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# PROPERTIES AND APPLICATIONS FOR ELECTRODEPOSITED NANOCRYSTALLINE Fe-Ni ALLOYS

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**Abstract.** Iron-Nickel alloys are of great commercial interest as a result of their soft magnetic and thermal expansion properties. A proprietary, high efficiency electrodeposition process has been developed to produce the full range of Fe-Ni alloys (Ni: 0-100%) as fully dense freestanding nanocrystalline material, with average grain sizes in the range of 10-15 nm. The Fe-Ni alloys can be produced in the form of either net shape components or continuous foil (5-250 μm thickness). In this presentation, the physical properties of the nanocrystalline Fe-Ni alloys will be presented and compared with their conventional counterparts to demonstrate performance improvement obtained through extreme grain refinement. Properties that will be addressed include: hardness, ductility, thermal expansion, ferromagnetism (maximum induction, permeability, coercivity), electrical resistivity and thermal stability. Potential industrial/commercial applications for these nanocrystalline Fe-Ni alloys will be discussed, with particular emphasis on emerging applications in the electronics industry and in magnetic shielding and power generation/transmission.

## 1. INTRODUCTION

Due to their unique low coefficient of thermal expansion (CTE) and soft magnetic properties, iron-nickel alloys have been used in industrial applications for over 100 years [1,2]. Typical examples of applications that are based on the low CTE of Fe-Ni alloys include: thermostatic bimetals, glass sealing, integrated circuit packaging, cathode ray tube shadow masks, composite molds/tooling and membranes for liquid natural gas tankers [1,2]; applications based on the soft magnetic properties include: read-write heads for magnetic storage, magnetic actuators, magnetic shielding and high performance transformer cores. Nanostructured Fe-Ni alloys made by electrodeposition provide material with significantly improved strength, increased wear resistance, and good soft magnetic properties, without compromising the CTE. The multifunctional properties of electrodeposited nanostructured Fe-Ni alloys make these alloys amenable to many of the applications where conventional materials are currently used, but offer improved material performance.

In the past twenty years tremendous progress has been made with regard to the synthesis and characterization of nanocrystalline materials [3]. One synthesis method that has emerged as a technologically and economically viable route to produce nanostructured metals, alloys and composite materials is electrodeposition [4]. Material can be produced in the form of coatings, continuous thin foil (10 – 250 μm thick), thick plate (greater than 5 mm) or can be electroformed to produce small to large-scale net shape components or microelectromechanical system (MEMS) devices.

In this paper the synthesis, structure and some of the properties of electrodeposited nanocrystalline iron-nickel alloys will be presented and (where possible) compared to conventional iron-nickel alloys. The potential for performance enhancement for various applications of Fe-Ni alloys arising from the enhanced properties due to the ultra-fine grain size of the alloys will also be reviewed for a few select applications.

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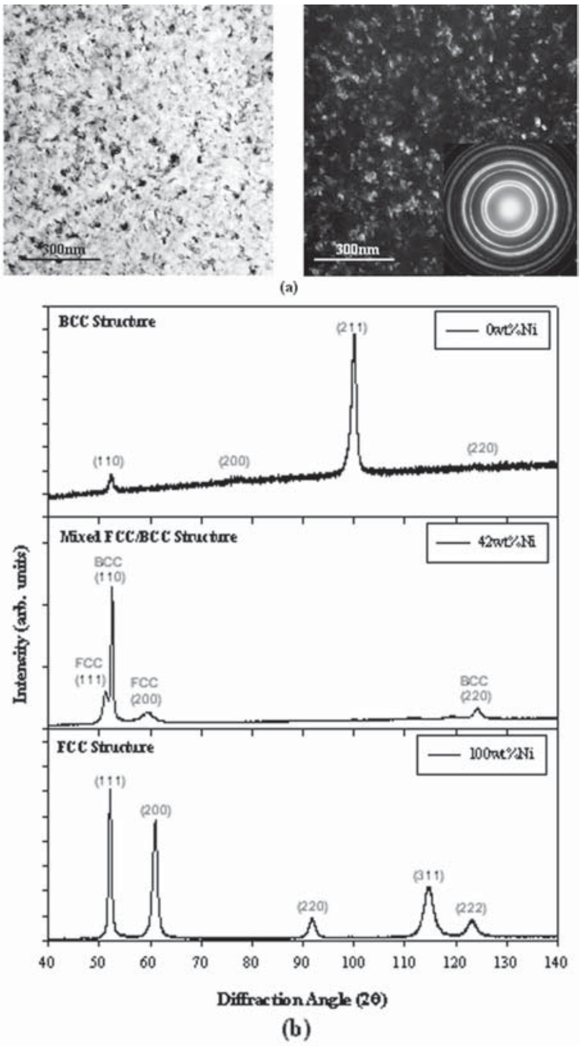


