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A potential Co$_{36}$Fe$_{36}$Si$_4$B$_{20}$Nb$_4$ nanocrystalline alloy for high temperature soft magnetic applications

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The paper addresses the structural, crystallization, soft magnetic and Curie temperature behaviour of Co$_{36}$Fe$_{36}$Si$_4$B$_{20}$Nb$_4$ alloy. The material, prepared in the form of ribbons by melt-spinning technique, was amorphous in the as-cast state. Differential scanning calorimetry (DSC) showed two stages of crystallization whereas thermal variation of electrical resistivity (TER) carried out to a higher range of temperature indicated three stages of crystallization. The first crystallization stage, which occurred at 845 K and 825 K in DSC and TER, respectively, was due to the formation of nanophase (CoFe)$_2$Si as evidenced by X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The formation of these nanoparticles reduced the magnetocrystalline anisotropy, thereby revealing good soft magnetic properties in the samples annealed between 825 K and 875 K with coercivity less than 49.9 A m$^{-1}$ (627 mOe) and susceptibility $\sim 0.72 \times 10^3$. In this optimum nanocrystalline state, the material also exhibited a high Curie temperature above 1100 K, opening the scope of the present nanocrystalline alloy for high temperature applications.

1. Introduction

In recent years there has been an increasing demand for soft magnetic materials in applications like rotor assemblies as well as the magnetic bearings of auxiliary power supplies in aircraft engines, high-frequency transformers and space power systems which encounter high temperatures during operation [1]. The conventional materials used for such applications were mainly polycrystalline materials such as the 50CoFe Permendur alloy that contains a high content of expensive cobalt and is brittle. Although ductility was achieved in materials like Hiperco-50 (49Co–49Fe–2V) by incorporation of vanadium, its addition not only lead to rapid deterioration in energy efficiency due to magnetic losses but also degraded its soft magnetic properties. Hence, these materials, although they had a high Curie

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temperature, ~1000 K, had inferior soft magnetic properties with coercivity above 1000 mOe [2, 3].

The enhancement in soft magnetic properties underwent a significant breakthrough with the advent of amorphous magnetic materials bearing low or negligible crystalline anisotropy. In subsequent developments, in addition to lowering of crystalline anisotropy, control of magnetostriction and higher electrical resistivity could be achieved in the new generation of FeNbCuSiB-based nanocrystalline systems [4]. These additional features increased the potential of these Fe-based nanocrystalline alloys in applications like transformer cores, choke coils, magnetic sensors, etc. [5], operating around room temperature. However, at elevated operating temperatures these materials lose their ferromagnetic stability due to their Curie temperature being below 700 K [6]. Hence, subsequent reports suggested the incorporation of Co in FeZrB-based systems [7–9] with a typical composition of Co_{44}Fe_{44}Zr_{7}B_{4}Cu. These alloys, although they have a fairly high Curie temperature above 1000 K, demand considerable attention due to the presence of oxidation-prone Zr in the system. In view of these limitations there was simultaneous work on the addition of Co to FeCuNbSiB-based nanocrystalline systems [10, 11]. In these alloys the data on enthalpy of mixing suggest that in comparison to Fe, the element Co has more affinity towards Cu [12, 13]. Therefore, the presence of Cu as a nucleating element is not required when Co is incorporated in the alloy system.

With due consideration of an element which would not only raise magnetic stability but also function as a nucleating element, the present work addresses structural and soft magnetic properties of an alloy where iron has been substituted by cobalt in the FeSiBNb system. This simple alloy system with minimum number of components was chosen in order to reduce structural complexities.

