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Magnetic properties of Ni–Co–Cr-base Elgiloy

J. C. HO
Department of Physics, Wichita State University, Wichita, KS 67260, USA
F. G. SHELLOCK
Shellock R&D Services, Inc. and School of Medicine, University of Southern California, Los Angeles, CA 90089, USA

The Ni–Co–Cr-base Elgiloy is one of the commonly used engineering materials. Most applications rely on its high strength, ductility, corrosion resistance and excellent fatigue life over a wide temperature range. However, in the medical application of cerebral aneurysm clips, the alloy is often subjected to strong magnetic fields associated with magnetic resonance imaging (MRI). Its paramagnetic behavior meets MRI safety requirements, but is the source of relatively large artifacts and thus less MRI-compatible for MRI procedure involving the brain. This article reports superconducting quantum interference device (SQUID) measurements on the magnetic properties of a series of Elgiloy wires in either as-drawn or heat-treated conditions. Furthermore, low-temperature calorimetry was employed to reveal the existence of submicroscopic clusters containing ferromagnetic elements such as Ni or Co in the macroscopically paramagnetic matrix.

1. Introduction

Ni–Co–Cr-base Elgiloy is a high-performance engineering material [1]. Along with a strong mechanical strength and excellent fatigue life, it has the ability to withstand corrosive environments and a wide temperature range. Therefore, it is an outstanding choice for a variety of applications in petrochemical, marine and aerospace industries. Also, its biocompatibility is applied in medical and dental practices for surgical implants and instruments, and orthodontic fixtures and probes. This work considers a special medical application of Elgiloy for manufacturing cerebral aneurysm clips. Following cerebral aneurysm repair, one or more metallic clips are often left in place by neurosurgeons. Such a long-standing practice began to face challenges after magnetic resonance imaging (MRI) routinely joined modern medical technology. The main concern centers around the magnetic behavior of clip materials in strong magnetic fields associated with MRI devices.

Magnetic moments can be induced in metallic materials placed in magnetic fields. The mass magnetic susceptibility is defined as $\chi = M/B$, where M is the induced magnetic moment per unit mass and B is the magnetic field. A ferromagnetic material has a large susceptibility as well as a residual magnetization after exposure to an external field, as revealed by a hysteresis loop in an M–B curve. When placed in a magnetic field, a ferromagnetic material experiences linear attraction and torque forces. Indeed, ferromagnetic aneurysm clips are rarely used nowadays. In contrast, paramagnetic materials display weak magnetic susceptibility, and develop an induced magnetization in direct proportion to the applied field. This induced magnetization is always in the direction of the applied field, so no torque would be expected. An object with mass m and magnetic moment $\mu = mM$, in a spatially varying magnetic field with field gradient, $\mathrm{d}B/\mathrm{d}z$, is also subjected to a force $F = \mu(\mathrm{d}B/\mathrm{d}z)$. The force tends to move the object in the field direction if the moment, the field gradient and the field are in the same direction (maximum force configuration as in the case of a paramagnetic clip in an MRI environment).

Prompted by an MRI-related death of a patient with a cerebral aneurysm clip, the US Food and Drug Administration stressed in 1993 the need for caution in this regard [2]. Even without any clip movement to present additional risk to the patient, the large induced magnetic moments in an MRI-safe clip with relatively strong paramagnetism would nevertheless affect the quality of diagnostic information for procedures involving examinations of the brain. Among the many types of aneurysm clips now commercially available, a majority of them are made of Elgiloy or its equivalent Phynox. Fig. 1 shows an artifact on MR imaging (1.5-Tesla Signa MR system of General Electric Co., Milwaukee, WI) of Elgiloy wires placed inside a turkey breast phantom to approximate tissue interaction. The following imaging parameters were used:

- fast, multi-planar, spoiled gradient echo in the steady state (GRASS) pulse sequence;
- axial plane;
- TR/TE, 50/4 ms;
- flip angle, 30°;
- field of view, 16 cm;
- number of excitations, four;
- imaging matrix, 256 × 128;
- section thickness, 3 mm.