**Fig. 1.** (a) Bright and dark field TEM micrographs and the corresponding selected area diffraction pattern (inset) of electrodeposited nanocrystalline Fe-42wt%Ni, and (b) X-Ray diffraction patterns of electrodeposited Fe-Ni alloys with various Fe concentrations.

## 2. SYNTHESIS AND STRUCTURE

When carried out under optimized conditions electrodeposition is a single step process that produces nanocrystalline materials with virtually zero porosity (as determined by density [5] and positron annihilation [6] measurements). High- resolution electron microscopy has demonstrated that grain boundary structures in electrodeposited bulk nanostructures are similar to structures found in conventional polycrystalline materials [7]. Unlike the columnar grain structure found in conventional nickel electrodeposits [8], an equiaxed grain structure is typically found in nanocrystalline electrodeposits [9]. By varying the plating parameters (including but not limited to: bath pH, current density, pulse parameters and bath additions), the average grain size and crystallographic texture of the deposits can be controlled. Cross-sectional examination of thin (< 3 μm) and thick (> 1mm) coatings has shown that the nanocrystalline structure is fully established right at the interface with the substrate and that the grain size is independent of coating thickness [10], in contrast to conventionally produced electrodeposits which often show considerable grain coarsening with increasing coating thickness [11].

In the present study Fe-Ni alloys were produced using a pulse electrodeposition technique [9,12] on either AISI 1010 mild steel or titanium cathodes from a bath containing nickel and ferrous salts, a buffer, a complexing agent and a grain refiner. Fig. 1a presents bright field and dark field TEM micrographs and a corresponding selected area diffraction pattern of nanocrystalline Fe-42wt%Ni. The material displays an equiaxed grain structure with a relatively narrow grain size distribution. Fig. 1b shows X-ray diffraction patterns of various nanocrystalline Fe-Ni electrodeposits ranging in Ni content from 0 to 100%. Fe-Ni deposits with low nickel concentrations were found to have a body centred cubic (BCC) structure, while those with high nickel concentrations had a face-centred cubic (FCC) structure. A mixed FCC/BCC structure was observed for nickel concentrations ranging by approximately ±10 wt% around 40 wt% Ni.

## 3. PROPERTIES

**Tensile Strength & Hardness.** Due to Hall-Petch strengthening, nanocrystalline alloys offer significantly increased strength and hardness over conventional alloys. Table 1 summarizes tensile test data for conventional Permalloy (Fe-80%Ni-4.8%Mo) and a nanocrystalline Fe-Ni alloy close to the Permalloy composition with an average grain size between 10-15 nm. Due to the decrease in grain size, the yield strength and ultimate tensile strength are seen to increase by approximately 8-fold and 4-fold, respectively, while retaining approximately 3-4% ductility.

Fig. 2a shows the Vickers hardness of nanocrystalline Fe-Ni alloys as a function of Fe content in the deposits along with the hardness values for various conventional Fe-Ni alloys. The average hardness of the nanocrystalline Fe-Ni alloys is approximately 4 to 7 times higher than that of the conventional alloys. Fig. 2a reveals that there is a moderate decrease in hardness with increasing Fe con-

**Table 1.** Mechanical Properties of Nanocrystalline Ni~20%Fe and conventional Permalloy.

| *Material* | *Yield Strength, 0.2% Offset* (MPa) | *Ultimate Tensile Strength* (MPa) | *% Elongation* | *Vicker's Hardness* (VHN) |
|---|---|---|---|---|
| Nano Ni-20%Fe | 1785 | 2250 | 3-4% | 550-600 |
| Conv. Permalloy | 207 | 550 | 30% | 100 |