2. Experimental

The Co_{36}Fe_{36}Si_{4}B_{20}Nb_{4} alloy was prepared in the form of ribbons by the melt-spinning technique. As these rapidly quenched ribbons are in a metastable state, their crystallization behaviour was investigated using a differential scanning calorimeter (Perkin-Elmer DSC-7). The electron transport properties during transformations were evaluated from thermal variation of electrical resistivity (Sinku Riko, TER-2000) measurements. Different phases generated during crystallization were identified using X-ray diffractometer (Siefert-PTS 3030) with Mo-Kα radiation. Structural evolutions were observed using transmission electron microscopy (Philips, CM-200). Magnetic coercivity was measured from the hysteresis loop obtained in open-flux configuration at a quasi-dc magnetizing frequency of 50 mHz. The ac susceptibility was measured using a lock-in amplifier (PARC, Model 5209), which was also used to determine the Curie temperature from the thermal variation in ac initial susceptibility. The samples for magnetic and structural studies were annealed at different temperatures in argon atmosphere for 15 min using an infrared gold image furnace.
3. Results and discussion

3.1. Crystallization behaviour

3.1.1. Differential scanning calorimetry (DSC). The DSC plot of the Co$_{36}$Fe$_{36}$Si$_{4}$B$_{20}$Nb$_{4}$ (at.%) as-cast ribbon obtained at a heating rate of 20 K min$^{-1}$ in argon atmosphere is shown in figure 1. The DSC exotherms indicate two stages of crystallization represented by temperatures $T_X1$ and $T_X2$ at 845 K and 930 K, respectively. The alloy also exhibited a distinct glass transition ($T_g$) with an onset of an endothermic peak at 800 K. The $T_g$, which is attributed to mechanical softening due to lowering of viscosity, was observed about 45K below the first crystallization temperature suggesting a fairly wide supercooled region also observed in some bulk glassy alloys [14].

As the primary crystallization process is the major factor for the change in the magnetic properties, the activation energy involved during this transformation was calculated using a modified Kissinger’s equation [15] written as

$$\ln\left(\frac{T_p}{S}\right) = \frac{E_{act}}{RT_p} + \ln\left(\frac{E_{act}}{Rk_0}\right)$$

where $T_p$ is the peak temperature of exothermic process completion, $E_{act}$ is the effective activation energy for the process associated with the peak, $S$ is the rate of thermal scanning, $R$ is the gas constant and $k_0$ is the pre-exponential factor in the Arrhenius equation for the rate constant $k$. The Kissinger plot shown in figure 2a was obtained with a good linear fit of $\langle R \rangle = 0.99$ from where the activation energy was found to be 83 kcal mol$^{-1}$. The time constant [2] for the primary crystallization
process was also determined from Kissinger analysis and shown in figure 2b. A good linear fit with a correlation factor $R = 0.99$ was obtained with the following expression:

$$\ln \frac{\phi}{T^2} = 41.37 \times 10^3 \times \frac{1}{T} - 42.737$$

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

3.1.2. Thermal variation of electrical resistivity (TER) and structural evolution. Figure 3 shows the TER plot of the Co$_{36}$Fe$_{36}$Si$_4$B$_{20}$Nb$_4$ (at.%) ribbon obtained at a scan rate of 10 K min$^{-1}$ in argon atmosphere. The resistivity data have been normalized with respect to room temperature. The resistivity increased monotonically from room temperature onwards which was attributed to electron–magnon and electron–phonon scattering till the first drop in resistivity was observed at 770 K. This characteristic temperature was identified as the glass transition temperature $T_g$ that was observed at 800 K in the DSC plot. The electrical resistivity exhibited a drastic decrease above $T_g$ shown by a negative temperature coefficient, $\alpha_g$, as reported by other researchers [16–19]. Although the exact phenomenon of electron transport behaviour is yet to be determined, recent reports suggest that such a resistivity drop is due to transition from a state of supercooled random structure with high resistivity to a glassy state with low resistivity [18]. In addition to this theory, it is known that with an increase in temperature, the viscosity drop around the glass transition leads to mechanical softening. As a result of this mechanical softening, stress relaxation takes place thereby increasing the conductivity of electrons leading to a decrease in thermal electrical resistivity at the glass transition, $T_g$. 

Figure 2. Plots of (a) Kissinger’s and (b) time constant for the as-cast Co$_{36}$Fe$_{36}$Si$_4$B$_{20}$Nb$_4$ (at.%) ribbon obtained using different scan rates.
Beyond \( T_g \), the change in electron transport behaviour became very significant and showed rapid changes in the TER profile, as shown in figure 3. The changes in the profile were analyzed and their coefficients of resistivity (TCR) around the characteristic temperatures are shown in table 1. Above the glass transition, the TER plot showed drastic drops in resistivity representing three crystallization stages at \( T_{X1}, T_{X2} \) and \( T_{X3} \), i.e. temperatures of 825 K, 890 K and 1000 K, respectively. The first two crystallizations corroborate with the DSC data; it was beyond the operating range of the DSC instrument to monitor the high temperature transition at \( T_{X3} \).

