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Modeling of self-controlling hyperthermia based on nickel alloy ferrofluids: Proposition of new nanoparticles

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ABSTRACT

In order to provide sufficient heat without overheating healthy tissue in magnetic fluid hyperthermia (MFH), a careful design of the magnetic properties of nanoparticles is essential. We perform a systematic calculation of magnetic properties of Ni-alloy nanoparticles. Stoner–Wohlfarth model based theories (SWMBTs) are considered and the linear response theory (LRT) is used to extract the hysteresis loop of nickel alloy nanoparticles in alternating magnetic fields. It is demonstrated that in the safe range of magnetic field intensity and frequency the LRT cannot be used for the calculation of the area in the hysteresis for magnetic fields relevant for hyperthermia. The best composition and particle size for self-controlling hyperthermia with nickel alloys is determined based on SWMBTs. It is concluded that Ni–V and Ni–Zn are good candidates for self-controlling hyperthermia.

1. Introduction

In the process of miniaturization in modern technology magnetic nanoparticles (MNPs) attract enormous interest, since they show fascinating properties resulting in applications as catalysts [1,2], single-electron devices [3] and biomedicine such as magnetic resonance imaging (MRI) contrast enhancement [4,5], drug delivery [6,7] and hyperthermia [8–12]. The magnetic properties of nanoparticles depend on the chemical composition and particle size and it is important to systematically analyze the effect of those parameters on the magnetic properties in order to tailor the properties of materials for specific applications. As an example, in magnetic fluid hyperthermia (MFH) it is crucial to carefully control the magnetic properties of MNPs to provide sufficient heat to destroy tumor cells without overheating healthy tissue.

In MFH, MNPs are dispersed in cancer tissue. Then an ac-magnetic field is applied. The field strength and the frequency have to be chosen carefully to heat the entire tumor. Temperatures of at least 42 °C have to be reached without exceeding 46 °C to prevent necrosis [11,12]. In order to minimize the concentration of the MNPs and reduce toxicity particles producing as much heat as possible are desirable.

Superparamagnetic iron oxide nanoparticles (SPIONs) are used for in-vitro and in-vivo hyperthermia [9–12]. However, the tumor and tissue temperature is difficult to control and the risk of damaging healthy tissue is large. One reason for this is that the particles retain their magnetic properties up to temperatures of 500 °C. One possible solution to this problem are MNPs with a Curie temperature in the range of 42–46 °C providing high enough heat production but preventing damaging of healthy cells. Substituted iron oxides have a lower Curie temperature [13,14] but at the same time their magnetization decreases significantly and metal alloy NPs, such as nickel alloys, are good alternative since their Curie temperature can be controlled by adding nonmagnetic atoms to the matrix [15–18] and retaining a high magnetic moment.

In past studies Ni–Cu [15–17] and Ni–Cr [18] nanoparticles have been synthesized. The studies focused on tuning the Curie temperature of the nanoparticles to the therapeutic range, i.e. 42–46 °C. However, from the theory it is also known that the size and the size distribution have to be carefully controlled in order to provide sufficient heat [19–24]. Regarding these facts it is important to take into account both the size as well as the chemical composition of the magnetic particles in order to locate the ideal candidate for self-controlling hyperthermia (SCH).

We have systematically calculated the magnetic properties of Ni-alloy NPs including the magnetic saturation, anisotropy constant and Curie temperature as a function of composition and size.

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In the second step the results are used to get a handle on the heat generation of the NPs in alternating magnetic fields and to calculate the best composition and particle size for SCH. The Curie temperature and specific absorption rate (SAR) are given for $Ni_{1-x}\beta_x$ (where β is V, Mo, Cr, Cu, Zn) NPs.

2. Theory

For MNPs in an alternating magnetic field with frequency f and amplitude $\mu_0 H_{max}$, the heat released during one magnetic field cycle equals the area of the hysteresis loop (A), which can be expressed by

$$A = \int_{-H_{max}}^{+H_{max}} \mu_0 M(H) dH \tag{1}$$

where $M(H)$ is the NP magnetization.

The SAR is given by

$$\mathrm{SAR} = \frac{Af}{\rho} \tag{2}$$

To calculate the SAR of MNP via the equations above, the area of the hysteresis loop, the density (ρ), the saturation magnetization of bulk (M_s) and the anisotropy constant (K) are needed. We use two different theories to measure the area of the hysteresis loop. In Section 2.3 we present a method to extract the physical properties of nickel alloys.

2.1. Linear response theory

The LRT is a model to describe the dynamic response of an assembly of MNPs using the Néel–Brown relaxation time assuming a linear response of the particles to the magnetic field. The LRT has been reported previously in several articles [19–24].