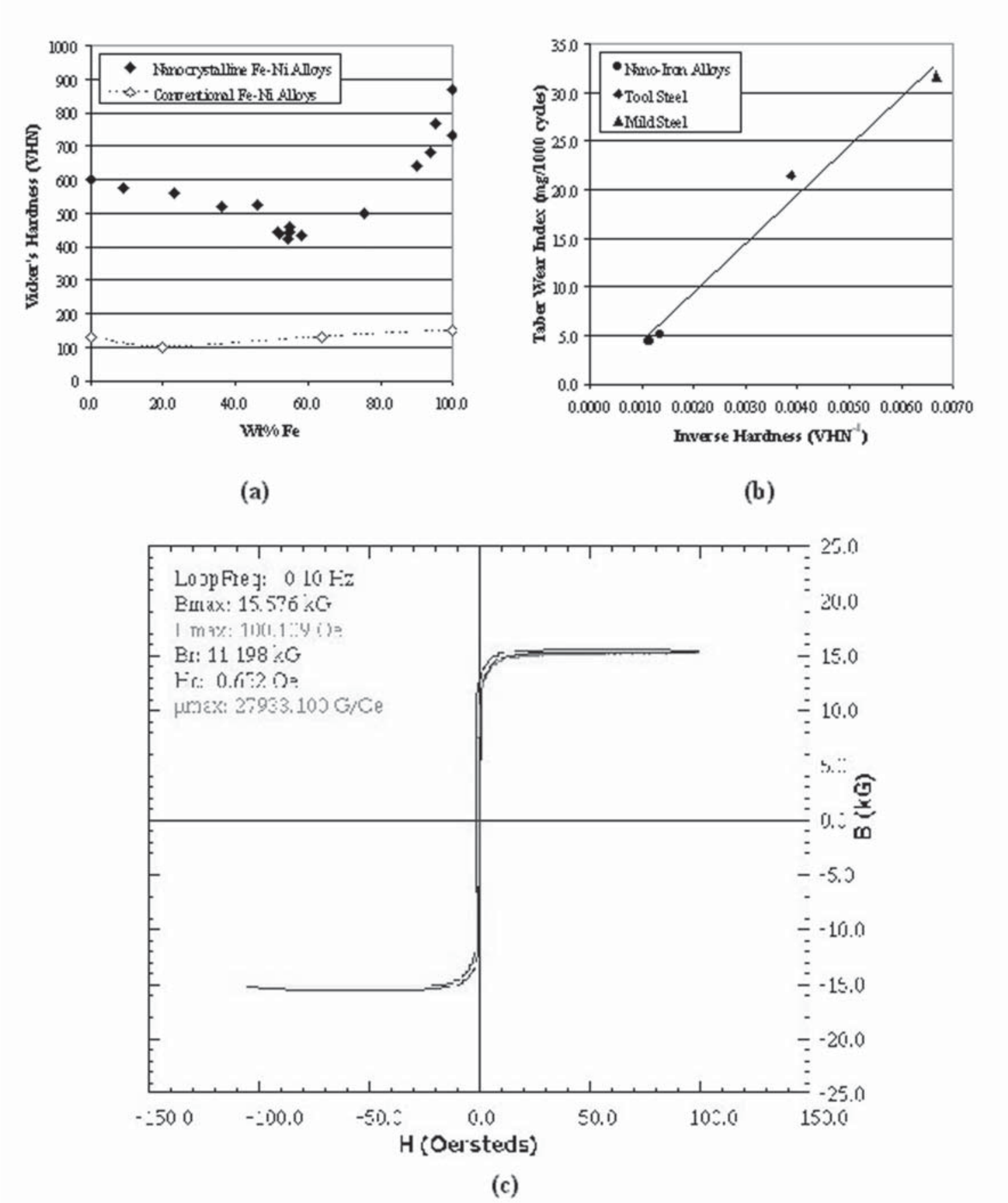


**Fig. 2.** (a) Vickers hardness as a function of iron content for various conventional and nanocrystalline Fe-Ni alloys, (b) Taber Wear Index as a function of inverse Vickers hardness for nanocrystalline Fe and conventional iron alloys, and (c) A B-H Loop measured at 0.1 Hz for nanocrystalline Fe-42wt%Ni in the as-deposited condition.

tent in the FCC range and a significant increase with Fe-content in the BCC range, with a minimum occurring at the FCC-BCC transition.