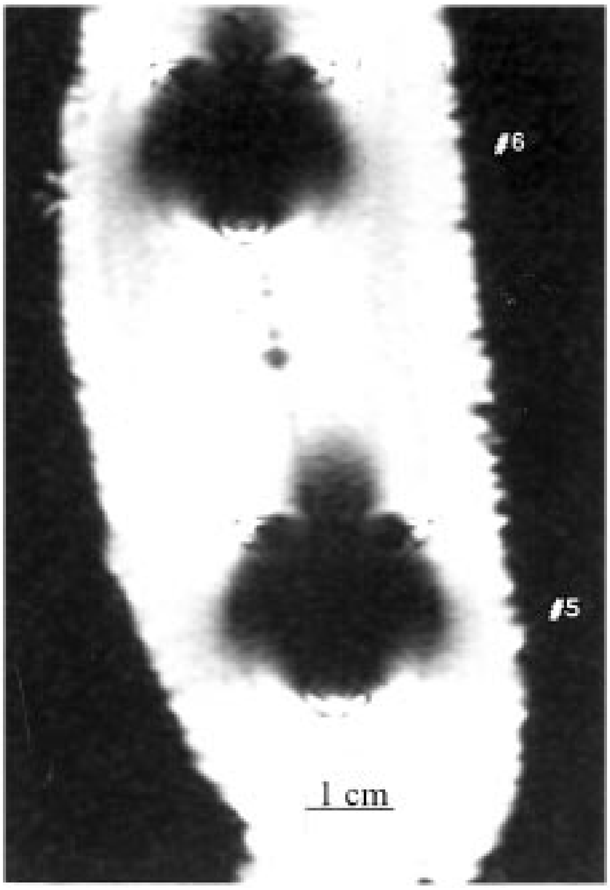

Figure 1 1.5-Tesla MRI artifacts as signal voids caused by 2-mm-diameter Elgiloy wires: No. 5, heat-treated; No. 6, as-drawn. See text for imaging parameters used in the fast, multi-planar, spoiled gradient echo in the steady state (GRASS) pulse sequence.

Using a plainimetry technique provided as part of the software on the GE MR system, the artifact areas are more than 200 times that of the 2.0-mm (0.080″) diameter wires. Similar results on several other Elgiloy wires will be reported elsewhere.

Elgiloy has typical compositions of 39.0–41.0 wt % Co, 19.0–21.0 wt % Cr, 14.0–16.0 wt % Ni, 6.0–8.0 wt % Mo, 1.5–2.5 wt % Mn, 0.10 wt % max. Be, 0.15 wt % max. C, and balance of Fe [1]. Nickel and cobalt constitute more than one-half of the alloy material. In pure form, nickel and cobalt are ferromagnetic. In an alloy, all ingredients are ideally mixed in a random fashion when solids are formed from melts. The resulting Elgiloy is paramagnetic in nature. However, elements like nickel and cobalt tend to stay together due to the lowering of energy through magnetic interactions. Therefore, even though the Elgiloy is non-ferromagnetic, one cannot rule out the possibility of nickel or cobalt cluster formation in the otherwise paramagnetic matrix. Nickel or cobalt clusters can be viewed as microscopic magnets. Their relative alignment, as well as growth in either number or size of individual clusters could change following mechanical and heat treatment. The effects would become more pronounced in strong magnetic fields. This article reports a comparative magnetic susceptibility evaluation among many Elgiloy specimens, complemented by a low temperature calorimetric study to verify the existence of the expected magnetic clusters.

2. Materials and methods

The magnetic measurements were carried out by examining 12 different Elgiloy wires as listed in Table I. They were kindly provided by Elgiloy Inc.

