_R$ was lower compared with that of glass transition induced TCR of $\alpha_3$ occurring above $T_g$. This spontaneously implies that conduction of electrons beyond $T_g$ was much higher than that above $T_X$ that may be attributed to higher electron conduction after enhanced stress relaxation around glass transition [25] as compared with the ordering of atoms during crystallization.

4.3. Soft magnetic and mechanical properties

The soft magnetic properties of the present bulk amorphous alloy was determined in its as-cast state.

Table 3: Soft magnetic and mechanical property of bulk amorphous alloy.

<table>
<thead>
<tr>
<th>Magnetic properties</th>
<th>Mechanical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curie temperature (K)</td>
<td>Coercivity (mOe)</td>
</tr>
<tr>
<td>595</td>
<td>212</td>
</tr>
</tbody>
</table>

Table 3 showing a summary of the magnetic and mechanical properties of the bulk amorphous alloy.

From the application point of view it is interesting to find that besides revealing a medium Curie temperature of 595 K and saturation induction of 12 kG, the material exhibited fairly superior soft magnetic properties with a low coercivity value of 212 mOe. This superior soft magnetic property compared with the conventional crystalline materials was also coupled with a very high mechanical hardness of 1250 Hv. This value is much higher compared with those of fairly hard crystalline soft magnetic materials like sendust (Fe : Al : Si :: 85:5:10) showing mechanical hardness in the range of 400–600 Hv [26]. Only some of the Fe-based amorphous systems like Fe₈₀B₉₀ and Fe₇₈B₇₈Si₁₂ show high Hv values of 1080 and 910, respectively [27]. Such high hardness in bulk amorphous alloys are attributed to the dense random packing of hard spheres (DRPHS) of atoms for amorphous structure. Besides this fundamental structural advantage of amorphous systems, in the present case the high mechanical hardness is due to consequent restriction to crystallization as observed from the highly reduced glass transition temperature $T_g$ of 0.56–0.58. The isotropy from these amorphous structures and wide supercooled region of 50–60 K led to the superior soft magnetic property [28]. The low magnetic softness coupled with high mechanical hardness opens up the scope for the bulk amorphous Fe₇₂Si₁₂B₇₀Nb₄ alloy in applications demanding soft magnetic properties and robustness.

5. Conclusion

The properties of bulk amorphous Fe₇₂Si₁₂B₇₀Nb₄ alloy in the form of rods were investigated. Before the onset of crystallization, the amorphous alloy showed distinct glass transitions from calorimetric and electrical resistivity measurements. These studies indicated a wide supercooled range, $\Delta T_X$ of about 50–60 K lower than the crystallization temperature. Such a wide supercooled region is helpful in developing a bulk amorphous alloy. Thermal scanning showed a sharp drop in electrical resistivity around the glass transition temperature. With the increase in temperature, such enhanced electrical conductivity was due to the stress relaxation effects arising from viscosity decrease around the glass transition. The subsequent decrease in electrical resistivity was due to crystallization-induced ordering. The alloy also exhibited a high value of the reduced glass transition temperature, $T_g$ of 0.56–0.58 which is attributed to the high isotropic dense atomic structure of the bulk amorphous alloy. The material displayed nonlinear thermal stability between the glass transition and crystallization temperature. The bulk amorphous alloy showed excellent soft magnetic properties with low coercivity of 212 mOe, saturation induction of 12 kG, moderate Curie temperature of 595 K and high mechanical hardness of 1250 Hv. These potential properties open up the scope of the material as a robust soft magnetic component.

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