**Wear - Abrasive (Taber).** Taber wear tests were performed on various nanocrystalline iron samples as well as various conventional Fe alloys with different hardnesses. Taber wear tests were performed using CS-17 abrasive wheels, with an applied load of 1 kg. The tests were performed for a total of 10,000 cycles and the Taber wear index (TWI) was calculated from the average weight loss every 1000 cycles. Similar to what has been observed in nanocrystalline nickel electrodeposits [13], the wear resistance of Fe was found to increase with an increase in hardness. This can be explained by Archard's Law, which relates the wear volume loss ($\Delta V$) in a material to the applied load ($L$), sliding distance ($S$) and hardness of the wear surface [14]:

$$\Delta V = k\frac{LS}{H}, \qquad (1)$$

where $k$ is the wear coefficient. Fig. 2b presents the Taber Wear Index as a function of inverse Vickers hardness for nanocrystalline iron and various conventional iron alloys with different hardness. From this curve the TWI is seen to vary with inverse hardness in accordance with Archard's law, demonstrating that an increase in hardness due to grain size reduction results in significantly improved wear resistance.

**Electrical and Magnetic Properties.** As the average grain size in nanocrystalline materials can approach critical magnetic length scales (such as the domain wall thickness or the ferromagnetic exchange length) found in conventional materials, considerable changes in the magnetic behaviour can occur. When the grain size is reduced to the extent that the domain wall thickness is comparable to the grain size, the coercivity is found to dramatically decrease [15]. Studies on the saturation magnetization ($M_S$) of electrodeposited nanocrystalline materials, have shown that the $M_S$ is relatively insensitive to grain size, with a maximum decrease of $M_S$ by only ~ 5% [16-19]. Fig. 2c shows a B-H Loop, measured at 0.1 Hz, of electrodeposited nanocrystalline Fe-42wt%Ni in the as-deposited condition. In general, magnetic measurements on nanocrystalline Fe-Ni alloys produced in this study have shown the alloys to have high saturation magnetization (8-16 kG), low coercivity (0.2-0.6 Oersteds) and high maximum permeability (10,000-30,000).

Another consequence of the ultra-fine grain size of nanocrystalline materials is an increased electrical resistivity over polycrystalline materials due to the high volume fraction of grain boundaries. The electrical resistivity of electrodeposited nanocrystalline Fe-Ni alloys has been found to be linearly proportional to the grain boundary surface area per unit volume in the material which increases considerably when the grain size decreases to less than 100 nm [20]. The effect of the grain boundaries on the electrical resistivity can be quantified in terms of a specific grain boundary resistivity ($\rho_{SGBR}$) and the total electrical resistivity ($\rho_{total}$) can thus be expressed as:

$$\rho_{total} = \rho_0 + 2.37\rho_{SGBR}/d, \qquad (2)$$

where: $\rho_0$ is the electrical resistivity due to phonons, impurities and dislocations and $d$ is the average grain size. The specific grain boundary resistivity determined for Fe-Ni alloys ranging in composition from 66 to 84wt%Ni was found to be approximately $3.03\times10^{-6}$ $\mu\Omega cm^2$ and was relatively insensitive to composition [21].

**Thermal Stability.** A consequence of the ultra-fine grain structure of nanocrystalline materials is a limited thermal stability. This is due to excess free energy stored at the grain boundaries, which results in a large driving force for grain growth. As the electrical resistivity is dependent on the grain size of the material, high temperature electrical resistivity measurements can be used to estimate the thermal stability of the material. By measuring the electrical resistivity at elevated temperatures, the point at which the material is no longer thermally stable can be determined by a sharp decrease in the electrical resistivity. Fig. 3a shows the electrical resistivity as a function of temperature from 200 °C to 450 °C for a nanocrystalline Fe-69wt%Ni sample. The figure shows that the onset of grain growth (as indicated by the large drop in resistivity) occurs at approximately 375 °C.