Note that, for the purpose of comparison, Nos 1, 6 and 9 in the as-drawn-wires list are the same as those of the heat-treated-wires list. It should also be pointed out that various manufacturers using Elgiloy as the raw material may very well have different heat-treatment schedules different from 980 °F/5 h and different mechanical processes from the wire-drawing. However, the only intention of this study is to demonstrate whether or how much the magnetic properties of various Elgiloy specimens can differ from each other when being drawn to different diameters or before and after a certain heat-treatment schedule.

3. Results

3.1. Magnetic measurements

A superconducting quantum interference device (SQUID) was used for magnetic measurements. Except for the as-drawn wire No. 7, the other 11 specimens had

TABLE I Elgiloy wires used for magnetic measurements

	Elgiloy Inc. wire stock number	Wire diameter (mm) (inch)
As-drawn wires		
1	32941 W (51530)	1.1 (0.043)
2	33441 W (52319)	1.2 (0.047)
3	32841 W (51653)	1.2 (0.048)
4	34232 W (52372)	1.2 (0.048)
5	32962 W (51469)	1.6 (0.062)
6	34871 W (53048)	1.6 (0.063)
7	31742 W (51100)	1.8 (0.072)
8	33861 W (52118)	2.0 (0.080)
9	31922 W (51020)	2.0 (0.080)
Heat-treated (980 °F, 5 h) wires		
1	32941 W (51530)	1.1 (0.043)
2	34871 W (53048)	1.6 (0.063)
3	31922 W (51020)	2.0 (0.080)

TABLE II Magnetization data of as-drawn Elgiloy wires

Wire No.	Diameter (mm)	Magnetization (emu g^{-1})				
		1 T	2 T	3 T	4 T	5 T
32491W (51530)[a]	1.1	0.3240	0.6501	0.9742	1.3023	1.6343
33441W (52319)	1.2	0.3806	0.7638	1.1488	1.4818	1.9080
32841W (51653)	1.2	0.3866	0.7717	1.1535	1.5392	1.9243
34232W (52372)	1.2	0.3883	0.7789	1.1564	1.5508	1.9586
32962W (51469)	1.6	0.3746	0.7497	1.1241	1.4937	1.8588
34871W (53048)[a]	1.6	0.3771	0.7584	1.1346	1.5765	1.9573
33861W (52118)	2.0	0.3874	0.7785	1.1599	1.5352	1.9050
31922W (51020)[a]	2.0	0.3718	0.7457	1.1213	1.4926	1.8562

[a] See Table III for data after being heat-treated.

TABLE III Magnetization data of heat-treated (980°F/5 h) Elgiloy wires

Wire No.	Diameter (mm)	Magnetization (emu g^{-1})				
		1 T	2 T	3 T	4 T	5 T
32491W (51530)	1.1	0.2550	0.5130	0.7652	1.0195	1.2812
34871W (53048)	1.6	0.2829	0.5659	0.8488	1.1311	1.4137
31922W (51020)	2.0	0.2905	0.5812	0.8703	1.1597	1.4486

their magnetization, M, determined at an applied magnetic field, B of 1, 2, 3, 4 and 5 T. Table II lists the magnetization data of eight as-drawn wires, five sets of which are shown in Fig. 2. The other three wires were also measured in their heat-treated (980 °F/5 h) condition with the results listed in Table III. Fig. 3 compares these three specimens before and after heat-treatment. Clearly, each set of data follow a linear relation between the magnetization and the applied magnetic field.

The linear dependence between M and B indicates the paramagnetic nature of these wires. To warrant the absence of ferromagnetism, the No. 7 as-drawn specimen was subjected to a magnetic loop test. The magnetic field was raised first from 0 to 4 T, then lowered through 0 to -4 T, and finally raised again from -4 T back to 0 T. Indeed, the results as summarized in Fig. 4 show no observable trace of a hysteresis.

