Magnetic induction heating of FeCr nanocrystalline alloys

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ABSTRACT

In this work the thermal effects of magnetic induction heating in (FeCr)_{73.5}Si_{13.5}Cu_{1}B_{9}Nb_{3} amorphous and nanocrystalline wires were analyzed. A single piece of wire was immersed in a glass capillary filled with water and subjected to an ac magnetic field (frequency, 320 kHz). The initial temperature rise enabled the determination of the effective Specific Absorption Rate (SAR). Maximum SAR values are achieved for those samples displaying high magnetic susceptibility, where the eddy current losses dominate the induction heating behavior. Moreover, the amorphous sample with Curie temperature around room temperature displays characteristic features of self-regulated hyperthermia.

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1. Introduction

High frequency (radio frequency, rf) induction heating represents a topic of growing interest during the last decade. Their main interest ranges within the biomedical applications in the design of new cancer therapies based on the fluid suspensions of ferromagnetic nanoparticles (magnetic hyperthermia) [1]. However, rf induction heating is a widely employed technique in different industrial applications ranging from the steel industry [2], household appliances (cooking) [3] or plastic industry [4]. Among these applications the ferromagnetic based composites (i.e. magnetic nanoparticles dispersed in polymer matrices) stand out, in the biomedical field (magnetic hyperthermia, cancer therapy) [5] and in the polymer industry (sealing, curing and repairing of polymers/epoxies) [6,7].

Magnetic induction heating is based on the heat generated as a consequence of the application of an alternating (ac) field to a magnetic material, both in bulk form (i.e. bars or needles) and nanoparticle systems. In bulk form, eddy-current losses dominate the rf dissipation behavior [8]. However, for magnetic nanoparticles in a viscous medium, the heat dissipation is mainly determined by the Néel and Brownian relaxations [9]. The use of ferromagnetic implants for magnetic hyperthermia, and in particular the necrosis of solid tumors, was recognized some decades ago as an adjuvant cancer therapy in the treatment of solid tumors [8,10–12]. Due to their multifunctional capacities (MRI resonance imaging, targetable drug carriers), the main recent efforts in this field have been focused on the study and applications of magnetic nanoparticles [13]. However, there are some aspects that prevent their extensive application in clinical use, as toxicity or inhomogeneous distribution in tumors. In fact, the achievement of a homogeneous temperature distribution represents the main challenge regarding solid tumor treatments [14]. In this sense, ferromagnetic needles have been recently shown to display higher efficiency rates than iron oxide ferromagnetic nanoparticles [15]. Therefore, the use of ferromagnetic implants in inductive heating applications, as hyperthermia treatments, represents a renewed research topic in the biomedical field. Besides the spatial distribution, the temperature control and stability is an additional parameter to take into account in the design of optimum rf heating systems. Accordingly, self-regulated systems have been proposed, where the Curie point of the ferromagnetic component controls the maximum heating temperature [16–19].

The main aim of the work is to explore the rf self-heating features in ferromagnetic FeCrSiBCuNb amorphous and nanocrystalline wires. The results indicate that the eddy-current losses basically dominate the induction heating phenomena. Moreover, in these alloys the control of the Curie temperature through the Cr content of the amorphous phase [20] enables the design of self-regulated rf induction systems.