It was observed that the negative temperature coefficients of resistivity showed an increasing trend beyond \( T_{X1} \). However, it was noted that above \( T_{X1} \) there was a gradual drop in resistivity shown by a slow increase in TCR value from \( \alpha_1 = -3.409 \) to \( \alpha_2 = -4.984 \). This indicates that a phenomenon like electron scattering by nanoparticles [20, 21] occurs beyond \( T_{X1} \), which restricted the drastic decrease in resistivity. This was evidenced from the structural evolution during nanocrystallization of the amorphous state initially shown by salt–pepper contrast in a TEM micrograph (figure 4a) and its corresponding selected area diffraction (SAD) which exhibits the characteristics of diffused ring pattern indicating an absence

![Figure 3. Thermal variation of electrical resistivity plot of as-cast Co\textsubscript{36}Fe\textsubscript{36}Si\textsubscript{4}B\textsubscript{20}Nb\textsubscript{4} (at.\%) ribbon. Scan rate 10 K min\textsuperscript{-1}.](image)

<table>
<thead>
<tr>
<th>Characteristic temperatures (K)</th>
<th>Temperature range (K)</th>
<th>Temperature coefficient, ( \alpha ) (( \times 10^{-4} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_g &lt; T &lt; T_{X1} )</td>
<td>771–807</td>
<td>( \alpha_g ) = 1.537</td>
</tr>
<tr>
<td>( T_{X1} &lt; T &lt; T_{X2} )</td>
<td>825–871</td>
<td>( \alpha_1 ) = 3.409</td>
</tr>
<tr>
<td>( T_{X2} &lt; T &lt; T_{X3} )</td>
<td>891–999</td>
<td>( \alpha_2 ) = 4.984</td>
</tr>
<tr>
<td>( T_{X3} &lt; T )</td>
<td>1001–1025</td>
<td>( \alpha_3 ) = 28.400</td>
</tr>
</tbody>
</table>

Table 1. Temperature coefficients determined from TER measurements.
of crystallinity. A broad maximum in the XRD peak (figure 5) also indicated the amorphous nature of as-cast alloy. When annealed around first crystallization temperature of \( T_{X1} = 825 \text{ K} \), dispersion of nanoparticles (\( \sim 12–15 \text{ nm size} \)) appears within the amorphous matrix. The second phase occurs in the form of isolated islands as well as clusters of varying shape (figure 4b). The distribution of fine second phases within the matrix is confirmed by the presence of few concentric diffraction maxima (figure 4b). The indexed ring pattern indicates the zone axis as \( Z = B = [121] \). The nanoparticles formed at this temperature, as per TER measurements, were identified to be nanophase \((\text{CoFe})_2\text{Si}\) as observed from XRD (figure 5). This nanocrystallization stage was also shown by DSC exotherm (figure 1) at higher

Figure 4. TEM micrograph of the alloy obtained in the (a) as-cast state and (b) annealed at 825 K. SAD pattern shown in the inset.
temperature of 845 K due to its low sensitivity than electrical resistivity measurements.

Beyond the second and third crystallization temperature, \( T_{X2} \) and \( T_{X3} \), respectively, the resistivity drop became drastic with the negative TCR value increasing from \( \alpha_2 = -4.984 \) to \( \alpha_3 = -28.400 \). This rapid fall in resistivity was attributed to ordering phenomena occurring during amorphous to crystalline transformation [22]. In the presence of nanophase \((\text{CoFe})_2\text{Si}\) formed at \( T_{X1} \), X-ray diffractograms of material annealed around 875 K showed the formation of such crystalline phases like \((\text{CoFe})_3\text{B}\). Further ordering due to formation of fcc Co and \((\text{CoFe})_3\text{Nb}\) phases at 925 K also shown in XRD plot was the cause of drastic decrease in resistivity around the third crystallization temperature \( T_{X3} = 1000 \) K.