The proportionality constant $\chi = M/B$ is the magnetic susceptibility. If M and B have the units of emu g^{-1} and gauss (1 T = 10 000 gauss) respectively, χ has the unit of cm^3 g^{-1}. Table IV lists the magnetic susceptibility values thus obtained from Figs 2 and 3. Judging from the χ values in Table IV, magnetic properties of different as-drawn specimens vary up to some 20%. Similarly, the same wires have their χ values reduced somewhat after heat-treatment. We believe them to be indicative of a lack of materials homogeneity. Existence of magnetic clusters can be at least partially the cause. In comparison, titanium is another material currently used in cerebral aneurysm clips [3, 4]. With a much lower magnetic susceptibility, titanium clips exhibit minimal artifact in MR imaging [5].

3.2. Low-temperature calorimetric measurements

Magnetic clusters in Elgiloy, if any, reflect compositional heterogeneity on an atomic scale and are not observable through standard metallurgical techniques. Instead, their

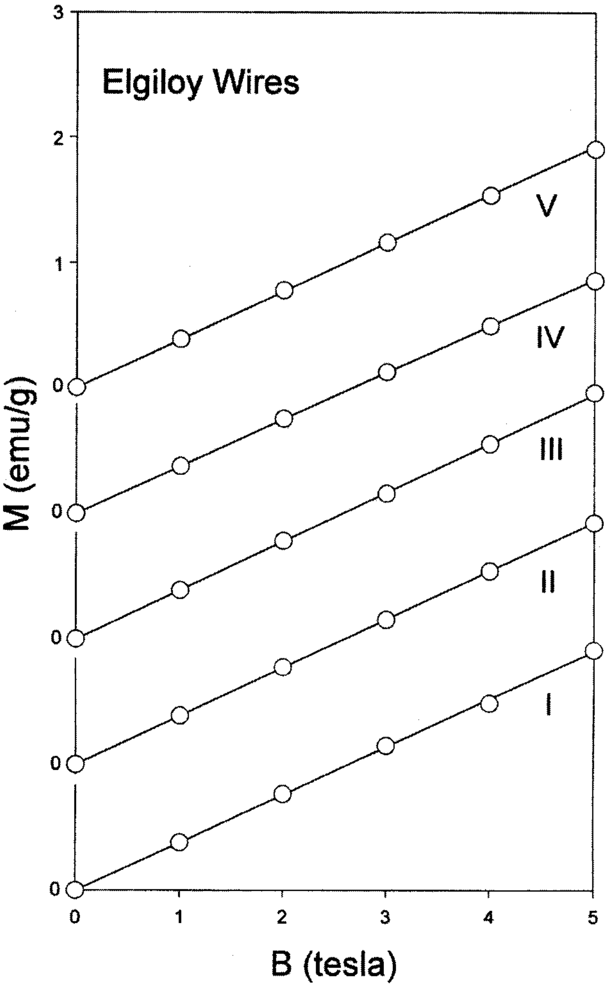

Figure 2 Linear fit to magnetic field dependence of magnetization of five as-drawn Elgiloy wires: (I) 33441W, (II) 32841W, (III) 34232W, (IV) 32962W, (V) 33861W. Note the successive 1-emu g^{-1} step shift in ordinate for each set of data.

