

Papers and their abstracts submitted by the PI of the University of Maryland portion under the auspices of DOE award DESC0005448 “Polymeric Multiferroics Collaborative Research Between University of Maryland and Kansas University”

1. Torben Dankwort, Julian Strobel, Christoph Chluba, Wenwei Ge, Viola Doppel, Manfred Wuttig, Eckhard Quandt and Lorenz Kienle, Martensite adaption through epitaxial nano transition layers in TiNiCu shape memory alloys, *J. Appl. Cryst.* (2016). 49, 1009–1015,

<https://doi.org/10.1107/S160057671600710X>

Abstract

Titanium-rich TiNiCu shape memory thin films with ultralow fatigue have been analysed for their structural features by transmission electron microscopy. The stabilization of austenite (B2) and orthorhombic martensite (B19) variants epitaxially connected to Ti₂Cu-type precipitates has been observed and found responsible for the supreme mechanical cycling capability of these compounds. Comprehensive ex situ and in situ cooling/heating experiments have demonstrated the presence of an austenitic nanoscale region in between B19 and Ti₂Cu, in which the structure shows a gradual transition from B19 to B2 which is then coupled to the Ti₂Cu precipitate. It is proposed that this residual and epitaxial austenite acts as a template for the temperature-induced B2-B19 phase transition and is also responsible for the high repeatability of the stress-induced transformation. This scenario poses an antithesis to residual martensite found in common high-fatigue shape memory alloys.

2. Chluba C, Ge W, Dankwort T, Bechtold C, Lima de Miranda R, Kienle L, Wuttig M, Quandt E., Effect of crystallographic compatibility and grain size on the functional fatigue of sputtered TiNiCuCo thin films. *Phil. Trans. R. Soc. A* 374, 2015 0311. <http://dx.doi.org/10.1098/rsta.2015.0311> DOI: 10.1098/rsta.2015.0311

Abstract

The positive influence of crystallographic compatibility on the thermal transformation stability has been already investigated extensively in the literature. However, its influence on the stability of the shape memory effect or superelasticity used in actual applications is still unresolved. In this investigation sputtered films of a highly compatible TiNiCuCo composition with a transformation matrix middle eigenvalue of 1±0.01 are exposed to thermal as well as to superelastic cycling. In agreement with previous results the thermal transformation of this alloy is with a temperature shift of less than 0.1 K for 40 cycles very stable; on the other hand, superelastic degradation behaviour was found to depend strongly on heat treatment parameters. To reveal the transformation dissimilarities between the differently heat-treated samples, the microstructure has been analysed by transmission electron microscopy, *in situ* stress polarization microscopy and synchrotron analysis. It is found that good crystallographic stability is not a sufficient criterion to avoid defect generation which guarantees high

superelastic stability. For the investigated alloy, a small grain size was identified as the determining factor which increases the yield strength of the composition and decreases the functional degradation during superelastic cycling.

3. Christoph Chluba, Wenwei Ge, Rodrigo Lima de Miranda, Julian Strobel, Lorenz Kienle, Eckhard Quandt, Manfred Wuttig, Ultra-Low Fatigue Shape Memory Alloy Films, *SCIENCE*, 348, 1006, 2015 • doi 10.1126/science.1261164

Abstract

Functional shape memory alloys need to operate reversibly and repeatedly. Quantitative measures of reversibility include the relative volume change of the participating phases and compatibility matrices for twinning. But no similar argument is known for repeatability. This is especially crucial for many future applications, such as artificial heart valves or elastocaloric cooling, in which more than 10 million transformation cycles will be required. We report on the discovery of an ultralow-fatigue shape memory alloy film system based on TiNiCu that allows at least 10 million transformation cycles. We found that these films contain Ti_2Cu precipitates embedded in the base alloy that serve as sentinels to ensure complete and reproducible transformation in the course of each memory cycle.

4. Wei Qin, Xiaomin Chen, Huashan Li, Maogang Gong, Guoliang Yuan, Jeffrey Grossman, Manfred Wuttig and Shenqiang Ren, Room temperature magnetism and multiferroicity in supramolecular charge-transfer co-crystals, *advanced materials*, *ACS Nano*, 2015, 9 (9), pp 9373–9379, DOI: 10.1021/acsnano.5b03558

Abstract

Room temperature multiferroics has been a frontier research field by manipulating spin-driven ferroelectricity or charge-order-driven magnetism. Charge-transfer crystals based on electron donor and acceptor assembly, exhibiting simultaneous spin ordering, are drawing significant interests for the development of all-organic magnetoelectric multiferroics. Here, we report that a remarkable anisotropic magnetization and room temperature multiferroicity can be achieved through assembly of thiophene donor and fullerene acceptor. The crystal motif directs the dimensional and compositional control of charge-transfer networks that could switch magnetization under external stimuli, thereby opening up an attractive class of all-organic nanoferronics.