2. Experimental procedure

Amorphous wires with nominal composition Fe_{73.5-x}Cr_{x}Si_{13.5}Cu_{1}B_{9}Nb_{3} (x=3, 7 and 10) were prepared by in-rotating-water quenching technique (diameter ≈ 130 μm). The devitrification process of the initial amorphous state was followed by Differential Scanning Calorimetry. The crystallization process takes place in two main
steps at $T_{a1}$ and $T_{a2}$ correlated to the precipitation of $a$-FeSi and boride phases, respectively [21]. The increase of the Cr content of the alloy promotes a shift of the first crystallization process towards higher temperatures [22]. The nanocrystalline structure, obtained through isothermal annealings at annealing temperatures $T_a \approx T_{a1}$, was confirmed through X-ray diffractometry in the annealed samples. Mean grain sizes around 10 nm were estimated in the nanocrystalline state through the Debye–Sherrer formula. Four samples were analyzed: one commercial FeSi and two nanocrystalline samples with $x=7$ and different crystalline fractions, $Cr_{7}nano(1)$ and $Cr_{7}nano(2)$ ($T_{ca}=818$ K, annealing time, $t_a=90$ and 210 min, respectively). With respect to the magnetic characterization, the temperature dependence of the self-inductance, $L$, was determined through a commercial LCR meter at 10 kHz and a ac excitation voltage of 1 V. An induction method was employed to determine at room temperature the ac hysteresis loops and the magnetic susceptibility, $\chi$ ($f=100$ Hz, amplitude magnetic field 95 A/m). The induction method consists of a long solenoid (1.2 (kA/m)/A) and two secondary coils (2000 turns) connected in series-opposition. In the case of the ac hysteresis loops the pick-up voltage was suitably integrated using a fluxmeter, while in the susceptibility measurements it was analyzed through a lock-in amplifier. The electrical resistivity, $\rho$, of the wires was determined through a four-probe technique. The heating effects on the wires were analyzed under the application of an ac magnetic field, $H_{ac}$, with the help of a home-made hyperthermia set-up. A single piece of wire (length, $l=5 \times 10^{-3}$ m, mass, $m_{w}=1.7 \times 10^{-3}$ kg) was immersed in a glass capillary filled with water. The capillary was subjected to the ac magnetic field generated by a water refrigerated coil and connected to a RF power amplifier (see Fig. 1). The temperature increase ($\Delta T=T(t)-T_0$, $T_0=291$ K) was registered as a function of time ($t$), using a fiber optic thermometer under the action of $H_{ac}$ (frequency 320 kHz). The measurements were repeated 5 times in order to estimate the mean heating response of the samples.

3. Results and discussion

Fig. 2a displays the temperature dependence of the self-inductance, $L$, for the wires in amorphous state. At this low frequency excitation ($f=10$ kHz), the skin effect can be disregarded and the electrical impedance can be expressed as

$$Z=R+i2\pi fL=R_{dc}+i(\langle E_z \rangle / I)l,$$

where $R_{dc}$ is the electrical resistance of the wire, $l$ the sample length, $I$ the electrical current flowing through the sample and $\langle E_z \rangle$ the average electrical field originated by the circumferential magnetization process ($\langle E_z \rangle \propto \mu_d$, circumferential magnetic permeability). Therefore, since $\mu_d(T)$ is the temperature dependence can be employed to determine magnetic transitions leading to sharp changes in $\mu_d(T)$ (i.e. the Curie temperature $T_C$) [23] or the martensitic transformation in ferromagnetic shape memory alloys [24], Fig. 2a shows that the Curie temperature can be easily characterized in the soft magnetic amorphous wires by a sharp decrease in $L$ around $T_C$. As previously reported, the substitution of Fe by Cr in the initial amorphous state promotes a linear decrease in the Curie temperature, $T_C$, of the alloy: $T_C(K)=630-30x[K%/Cr]$. Thus, for $x=10$ the amorphous alloy displays a Curie point around room temperature. With respect to the nanocrystalline state, it is extensively reported the occurrence of a magnetic transition associated with the magnetic decoupling process of the ferromagnetic crystallites around the Curie temperature of the residual amorphous phase, $T_{ca}$ [24–26]. This magnetic transition leads to a sharp decrease in $\mu_d$ at temperatures around $T_{ca}$ and can be characterized by a parallel abrupt diminution in L. Fig. 2b shows the temperature dependence of $L$ for the nanocrystalline wire with $x=7$ (annealing temperature, $T_{ca}=818$ K) and two different crystalline fractions (annealing time, $t_a=90$ and 210 min, $Cr_{7}nano(1)$ and $Cr_{7}nano(2)$, respectively). As expected, the nanocrystallization process leads to a significant decrease in $T_{ca}$ as a consequence of the enrichment in Cr of the residual amorphous phase. Thus, the Curie point of the residual amorphous phase can be suitably controlled through the annealing conditions. In particular, values of $T_{ca}$ around 300 K are achieved in the nanocrystalline wire ($x=7$) for the highest annealing times ($Cr_{7}nano(2)$).

With respect to the induction heating characteristics of the wires, Fig. 3 shows the temperature rise, $\Delta T$, (from $T_0=291$ K versus time, $t$, under the action of the ac magnetic field (amplitude 4 kA/m). Maximum $\Delta T$ values are found for the amorphous wire with $x=3$ ($Cr_{3}amorp$) and the nanocrystalline sample $Cr_{7}nano(1)$ ($T_{ca} \geq 350$ K). For comparison, the heating curve of a Cu wire with similar mass and geometric characteristics is also displayed. The detected slight temperature decrease should be correlated to the effect of the coil refrigeration. Therefore, the observed heating effects in the FeCr wires should be interpreted as a direct consequence of the ferromagnetic nature of the samples.