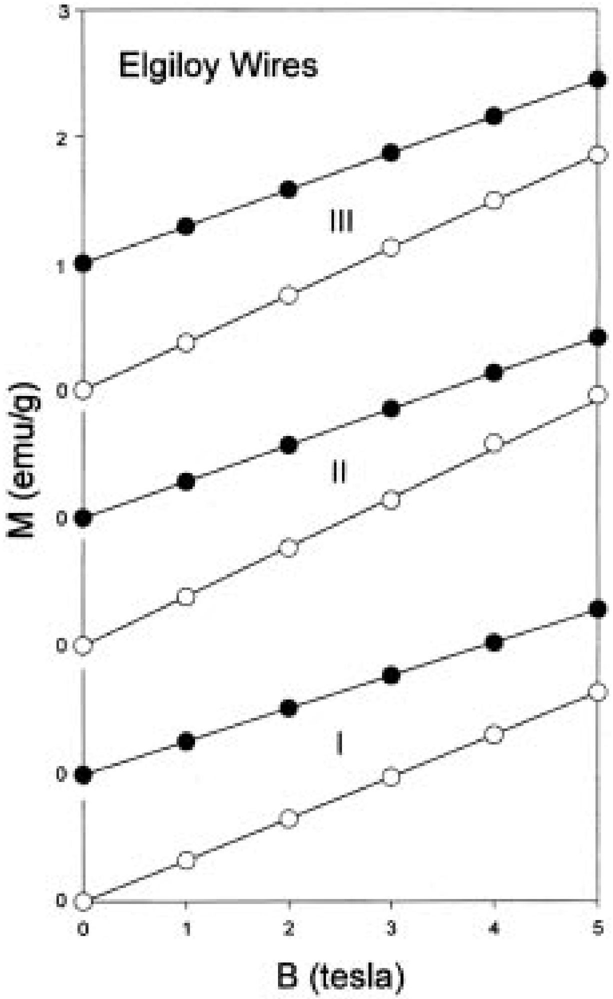

Figure 3 Linear fit to magnetic field dependence of magnetization of three Elgiloy wires: comparison between as-drawn (○) and heat-treated (●) conditions: (I) 32491W, (II) 34871W, (III) 31922W. Note the successive 1-emu g^{-1} step shift in ordinate for each set of data.

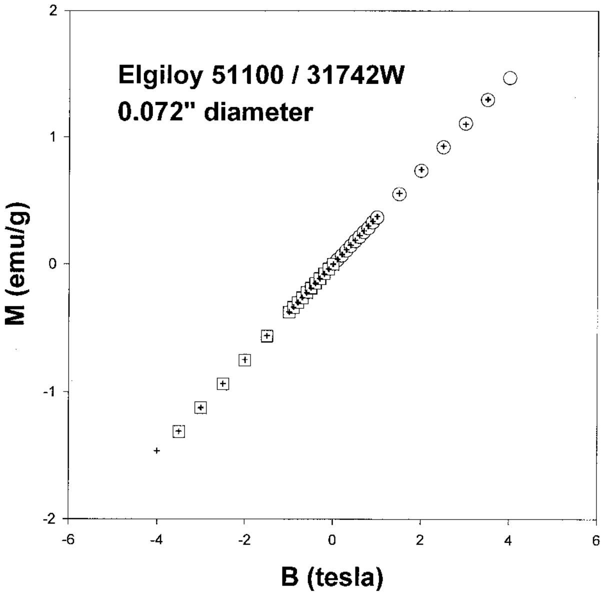

Figure 4 Hysteresis curve of an Elgiloy wire. The reversible magnetization indicates the absence of ferromagnetism: (○) increasing field from 0 to 4 T, (+) decreasing field from 4 to −4 T, (□) increasing field from −4 to 0 T.

presence can be verified by low-temperature heat capacity measurements. The thermodynamic quantity of heat capacity is defined as the amount of heat required to raise the temperature of a specimen by 1°. For a normal metallic solid, the rising temperature yields an increase in conduction electrons excitation and also atomic vibration, with corresponding contributions to heat capacity proportional to T and T^3, respectively, at low temperatures near the absolute zero

$$C = \gamma T + \beta T^3 \qquad (1)$$

where γ and β are the electronic and lattice heat capacity coefficients, respectively.

Additional contributions to the measured heat capacity can arise from other factors, including magnetic clusters. Each magnetic cluster would have a preferred orientation dictated by the surrounding atoms. To raise the specimen temperature additional heat would then be needed to help enhance the clusters' oscillation around this preferred orientation. Consequently, a higher heat capacity prevails. This additional contribution to heat capacity is more pronounced at very low temperatures, where the background of lattice and electronic terms becomes less dominant. Therefore, measurements in this work were made at temperatures far below that of the ambient. This may be viewed as analogous to MRI, which is performed using static magnetic fields much higher than the earth field one normally experiences, thus to facilitate the imaging process.