**Coefficient of Thermal Expansion.** It has been previously determined that grain size reduction to about 10 nm in fully dense electrodeposited materials has no major effect on the thermal expansion [6]. In the current study, the coefficient of thermal expansion of Fe-43wt%Ni was determined from linear thermal expansion measurements (from –50 °C to 400 °C) using a dual push-rod dilatometer (Theta Dilatronics II), following ASTM standard testing procedure E228. Two scans were performed on the same sample to determine the effect of grain growth on the CTE, as the testing temperature exceeded

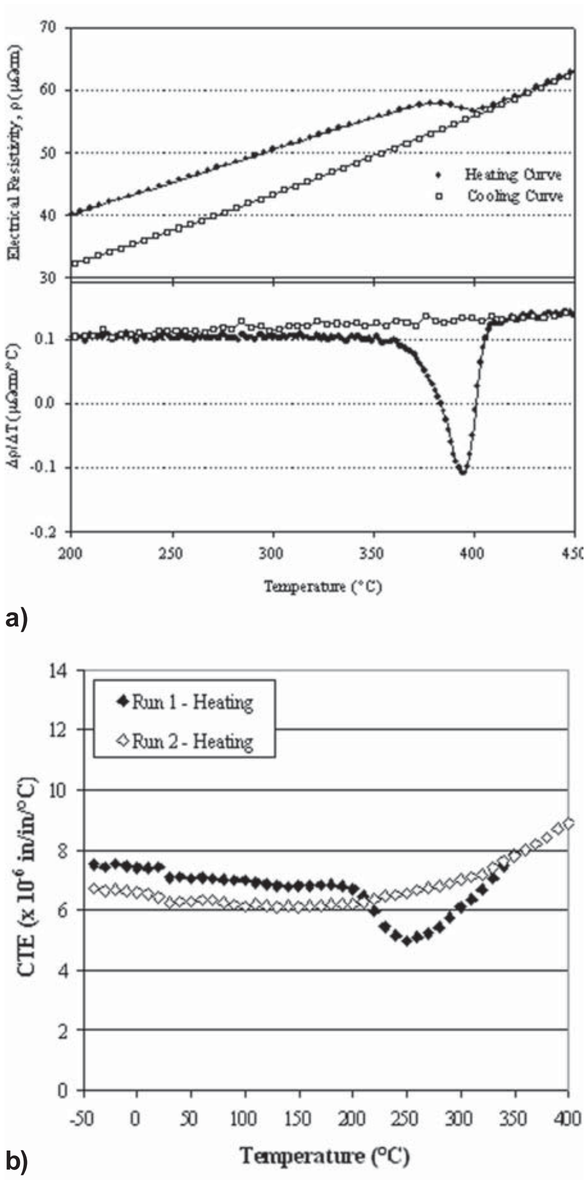


**Fig. 3.** (a) Heating and cooling isokinetic electrical resistivity curves (upper graph) and the rate of change of resistivity with respect to temperature curves (lower graph) for electrodeposited nanocrystalline Fe~80wt%Ni, and (b) The coefficient of thermal expansion for a Fe-43wt%Ni alloy as a function of temperature from –50 to 400 °C.

the thermal stability of the material. Fig. 3b shows the CTE as a function of temperature for the temperature range tested. As seen from the figure, the CTE is relatively constant with temperature and is found to slightly decrease (by approximately 10%) during the first scan upon heating through the temperature region in which grain growth occurs. During the second scan, no decrease in CTE was observed and the CTE values are very similar to what would be expected for a conventional Fe-Ni alloy of the same composition.

## 4. APPLICATIONS

**Low Thermal Expansion Applications.** The most promising applications for nanocrystalline Fe-Ni alloys are those where a low CTE is required and additional strength would be beneficial. Two applications in particular are for use in integrated circuit packaging and shadow masks for cathode ray tubes.

Integrated circuit packaging requires materials with thermal expansion coefficients matched to those of silicon to prevent the formation of cracks, delamination and/or de-bonding of the different materials during thermal cycles to which the component is exposed. The first Fe-42%Ni supports for silicon chips were introduced in the 1970's and still remain in widespread use today [22]. Present trends, however, are leading towards the use of ultra-thin supports that require high strength.