The obtained results indicate that the experimental set-up departures from an ideal adiabatic zero thermal losses calorimeter. Under the ideal adiabatic conditions, the achieved temperature, $T$, under the application of the ac magnetic field should linearly increase as a function of time, $t$ [27]. However, the experimental data can be suitably fitted to an exponential law:

$$\Delta T = T(t)-T_0 = A-Be^{-ct}$$

(1)

This exponential law can be derived taking into account the modified heat equation considering the heat transfer...
contribution [28]:

\[
\frac{dT}{dt} = mc_p \frac{dT}{dt} + \frac{1}{R_e} (T - T_0)
\]  

with \(Q\) the thermal energy (heat), \(mc_p = m_i c_w + m_{H_2O} c_{H_2O}\) (\(m_i\) and \(c_i\): mass and specific heat for \(i = w\) and \(H_2O\), wire and water, respectively). The second term in Eq. (2) represents the heat transfer with the environment, where \(R_e\) is the thermal resistance that in the case of radial heat transfer with cylindrical geometry is given by \(R_e = L n(r/T_0) / 2 \pi L k\) (\(L\): axial length, \(r\) and \(t_0\) radial coordinates at \(T\) and \(T_0\) respectively), being \(k\) the thermal conductivity and \(T_0\) the external or environment temperature [29]. This thermal resistance would comprise the heat transfer within the wire and the water bath. Thus, the total heat generated by the ferromagnetic wires can be expressed as that absorbed by the water and the transferred losses to the environment. If we considered \(T'\) as that displayed in Eq. 1 with \(m_i\) and \(c_i\) the solution of Eq. (3) displays an exponential time dependence \((t \rightarrow \infty)\) and the time constant \(\gamma = \sqrt{1/\pi L k}\). Table 1 displays the fitting parameters obtained from the experimental curves of Fig. 3. As expected from the above discussion, the fitting parameters fulfill \(A \approx B\). Those samples with the highest Curie temperatures of the amorphous phase (\(Cr_3amorp\) and \(Cr_7nano(1)\)) display maximum \(T_{max} - T_0\) values. Moreover, since the wires display similar geometrical features and equivalent bath water mass is employed, the time constant \(\gamma\) would come mainly determined by the thermal conductivity of the wires. In metallic systems there is a direct relationship between the thermal conductivity and the electrical resistivity (Wiedemann–Franz law) [30]. Table 1 shows the electrical resistivity, \(\rho\), for the set of the analyzed wires. As expected, the lowest time constant \(\gamma\) is found in the amorphous sample with the highest electrical resistivity.

In order to further analyze the induction heating features of the samples, the equivalent Specific Absorption Rate (SAR) was estimated through the initial slope of the heating curves, \((dT/dt)_{t=0}\) according to the following expression:

\[
\text{SAR} = \frac{m_w c_w + m_{H_2O} c_{H_2O}}{m_w} \left(\frac{dT}{dt}\right)_{t=0}
\]  

with \(m_w = 1.7 \times 10^{-6} \text{ kg},\ m_{H_2O} = 2 \times 10^{-4} \text{ kg},\ c_w = 0.53 \times 10^3\ \text{ J kg}^{-1} \text{ K}^{-1}\) [31] and \(c_{H_2O} = 4.18 \times 10^3\ \text{ J kg}^{-1} \text{ K}^{-1}\). The initial heating rate, \((dT/dt)_{t=0}\), can be easily calculated through the derivation of Eq. (1): \((dT/dt)_{t=0} = (T_{max} - T_0)/\gamma\). Table 1 summarizes the obtained SAR values according Eq. 4 and the calculated \((dT/dt)_{t=0}\) considering \((T_{max} - T_0) = (A + B)/2\). As expected from the analysis of the temperature heating curves (see Fig. 3), maximum SAR \((15.2 \times 10^3 \text{ W/kg})\) is found in the amorphous wire \(Cr_3amorp\) with the highest Curie point. These SAR values are below the reported values in Fe-based nanoparticles [32–34].

The physical mechanisms associated to the induction heating can be classified in three main contributions: (i) eddy-current losses, (ii) magnetic hysteresis losses and (iii) relaxation losses (Néel and/or Brown rotations). In all the cases, the power dissipation (heat) should be interpreted as a consequence of the magnetization lag with respect to the applied magnetic field. In metallic (bulk) implants the eddy-current losses dominate the heating behavior, while the hysteresis and relaxation losses are the main contribution in the case of nanoparticle systems [35,36].