Calorimetric measurements were made on one as-drawn and one heat-treated Elgiloy 31922W (51020) wire (2 mm diameter, see Table I). Inside a thermal-relaxation calorimeter in a ^{3}He cryostat, the specimen was thermally anchored with a minute amount of grease to a sapphire holder on which thin films of ruthenium oxide and nickel–chromium alloy were deposited to serve as a temperature sensor and joule heating element, respectively. The temperature scale was based on a precalibrated germanium thermometer. The holder was thermally linked by four Au–Cu alloy wires to a temperature-regulated copper block. Following each heat pulse, the specimen temperature relaxation rate was monitored to yield the time constant, τ. The heat capacity value was then calculated from $C = k\tau$, where k is the thermal conductance of the Au–Cu wires. The heat capacity of the specimen holder was separately measured for addenda correction. Overall uncertainties in the final results were within a few per cent judging from the measurements on a copper standard.

The experimental results are shown in Fig. 5. Also included for comparison are heat capacities for titanium [6]. Clearly, Elgiloy in both as-drawn and heat-treated conditions has much higher values. Its temperature dependence reveals the presence of magnetic clusters as expected. This is better demonstrated by rewriting Equation 1 as

$$C/T = \gamma + \beta T^2 \qquad (2)$$

Having only the basic heat capacity contributions from lattice vibration and conduction electrons, the titanium data can be well fitted by a straight line in a C/T versus T^2 plot as shown in Fig. 6. Its intercept and slope yield

TABLE IV Magnetic susceptibility of Elgiloy wires

Wire No.	Diameter (mm)	Magnetic susceptibility, χ^a (10^{-6} cm^3 g^{-1}) As-drawn	Magnetic susceptibility, χ^a (10^{-6} cm^3 g^{-1}) Heat treated (980 °F/5 h)
32491W (51530)	1.1	32.63	25.55
33441W (52319)	1.2	37.95	—
32841W (51653)	1.2	38.53	—
34232W (52372)	1.2	38.85	—
32962W (51469)	1.6	37.39	—
34871W (53048)	1.6	38.40	28.29
33861W (52118)	2.0	38.56	—
31922W (51020)	2.0	37.26	29.02

[a] $\chi(\mathrm{cm}^3\ \mathrm{g}^{-1}) = M(\mathrm{emu\ g}^{-1})/B$ (gauss); 1 T = 10000 gauss.

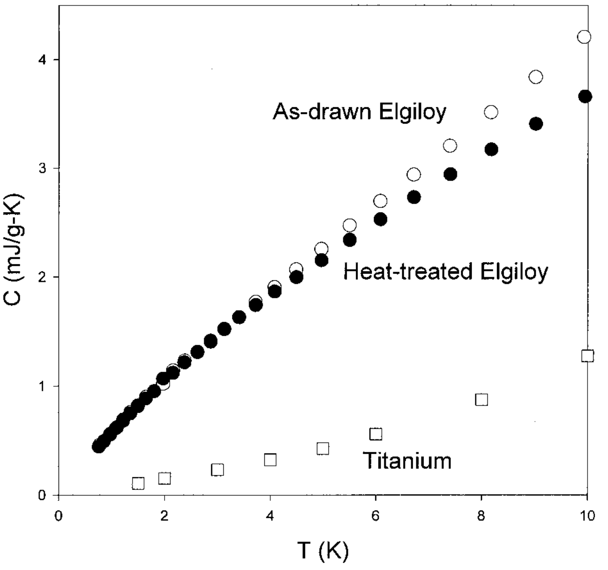

Figure 5 Temperature dependence of heat capacity of an Elgiloy wire [31922W (51020), 2-mm diameter] in as-drawn and heat-treated conditions, respectively. The titanium data are included for comparison.

