Magnetic Field Induced Transformation Strain in Kinetically Arrested NiCoMnIn

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1. Introduction

Ni-Co-Mn-X (X=Al, Sn, Sb, In) metamagnetic shape memory alloys (MMSMAs) are a special class of smart material that can undergo field induced martensitic phase transformation [1-2]. By applying a biased stress field, the martesitic phase transformation can produce large transformation strains by temperature or magnetic field changes. This can allow their future use in actuation, sensing and energy harvesting applications. Unfortunately, a phenomenon dubbed Kinetic Arrest (KA) in the literature has been shown to prevent the thermally induced martensitic transformation from below a critical temperature. The exact cause for this halting of the thermal martensitic phase transformation is not fully understood, but has been attributed to the difference in entropy between austenite and martensite going to zero, but rate dependent effects and isothermal relaxation have been observed [3]. Interestingly, a similar response has been observed in Ni-rich NiTi and TiNiFe shape memory alloys and is attributed to a glass transition temperature around 160 K [4-5]. These studies on NiTi also showed that although the martensite phase could not be thermally stabilized because the transformation temperatures are below the glass transition, stress could stabilize the martensite above and below the glass transition temperature. The present work utilizes NiCoMnIn single crystals to explore the magnetic field induced phase transformation in a fully arrested material. The objectives are to show a fully arrested MMSMA can undergo magnetic field induced phase transformation (MFIPT) and determine the phase diagram above and below the kinetic arrest temperature. This will help in understanding if the KA is caused by a change in the thermodynamic equilibrium between austenite and martensite, in other words the entropy difference going to zero, or by a shift from an athermal to isothermal martensitic transformation brought on by a strain glass.

2. Experimental procedure

$Ni_{45}Co_5Mn_{36.5}In_{13.5}$ single crystals were grown in a He atmosphere using the Bridgeman technique and 2×2×4 mm compression specimens were wire electro discharge machined with the loading axis along austenite's [100] crystallographic direction. The specimens were then sealed in quartz tubes under an ultra-high-purity Ar atmosphere and subjected to a step heat treatment of 1173 K for 24 hours then 673 K for 3 hours. Water quenching was used after each heat treatment step. The specimens were then loaded to a desired stress in a custom Micro Magneto-Thermo-Mechanical (Micro MTM) cell designed to fit inside the 10 mm bore of typical SQUID magnetometers. The load is held within relative ±10% of the room temperature value across the thermal variation. A displacement sensor was then fixed to the Micro-MTM and the apparatus was lowered into a 16.5 T SQUID magnetometer for testing. The temperature was ramped to a desired test temperature and then held constant as the magnetic field was rammed. The displacement and magnetization were measured simultaneously during the ramping process.

3. Results and discussion

Figure 1 displays the material's magneto-thermo response under 0.05 T and 7 T after heat treatment. There is no evidence of martensitic transformation from

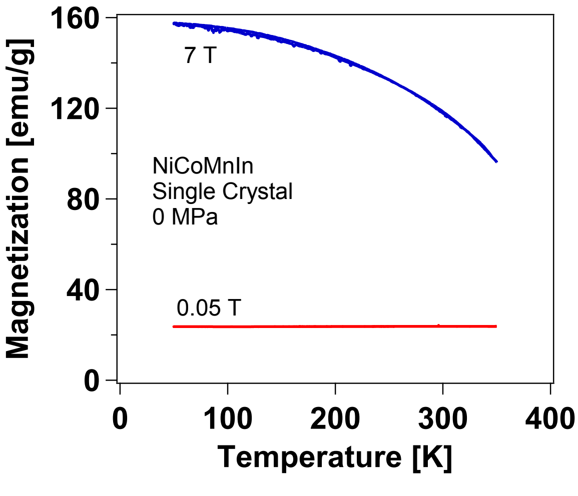

Fig. 1 Magnetization as a function of temperature for the heat treated $Ni_{45}Co_5Mn_{36.5}In_{13.5}$ single crystal.

ferromagnetic austenite to paramagnetic martensite. The changes in magnetization with temperature and magnetic field are indicative of the ferromagnetic austenite phase. This halting of the phase transformation is brought about by the heat treatment which is believed to change the order and point defect concentration of the material which in turn shifts the martensitic transformation temperatures below the 150 K kinetic arrest temperature [6].