The energy loss associated to eddy-currents in a metallic medium is proportional to the integral of \(\rho_j^2\) \((\rho):\) electrical resistivity, \(j:)\ current density \) over the volume of the material. In particular, at high frequencies when the penetration of the applied ac field is incomplete the power loss, \(P_{ec}\), can be expressed as [37]:

\[
P_{ec} = \varepsilon^* \chi^* / \mu_0 H_{ac}^2
\]  

with \(\mu = \mu_0 (1 + \chi)^\ast\), the static (low frequency) magnetic permeability. However, in the case of hysteresis loss, the power loss is a function of the area of the hysteresis loops [38]:

\[
P_{hys} \propto f \int H dM
\]  

(6)

Finally, the power loss associated to the relaxation losses (Néel and/or Brown rotations) are usually expressed as a function of the imaginary component of the magnetic susceptibility \(\chi^*\):

\[
P_{rel} = \chi^* / \mu_0 H_{ac}^2
\]  

(7)

However, it has been recently shown that Eq. (7) is just a particular case of Eq. (6) under linear response theory \((M\) linear with \(H\)) taking into account the Néel–Brown relaxation times [38].

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**Figure 3.** Temperature rise, \(\Delta T = T(t) - T_0\) \((T_0 = 291 \text{ K})\), as a function of time, \(t\), for the amorphous \((x = 3, \text{ Cr}_3\text{amorp})\) and \(x = 10, \text{ Cr}_3\text{amorp})\) and nanocrystalline wires \((\text{Cr}_7\text{nano}(1): t_0 = 90 \text{ min}, \text{Cr}_7\text{nano}(2): t_0 = 210 \text{ min}, x = 7)\). For comparison the results in a Cu wire are also included. \((H_{ac} = 4 \text{ kA/m})\).

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(A) (K)</th>
<th>(B) (K)</th>
<th>(C) (s(^{-1}))</th>
<th>(\rho) ((\Omega) m)</th>
<th>SAR (W/kg)</th>
<th>(\chi) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cr}_3\text{amorp}) ((x = 3) amorphous)</td>
<td>7.1</td>
<td>7.7</td>
<td>4.3 \times 10^{-3}</td>
<td>1.82 \times 10^{-6}</td>
<td>15.2 \times 10^3</td>
<td>7695</td>
</tr>
<tr>
<td>(\text{Cr}_3\text{amorp}) ((x = 10) amorphous)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.4 \times 10^{-3}</td>
<td>1.81 \times 10^{-6}</td>
<td>2.4 \times 10^3</td>
<td>3635</td>
</tr>
<tr>
<td>(\text{Cr}_7\text{nano}(1): t_0 = 90 \text{ min})</td>
<td>7.4</td>
<td>8.1</td>
<td>3.5 \times 10^{-3}</td>
<td>1.50 \times 10^{-6}</td>
<td>13.5 \times 10^3</td>
<td>3812</td>
</tr>
<tr>
<td>(\text{Cr}_7\text{nano}(2): t_0 = 210 \text{ min})</td>
<td>3.6</td>
<td>4.0</td>
<td>4.4 \times 10^{-3}</td>
<td>1.39 \times 10^{-6}</td>
<td>8.2 \times 10^3</td>
<td>934</td>
</tr>
</tbody>
</table>
To discern the main contribution to the induction heating process, the ac hysteresis loops were determined as function of the exciting ac frequency, \( f \). Fig. 4 shows the frequency dependence of the coercive field, \( H_c \), for the analyzed wires. As expected, the highest \( H_c \) values are found in the nanocrystalline sample with lowest Curie temperature of the amorphous phase (\( Cr\text{-nano}(2) \), \( T_{Ca} < 300 \) K). In this sample the nanocrystalline grains are partially decoupled as a consequence of the decrease in the exchange correlation length due to the paramagnetic state of the residual amorphous phase [26]. However, the nanocrystalline wire with \( T_{Ca} > 300 \) K (\( Cr\text{-nano}(1) \)) displays similar low coercive fields that the amorphous samples. In fact, nearly anhysteretic hysteresis loops are found in these soft magnetic samples (see inset of Fig. 4) in spite of their self-heating characteristics. Thus, hysteresis losses should be disregarded as the mean mechanism of the detected induction heating phenomena.