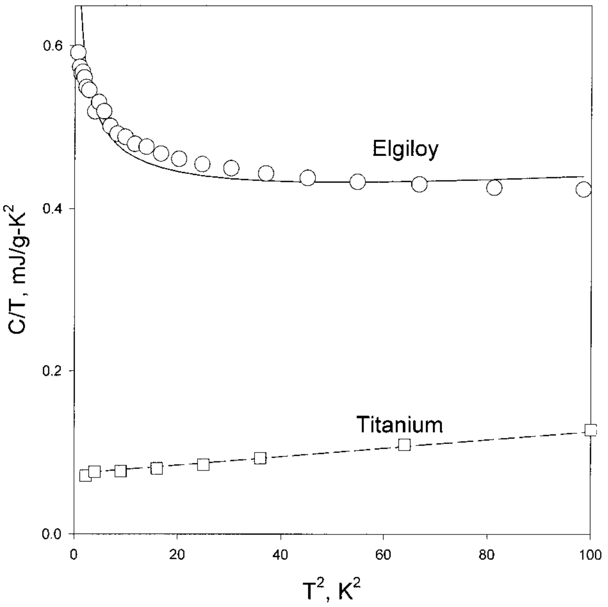

Figure 6 A plot of C/T versus T^2 showing a linear fit to the titanium data (Equation 2), but an additional, temperature-independent term (Equation 3) for the as-drawn Elgiloy [31922W (51020) wire, 2-mm diameter] data.

the values of γ and β, respectively. In contrast, an additional, temperature-independent term A is needed to fit the as-drawn Elgiloy data

$$C/T = A/T + \gamma + \beta T^2$$

or

$$C = A + \gamma T + \beta T^3 \tag{3}$$

As mentioned above, magnetic clusters in a paramagnetic matrix reflect compositional hetereogeneity on the atomic scale. They were first identified by Schröder and Cheng [7] through a temperature-independent term in heat capacity. A simple interpretation can be given as follows: each cluster interacts with the surrounding atoms. Such interaction is usually very weak. Therefore, even at a few degrees Kelvin, the cluster would behave as a classical oscillator around its preferred orientation with an energy of the order of k_BT (k_B being the Boltzmann constant). The corresponding heat capacity would be then a constant of the order of Nk_B, where N is the number of clusters. Similar observations have been reported by Ho and coworkers for Ni–Al [8], Al–Ce–Fe [9], W-2 (a heavy tungsten alloy containing Fe–Ni–Cu particles) [10] and Ni-base superalloys (MAR-M200, René N4 and DSR 80H) [11].

The A, γ and β values thus obtained are summarized in Table V. More relevant to this work are the two A values, which correspond to about 10^{19} clusters g^{-1} in the as-drawn as well as the heat-treated specimens. In comparison, there are a total of approximately 10^{22} atoms g^{-1} in the bulk material. This confirms the expectation that cluster formation occurs in the molten phase and persists to the solid state. During moderate-temperature heat treatment some of them could break up to become smaller clusters, leading to lower magnetic susceptibility as mentioned earlier. Meanwhile, with each cluster having a size-independent heat capacity of the order of k_B, the increase in number of clusters yields the slightly larger A value after heat treatment.

4. Conclusions

Elgiloy exhibits relatively strong paramagnetism. Heat treatments reduce slightly the magnetic susceptibility. More important, clusters of magnetic elements prevail in these Ni–Co–Cr-base materials as expected. While representing compositional hetereogeneity on the

TABLE V Calorimetric parameters of Elgiloy and titanium

Material	A (mJ g^{-1} – K^{-1})	γ (mJ g^{-1} – K^{-2})	β (mJ g^{-1} – K^{-4})
As-drawn Elgiloy	0.30	0.37	0.000 40
Heat-treated Elgiloy	0.39	0.32	0.000 40
Titanium	0	0.074	0.000 51

atomic scale, magnetic clusters affect significantly the magnetic properties of the bulk material. They are likely to be the source, at least partially, of relatively large artifacts in MR imaging of patients with Elgiloy cerebral aneurysm clips. For this special application, therefore, one needs to consider materials selection and control of processes carefully.

Acknowledgment

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