3.2. Magnetic behaviour

3.2.1. Soft magnetic properties. Figure 6 shows the effect of annealing on the coercivity and ac susceptibility of the as-cast \( \text{Co}_{36}\text{Fe}_{36}\text{Si}_{4}\text{B}_{20}\text{Nb}_{4} \) (at.\%) alloy.
On heat treatment above room temperature, the material did not show any significant change in coercivity. However, the susceptibility value showed an increasing trend with annealing up to 800 K owing to its measurement at low applied field that bore a sensitive change to magnetoeleastic anisotropy. Hence, the improvement in soft magnetic property below the first crystallization onset was attributed to structural relaxation. At an annealing temperature of 825 K, the alloy exhibited soft magnetic properties with coercivity \( \sim 14 \text{ A m}^{-1} \) (175 mOe) and susceptibility \( \sim 4 \times 10^3 \). The \((\text{CoFe})_2\text{Si}\) nanoparticles of \( \sim 12–15\text{ nm} \) in size formed at this temperature (figure 6) have a tendency to randomly average out their individual anisotropies and thereby reduce the overall anisotropy of the system to exhibit soft magnetic properties [23]. According to this model, the relation between coercivity and magnetocrystalline anisotropy of the nanoparticles derived from effective anisotropy of the system [24] could be approximated as

\[
H_c = P_c \frac{K_1 D^6}{A^3 J_s}
\]

where \( P_c \) is a pre-factor that according to the fine-particle theory becomes 0.64. \( K_1 \) is the magnetocrystalline anisotropy of the nanoparticles, which is \( 8 \text{ kJ m}^{-3} \) [25]. \( A = 10^{-11} \text{ J m}^{-1} \) [26] is the exchange stiffness constant of the system. In the present \( \text{Co}_{36}\text{Fe}_{36}\text{Si}_{4}\text{B}_{20}\text{Nb}_{4} \) (at.\%) alloy, \( J_s \) was found to be 1.13 T obtained from approach to saturation at high magnetizing field. \( D \) is the particle size which was \( \sim 14 \text{ nm} \) for sample annealed at 825 K. With the above material parameters, coercivity was calculated according to equation (3) and was found to be 17.44 A m\(^{-1}\), close to the experimental value of 14.01 A m\(^{-1}\).

Annealing beyond 825 K up to 875 K led to gradual deterioration in soft magnetic properties with increase in coercivity and a decrease in susceptibility which may be attributed to increase in size of \((\text{CoFe})_2\text{Si}\) nanoparticles. However, in this temperature range, the thermal degradation of soft magnetic properties was slow.
enough to corroborate its effect with the retarded growth of (CoFe)$_2$Si nanoparticles. Such restriction to anomalous growth of nanoparticles was brought about by the presence of large sized refractory element Nb [27]. The distribution of these slowly growing nanoparticles even up to 875 K were effectively averaging their individual anisotropy thereby reducing the net anisotropy of the system and thus maintaining fairly soft magnetic properties with coercivity $\sim 627$ mOe (49.90 A m$^{-1}$) and susceptibility $\sim 0.72 \times 10^3$.

Above 875 K, magnetic hardening became prominent with a rapid increase in coercivity and corresponding decrease in susceptibility. This deterioration in the soft magnetic properties above 875 K is attributed to the formation of strongly anisotropic boride phases identified using X-ray analysis (figure 5). The magnetic degradation became drastic above 925 K which was caused not only by to the enhanced anisotropy with the formation of additional fcc Co and (CoFe)$_3$Nb crystalline phases but also by their rapid growth which impeded domain wall movement.