On the other hand, assuming that the eddy-current losses dominate the power loss dissipation, SAR values should scale as \((\chi p)^{1/2}\) (Eq. (5)). Fig. 5 shows such a relationship (SAR versus \((\chi p)^{1/2}\); \( \chi \) low frequency values). A linear behavior is found for the samples with higher induction heating power (\( Cr\)amorp and \( Cr\text{-nano}(1,2) \)), confirming the relevant role of the eddy-current losses in the induction heating process. It should be noted that the nanocrystalline wire with the higher crystalline fraction (\( Cr\text{-nano}(2) \)) displays a value of \( T_{Ca} \) according to Fig. 2b, below \( T_0 \). Then, its self-heating capacity at 291 K should be interpreted as a result of the dependence of the magnetic transition associated to the magnetic decoupling of the ferromagnetic crystallites on the amplitude of the applied magnetic field. Shifts of the effective transition temperature close to 75 K are detected in FeSiCuNbB nanocrystalline wires. Such an increase is interpreted in terms of magnetization process of the decoupled ferromagnetic grains [23,25].

In the present case, due to closeness of \( T_{Ca} \) to the initial measuring temperature (\( T_0=291 \) K), the application of \( H_{ac} \approx 4 \) kA/m would be able to magnetize the ferromagnetic grains and thus to shift the effective magnetic transition above \( T_{Ca} \). However, the amorphous wire with \( T_{C} \approx 300 \) K \((x=10)\) displays a significant lower heating capacity (see Fig. 3). In fact, as Fig. 5 shows, this sample departs from the general linear trend (SAR versus \((\chi p)^{1/2}\)). This contradictory behavior should be interpreted as a consequence of the features of the \( \chi - T \) curves in these amorphous systems. Firstly, the absence of any significant increase in \( T_{C} \) with the applied magnetic field [23]. Secondly, the occurrence around \( T_{C} \) of a sharp Hopkinson peak in \( \chi (T) \) that disappears after nanocrystallization [39]. Therefore, starting from \( T \approx T_{C} \), a slight increase in temperature would promote a sharp decrease in \( \chi \) that would drastically decrease the power losses in the sample.

Finally, in order to check the self-regulated characteristics of the samples, the experimental set-up was modified in order to reduce the heat losses with the environment. Beside this, to enhance the heating capacity of the samples, the effective mass of the wires was increased and the measurements were taken under a higher magnetic field (\( H_{ac}=29 \) kA/m). Fig. 6 shows the obtained heating curves (\( \Delta T \) versus \( t \)) for both amorphous samples (\( m_{w,Cr\text{-amorp}}=19.5 \times 10^{-6} \) kg; \( m_{w,Cr\text{-nano}}=34 \times 10^{-6} \) kg; \( m_{w,Cr\text{-amorp}}=0.15 \times 10^{-3} \) kg). For the wire with higher Curie temperature, \( Cr\text{-amorp} \), \( T \) sharply increases within the measuring temperature range. A similar behavior, that is, a continuous increase of \( T \), is detected in the nanocrystalline wires. Conversely, the \( Cr\text{-amorp} \) wire shows an initial sharp temperature increase.
followed by clear stabilization around $T_c$. This result clearly proves the self-regulated characteristics of this amorphous system, where the Cr content can be suitably tailored to control the maximum temperature distribution. Finally, the estimated SAR values are in this case $3 \times 10^5$ and $0.3 \times 10^5$ W/kg for Cr$_{10}$amorp and Cr$_{7}$amorp, respectively. These values come closer to the reported values in Fe-based nanoparticles [30–34] and metallic iron nanostructures [40].

4. Conclusions

In conclusion, the magnetic induction heating effects in amorphous and Fe$_{73.5}$–$_{1}$Cr$_{10}$Si$_{13.5}$Cu$_{1}$B$_{9}$Nb$_{3}$ ($x=3, 7$ and $10$) nanocrystalline wires have been analyzed. The application of a $\sigma$ magnetic field gives rise to power losses that are able to increase the mean temperature of a capillary water bath where the samples are immersed. The Specific Absorption Rate (SAR) determined through the initial temperature rise of the system (wire plus water bath). Maximum SAR values are achieved for those samples displaying high magnetic susceptibility and Curie temperature above the initial measuring point (300 K). The analysis of the magnetic susceptibility indicates that the eddy current losses mainly dominate the heating phenomena. In order to explore the self-heating induction characteristics, samples (amorphous and nanocrystalline) with Curie temperature (amorphous phase) around 300 K were analyzed. The different heating response of the amorphous and nanocrystalline samples is analyzed in terms of the main features of the susceptibility–temperature curves. Self-regulated features are found in the amorphous alloy at temperatures around the corresponding Curie point.

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