Figure 2 shows the magnetization, solid lines, and strain, dashed lines, dependence on magnetic field at selected constant temperatures for experiments under a constant 80 MPa load. For clarity, the strain and magnetization paths during magnetic field ramping are shown for the 150 K experiment. The material begins at 0 emu/g and -4.2 % strain with respect to austenite at room temperature. The magnetization rapidly increases then saturates at a low value and the strain stays fairly constant as the magnetic field is increased to 2.5 T, the martensite to austenite transformation begins causing a sharp drop in the strain and an increase in the magnetization. The strain and magnetization continue to evolve as the magnetic field is increased and more austenite is stabilized. The transformation is completed above 5.6 T as shown by the saturation magnetization and strain values with further increases in magnetic field. Upon unloading the magnetic field, the magnetization and strain remain constant until 2.7 T where the reverse transformation occurs. This causes a decrease in the magnetization and increase in compressive strain. As the magnetic field reaches zero, the compressive strain returns to its original value and the magnetization drops to zero. The critical fields for transformation are extracted from the strain and magnetization data using the slope intercept method as shown in the 110 K tests in figure 2.

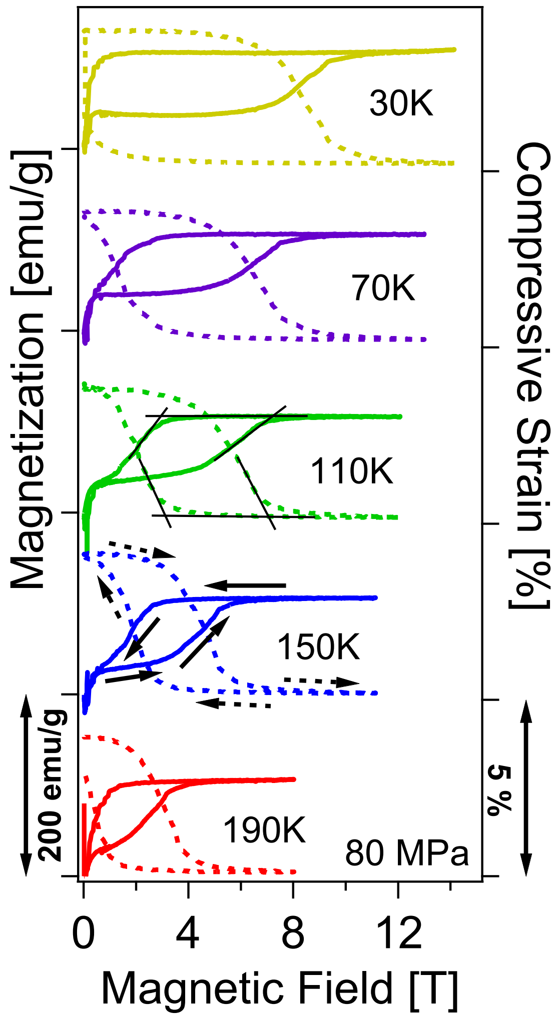

Fig. 2 The magnetization, solid lines, and compressive strain, dashed lines, as a function of magnetic field for the experiments conducted under 80 MPa and various constant temperatures.

Figure 3 displays the extracted critical magnetic fields for the austenite finish (H_{Af}) and martensite start (H_{Ms}) data points from all the experiments conducted at 80 MPa and 135 MPa constant stresses. The thin and thick lines represent the data extracted from magnetization and strain measurements, respectively. The equilibrium magnetic field (H_o) is calculated with the assumption that the forward and reverse transformations occur at the same rate and gives an indication of the relative thermodynamic stability of the austenite and martensite phases. The points below 150 K for the 135 MPa experiments have open markers to indicate that the extracted data points are not strictly reliable because the magnetic field was not strong enough to complete the phase transformation.