5. Maogang Gong, Alec Kirkeminde, Manfred Wuttig and Shenqiang Ren*, "Phase Transformation Induced Tetragonal-FeCo Nanostructures", *Nano Letters*, DOI:10.1021/nl5030485 (2014).

Abstract

Tetragonal FeCo nanostructures are becoming particularly attractive because of their high magnetocrystalline anisotropy and magnetization achievable without rare-earth elements, . Yet, controlling their metastable structure, size and stoichiometry is a challenging task. In this study, we demonstrate AuCu templated FeCo shell growth followed by thermally induced phase transformation of AuCu core from face-centered cubic to L1₀ structure, which triggers the FeCo shell to transform from the body-centered cubic structure to a body-centered tetragonal phase. High coercivity, 846 Oe, and saturation magnetization, 221 emu/g, are achieved in this tetragonal FeCo structure. Beyond a critical FeCo shell thickness, confirmed experimentally and by lattice mismatch calculations, the FeCo shell relaxes. The shell thickness and stoichiometry dictate the magnetic characteristics of the tetragonal FeCo shell. This study provides a general route to utilize phase transformation to fabricate high performance metastable nanomagnets, which could open up their green energy applications.

6. Wei Qin, Maogang Gong, Xiaomin Chen, Tejas A. Shastry, Ridwan Sakidja, Guoliang Yuan, Mark C. Hersam, Manfred Wuttig and Shengqiang Ren*, "Multiferroicity of Carbon-Based Charge Transfer Magnets", *Advanced Materials*, DOI:[10.1002/adma.201403396](https://doi.org/10.1002/adma.201403396) (2014)

Abstract

A new type of carbon charge-transfer magnet, consisting of a fullerene acceptor and single-walled carbon nanotube donor, is demonstrated, which exhibits room temperature ferromagnetism and magnetoelectric (ME) coupling. In addition, external stimuli (electric/magnetic/elastic field) and the concentration of a nanocarbon complex enable the tunabilities of the magnetization and ME coupling due to the control of the charge transfer.

7. Wei Qin, Daniel Jasion, Xiaomin Chen, Manfred Wuttig and Shengqiang Ren, Charge Transfer Magnetoelectrics of Polymeric Multiferroics, *ACS Nano*, 2014, 8 (4), pp 3671–3677, DOI: 10.1021/nn500323j

Abstract

The renaissance of multiferroics has yielded a deeper understanding of magneto-electric coupling of inorganic single-phase multiferroics and composites. Here, we report charge-transfer polymeric multiferroics, which exhibit external field-controlled magnetic, ferroelectric, and microwave response, as well as magneto-dielectric coupling. The charge-transfer-controlled ferroic properties result from the magnetic field-tunable triplet exciton which has been validated by the dynamic polaron bipolaron transition model. In addition, the temperature-dependent dielectric discontinuity and electric field-dependent polarization confirms room temperature ferroelectricity of crystalline charge-transfer polymeric multiferroics due to the triplet exciton, which allows the tunability of polarization by the photoexcitation.

8. Jessica Lohrman , Shaofeng Duan, Yueying Liu, Xiaoyong Zhao, Manfred Wuttig, and Shengqiang Ren, All Conjugated Copolymer Excitonic Multiferroics , Advanced Materials 25, 783–787, 2013, <http://dx.doi.org/10.1002/adma.201204113>

Abstract

A substantial magnetoelectric coupling effect of an excitonic all-conjugated block copolymer multiferroics consisting of electronically distinct polythiophene derivatives is reported. The observations open new avenues for the multifunctional all-conjugated block copolymer synthesis and electric field tunable multiferroic devices.

9. Shengqiang Ren and Manfred Wuttig, Organic Exciton Multiferroics, Advanced Materials 24, 724, 2012; DOI: 10.1002/adma.201104250

Abstract

For the first time the observation of substantial visible light-, electrically and mechanically induced changes of the magnetization of an organic exciton multiferroic consisting of single crystal P3HT doped with C₆₀ is reported. The observations open new avenues for exciton based spintronic devices.