In colour cathode ray tube televisions and computer monitors, the shadow mask is a perforated metal sheet that the electrons from the electron gun must pass through before reaching the phosphor screen. The role of the shadow mask is to ensure that the electron beam hits only the correct coloured phosphor dots and does not illuminate more than the one that was intended. Only 20% of the electrons pass through the shadow mask, thereby absorbing the other 80%, which leads to an increase in temperature in the mask. The resulting thermal expansion can disturb the alignment between the apertures and the phosphor triads, leading to a distorted image. This effect is known as "doming". To minimize the "doming" effect, Fe-Ni (Invar) alloys have recently replaced aluminum-killed (AK) plain carbon steel for use in shadow masks in high-resolution televisions and computer monitors [23].

In both of the above-mentioned applications finished parts are manufactured by a photo-engraving process known as "chemical machining", thus requiring the material to have good etchability. In light of the above information, the main advantages of using electrodeposited nanocrystalline Fe-Ni alloys over conventional Fe-Ni alloys for use in integrated circuit packaging and shadow masks for CRTs include:

- Single step process to produce foils ranging in thickness from 15 to 500 μm;
- High mechanical strength (>450 VHN);
- Isotropic properties due to fine equiaxed grain structure;
- Improved chemical machining performance:

– Finer pitch possible due a decrease in grain size and higher strength;
– High etch rates due to increased grain boundary volume fraction.

**Microelectromechanical Systems.** Many microelectromechanical system (MEMS) components are manufactured by electrodeposition using the LIGA (Lithographie Galvanoformung Abformtechnik) technique, which makes use of a thick photoresist (< 200 μm) to allow for the fabrication of high aspect ratio structures. Conventionally produced LIGA and other electrodeposits, however, have been shown to suffer from severe reliability problems in terms of unpredictable properties. A columnar grain structure (similar to what is found in conventional electrodeposited nickel) is typically found in LIGA Ni, which has been identified as the cause of the reliability problems, as not all material properties are isotropic [24]. The use of electrodeposited bulk nanostructures for MEMS devices would improve the reliability of the devices by providing a fine (10-20 nm) equiaxed grain structure throughout the device. This would increase the reliability of the device, by averaging the anisotropic properties over many grain diameters across the length of the MEMS structure. In addition, the increased strength and low CTE of the Fe-Ni alloys can improve the overall performance of the component in terms of specific strength, elastic energy storage capacity and thermal shock resistance [24]. Good soft magnetic properties are also of importance for electromagnetic applications such as magnetic actuators and motors.

**Magnetic Applications.** For soft magnetic applications, ranging from electromagnetic shielding, transformer materials, read-write heads, high efficiency motors or emerging microelectromechanical system components, magnetic materials that exhibit small hysteresis losses per cycle are required. More specifically, materials with: (i) high permeability (the parameter which describes the flux density in very small fields), (ii) low coercivity, (iii) high saturation and remnant magnetization, (iv) high electrical resistivity (to minimize losses due to eddy current formation) and (v) high Curie temperatures are required. Electrodeposited nanocrystalline Fe-Ni alloys fulfil the above requirements with the added benefit of high strength and good wear resistance. In the case of magnetic shielding, the ability of producing high strength net shape components with good soft magnetic properties is highly desirable.

**Other Applications.** As the abrasive wear performance of nanocrystalline iron with a 10-15 nm grain size (TWI of ~4.5mg/1000cycles) is similar to that of hard chrome (TWI of ~4.5mg/1000cycles), electrodeposited nanocrystalline Fe alloys would be ideal for hardfacing coatings where corrosion is not an issue (such as machine parts operating in an oil environment). The wear resistance of the coatings could be further reduced by co-depositing hard ceramic particles such as $B_4C$, SiC or $Al_2O_3$ [25]. As the composition of Fe-Ni can be varied to match the low CTE of the ceramic particles, a nanocrystalline Fe-Ni composite electrodeposit would be an excellent hardfacing coating in applications where large thermal gradients exist and close dimensional tolerance is required.

## 5. CONCLUSIONS

Electrodeposited nanostructured Fe-Ni alloys exhibit excellent mechanical, wear, thermal and magnetic properties and can readily be produced in large quantities and in many different forms and shapes including: thin and thick coatings, free-standing foil, sheet, tubes and wires as well as complex geometries. Based on the outstanding properties a number of advanced applications for electrodeposited Fe-Ni nanostructures have been considered and presented herein.

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