There are three distinct regions observed in the data: 1) above 150 K, 2) between 90 K and 150 K and 3) below 150 K. Above 150 K, the magnetic hysteresis, shown by the difference between H_{Af} and H_{Ms}, is small and the Clausius Clapeyron (CC) slope, given by the change in critical magnetic field with temperature dH/dT, of H_o is negative and fairly steep. This negative slope indicates that the martensite is more stable than the austenite in the temperature range and the magnetic field is required to stabilize austenite. Between 90 K and 150 K, the magnetic hysteresis begins to increase indicating greater kinetic effects and the H_o CC slope, while still negative, becomes less steep indicating that the relative stability of austenite and martensite is changing. Below 90 K, the CC slope becomes positive for the 80 MPa experiments. This inflection point is very important as it indicates that the austenite is now more stable than the martensite at these reduced temperatures. This is similar to the idea that the difference in entropy between austenite and martensite goes to zero.

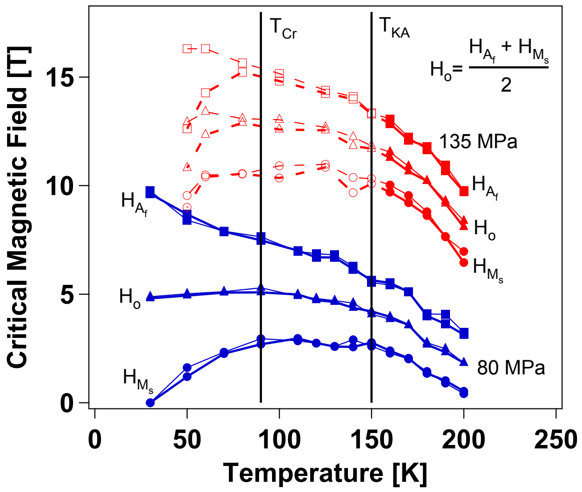

Fig. 3 The critical and equilibrium magnetic fields extracted from magnetization, thin lines, and strain, thick lines, data.

The KA temperature (T_{KA}) of 150 K, determined by Xu et al [6], obviously plays an important role even in a fully arrested material. The magnetic hysteresis above T_{KA} is small and the CC relationship corresponds well with thermo-mechanical data, not shown here. As the test temperature is decreased below 150 K, the martensitic transformation can still be magnetically stabilized, but the hysteresis begins to increase. This increase in hysteresis is believed result from kinetic affects that slow down the martensitic transformation and the 150 K threshold may be similar to the glass transition temperature observed in NiTi.

Below a critical temperature (T_{Cr}) of 90 K, exponential increases in the hysteresis with decreasing temperature are observed showing that the kinetic effects are increasing with decreasing temperature. The rapid increases in hysteresis are also accompanied by a change from a negative to positive CC slope that indicates the austenite is more stable than the martensite at these low temperatures. In traditional structural glass theory this is known as a Kauzmann point and is a true thermodynamic equilibrium if the forward and reverse transformations are considered to occur at the same rates [7].

4. Conclusion

A fully arrested MMSMA was shown to undergo magnetic field induced phase transformation under a biasing stress. Changes in the transformation rate below T_{KA} correspond well with previous data and are attributed to glassiness between the austenite and martensite phases. It was found that the austenite becomes more stable below a below T_{Cr} of 90 K. The T_{KA} corresponds to a decrease in the transformation rate while the T_{Cr} point corresponds to a shift in the thermodynamic equilibrium of each phase. The current literature does not distinguish between these two separate points, but this work shows that they both exist and occur at different temperatures.

References

[1] Y. Sutou, Y. Imano, N. Koeda, T. Omori, R. Kainuma, K. Ishida, and K. Oikawa, Appl. Phys. Lett., 85 (2004) 4358-4360.

[2] S. Morito, T. Kakeshita, K. Hirata, and K. Otsuka, Acta Mater., 46 (1998) 5377-5384.

[3] Y. Lee, M. Todai, T. Okuyama, T. Fukuda, Scripta Mater., 64 (2011) 927–930.

[4] Y. Wang, X. Ren, K. Otsuka, A. Saxena, Acta Mater., 56 (2008) 2885–2896.

[5] X. Ren, Y. Wang, K. Otsuka, P. Lloveras, T. Castán, M. Porta, A. Planes, A. Saxena, MRS Bulletin, 34 (2009) 838-846.

[6] X. Xu, W. Ito, R.Y. Umetsu, R. Kainuma,K. Ishida, App. Phys. Lett., 95 (2009) 181905.

[7] F.H. Stillinger, P.G. Debenedetti, T.M. Truskett, J. Phys. Chem. B, 105 (2001) 11809-11816.