The alternating magnetic field is described as follows:

$$H(t) = H_{max}\cos(\omega t) \tag{3}$$

where H_{max} and ω are the amplitude and angular frequency of the magnetic field, respectively. The hysteresis area for randomly oriented MNPs is

$$A = \frac{\pi \mu_0^2 H_{max}^2 M_s^2 V}{3 k_B T} \frac{\omega\tau}{(1+\omega^2\tau^2)} \tag{4}$$

where μ_0 symbolizes the permeability of the vacuum, M_s the saturation magnetization for the bulk material, V the volume of the MNPs, k_B the Boltzmann constant, T the absolute temperature (Kelvin) and τ is the Néel–Brown relaxation time which can be expressed as

$$\tau = \tau_0 \exp\left(\frac{K_{eff} V}{k_B T}\right) \tag{5}$$

here K_{eff} is the effective uniaxial anisotropy constant, and τ_0 is the frequency factor of the Néel–Brown relaxation time ($=10^{-9}$–10^{-12} s). This theory is valid for strong anisotropy and low magnetic field, i.e. the LRT allows one to calculate the hysteresis loop shape when the magnetization is linear with magnetic field ($\xi = \mu_0 M_s V H_{max}/k_B T < 1$). Moreover, at $2\pi f\tau = 1$ the transition between the superparamagnetic regime ($2\pi f\tau < 1$) and the ferromagnetic regime ($2\pi f\tau > 1$) is found. Exactly at this point, the hysteresis loop area displays a maximum for small magnetic fields. The LRT is still valid in this region and can be used to calculate minor hysteresis loops.

2.2. Stoner–Wohlfarth theory

The original Stoner–Wohlfarth model does not take into account thermal activation. This is justified for $T=0$ or in the limit of infinite field frequency ($f \to \infty$). In the case of randomly oriented MNPs, the area of the hysteresis loop can be calculated as follows [24]:

$$A = 2\mu_0 H_c M_s \tag{6}$$

where H_c is coercive field. For finite frequency and $T \neq 0$, the hysteresis loop area can be represented as

$$A(T,f) = 2\mu_0 H_c(T,f) M_s \tag{7}$$

Garcia-Otero et al. [25] obtained an analytical expression for a temperature dependant coercive field based on an approximation of the measurement time.

$$\mu_0 H_c = 0.48\mu_0 H_K \left[1 - \left(\frac{k_B T}{K_{eff} V}\left(\ln\frac{\tau_m}{\tau_0}\right)\right)^{3/4}\right] \tag{8}$$

here $\mu_0 H_K = 2K_{eff}/M_s$ is the anisotropy field.

In addition, the magnetic field necessary to saturate an assembly of MNPs is approximately twice its coercive field ($\mu_0 H_c = 0.5\mu_0 H_{max}$). In view of the fact that some of the MNPs may not be switched by the applied magnetic field the hysteresis loop area is slightly bigger. Therefore it is better to target a coercive field slightly higher. The best compromise has been found by numerical calculations [24] and is slightly dependent on the exact shape of the hysteresis loop as

$$\mu_0 H_c = (0.81 \pm 0.04)\mu_0 H_{max} \tag{9}$$

with this optimum coercive field, the area is

$$A = (1.56 \pm 0.08)\mu_0 M_s H_{max} \tag{10}$$

The SWMBTs are suitable to describe the NP hysteresis loops if the NPs are not too close to the superparamagnetic–ferromagnetic transition. For this reason, this theory is valid to calculate the hysteresis loop area when a dimensionless parameter κ ($\kappa = \frac{k_B T}{K_{eff} V}\ln\left(\frac{k_B T}{4\mu_0 H_{max} M_s V f \tau_0}\right)$) is smaller than 0.7 [24]. For more information about the validity of different theories we refer the reader to Carrey et al. [24].

In order to decide which model is most suitable for the optimization of particles in MFH, we have to carefully analyze and take into account the validity and limitations of the different theories. In our calculation we consider a random orientation of MNPs.

2.3. Physical properties of nickel alloy NPs

As mentioned previously, density (ρ), saturation magnetization of bulk (M_s) as well as the anisotropy constant (K) are required to calculate the SAR of a MNP. The density of a binary substitutional solid solution alloy can be calculated as function of composition based on Chen et al.'s method [26]. For a nickel alloy $Ni_{1-x}\beta_x$ this results is

$$\rho_{Ni_{1-x}\beta_x} = \rho_{Ni} \frac{1-\left(1-\frac{M_\beta}{M_{Ni}}\right)x}{1-\left(1-\frac{M_\beta \rho_{Ni}}{M_{Ni}\rho_\beta}\right)x} \tag{11}$$

where ρ_{Ni}, ρ_β, M_{Ni} and M_β are the density and the atomic weight of nickel and solute, respectively. Table 1 summarizes calculated density values of several nickel alloys of different composition. The density and the atomic weight of the different elements have been extracted from [28].

The moment per atom for different alloy concentrations (x) and for sufficiently large excess nuclear charge (i.e. the difference in the number of valance electrons between the impurity and the matrix) can be obtained by Friedel's virtual bound state (VBS) model [29,30]. The model predicts that

$$\mu_{av} = \mu_{matrix} - (z+10)x\ \mu_B \tag{12}$$