3.2.2. Curie temperature. With consistent soft magnetic properties revealed by the present alloy, Curie temperature behaviour was a significant issue for high temperature applications. For this, thermal variation of ac susceptibility was measured for the as-cast and annealed ($T_A$) samples, as displayed in figure 7. The sharp drop in the susceptibility indicated the transformation of the material from ferromagnetic to paramagnetic state. The Curie temperature was calculated from the derivative of the normalized susceptibility plot, indicated by an arrow in figure 7. Up to an annealing temperature of 800 K the first transitional drop at 700 K did not indicate any change in the Curie temperature of the amorphous phase. However, annealing in the range between 825 K and 875 K raised the Curie temperature of the amorphous matrix from 715 K to 775 K. The initial drop in ac susceptibility was followed by an increase in susceptibility above 825 K, as shown in figure 8 after re-scaling, indicating structural modification. This subsequent ferromagnetic ordering state indicated that the Curie temperature was above 1000 K. The increase of magnetization with annealing indicated that the (Co$_x$Fe$_{1-x}$)$_2$Si nanoparticles were formed after annealing. With progressive heating there was a change in this stoichiometry till the magnetization level became considerably high with the ratio of Co : Fe approaching $1 : 1$ [28].

TEM and X-ray analysis confirmed that this magnetization increased due to the formation of (CoFe)$_2$Si nanophase. The increase in volume fraction of this nanophase with further annealing to 875 K showed prominent increase in ferromagnetic ordering (figure 7) with increase in ac susceptibility above 900 K. The present Co$_{36}$Fe$_{36}$Si$_4$B$_{20}$Nb$_4$ (at.%) alloy showed a Curie temperature above 1100 K which is much higher than the Fe-based alloys. A typical comparison of Curie temperature behaviour with that of our earlier reported Fe-based alloy [6] is shown in figure 9. In the Fe-based alloy, the initial drop in the susceptibility indicating a ferromagnetic–paramagnetic transition of the amorphous matrix was much lower compared to the present CoFe-based alloy. Even after nanocrystallization, the Curie temperature of the Fe-based alloy was below 700 K, attributed to depletion of iron from the amorphous matrix. However, in the Co$_{36}$Fe$_{36}$Si$_4$B$_{20}$Nb$_4$
Figure 7. Thermal variation of normalized ac susceptibility plots of alloy in the as-cast state and at different heat annealing temperatures, $T_A$.

Figure 8. Thermal variation of normalized ac susceptibility plot of alloy at annealing temperature of 825 K showing high temperature ferromagnetic transitions.
(at.%) alloy such depletion of Fe from the amorphous matrix was compensated by the presence of Co that did not allow rapid loss in ferromagnetic ordering of the amorphous phase. As a result, there was an enhanced ferromagnetic coupling between (CoFe)$_2$Si nanoparticles via the amorphous matrix leading to increase in Curie temperature of the system. The noticeable depletion of Co together with Fe takes place to form (CoFe)$_3$Nb at much higher temperature of 925 K whereby the Curie temperature of the amorphous matrix is reduced from 775 K to 660 K, as observed in figure 7. In the 925 K annealed sample, this reduced Curie temperature of the amorphous matrix had a tendency to decouple the ferromagnetic nanoparticles, thereby leading to greater drop in magnetization as compared to 825 K and 875 K annealed samples.

4. Conclusion

A Co$_{36}$Fe$_{36}$Si$_4$B$_{20}$Nb$_4$ (at.%) nanocrystalline alloy was prepared in the form of amorphous ribbons by the melt-spinning technique. Differential scanning calorimetry (DSC) and thermal variation of electrical resistivity (TER) studies indicated a glass transition stage before the occurrence of subsequent crystallization stages. In the optimum heat-treatment temperature range of 825–875 K, the Curie temperature of the amorphous alloy increased with the generation of a ferromagnetic nanocrystalline phase. Microstructural study of 825 K annealed material indicated the formation of 12–15 nm sized (CoFe)$_2$Si nanoparticles dispersed in the amorphous matrix. In the optimum nanocrystalline state, the nanophase not only raised the overall magnetization of the alloy system with a Curie temperature above 1100 K but also revealed good soft magnetic properties with coercivity below 49.9 A m$^{-1}$ (627 mOe) and susceptibility $\sim 0.72 \times 10^3$. 

Figure 9. Thermal variation of normalized ac susceptibility plot of CoFe and Fe-based alloy after annealing at 875 K.
The combination of high Curie temperature and superior soft magnetic properties makes the material a potential candidate for high temperature soft magnetic applications.

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