Abstract of PhD Thesis

Elastic and dissipative energies in phase transformations of Cu-based shape memory alloys

Tarek Yousif AbdelRaoof El Rasasi

Supervisor

Prof. Dezső Beke

University of Debrecen
PhD School in Physics

Debrecen

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PhD School in Physics
and
The Department of Solid State Physics

Introduction

The amazing shape memory property of shape memory alloys (*SMAs*) attracted the attention of many scientists and engineers in the last decades, because of a wide range of important technical applications. Many models have been published for the description of the shape memory property as well as for the determination of critical parameters important for the technology. Furthermore, many experiments have also been carried out to understand the basic mechanisms and the details of the shape memory effect (*SME*).

In my thesis - after an introduction containing the most important definitions, notions and terminologies - I describe in details one of the above models (developed in Debrecen) and use it for analysis of the experimental results obtained in Cu based single and polycrystalline samples with compositions CuAl(15.9wt%)Ni(4.9wt%) and CuAl(11,6wt%)Be(0.36wt%), respectively. By using this model I was able for the first time to calculate the non chemical (elastic and dissipative) free energy terms and their contributions to the austenite (β)/martensite (β', i.e. *18R*) phase transformation and could also obtain the stress and temperature dependence of these energies. Furthermore, I also determined the dependence of the above energies on the number of thermal as well as mechanical cycles.

Experimental

Hysteresis loops of thermally and stress induced martensite transformations where investigated. The strain-stress ($\varepsilon \sim \sigma$) loops were obtained by the use of the Chatillon TCD225 tensile machine while a set up developed in our Laboratory was applied for the determination of the strain-temperature ($\varepsilon \sim T$) as well as the resistance-temperature ($R \sim T$) loops. Normalizing the strain axis by the maximal strain (transformation strain) or by the maximal value of the resistance the martensite volume fraction, ξ, was calculated and the $\sigma \sim \xi$ as well as $\xi \sim T$ hysteresis loops were constructed.

Differential scanning calorimeter (DSC) was used at zero uniaxial stress to measure the released and gained heat energy during the martensite transformation as well as to determine the effect of thermal cycling on the transformation heats. For obtaining the martensite volume fraction as the function of the temperature, the ratio of the partial and full integral of the DSC curves (integrating Q/T between e.g. the martensite start temperature, M_s, and T as well as between M_s and martensite finish, M_f temperature, respectively) has been taken.

Analysis of the results

The calculated hysteresis loops were analyzed in the framework of the model developed in Debrecen, allowing the determination of the stress and temperature dependence of the transformation strain, the elastic and dissipative energy contributions as well as the stress and temperature dependence of the equilibrium transformation temperature and stress.

Aims

Experimental investigation of hysteresis of thermal and stress induced martensitic transformations in single and polycrystalline Cu-based shape memory alloys. Using the model developed in Debrecen, carry out the separation of the non-chemical energy contributions (dissipative and elastic energies) from the free energy of the transformation. Determine how the dissipative and elastic energies depend on the stress and temperature as well as on the number of the thermal mechanical cycles. Since in the interpretation of data obtained the stress and temperature dependence of the transformation strain has a central role, these functions also have to be determined experimentally.

My work was

- Finding the full transformation strain as the function of temperature (for mechanically induced transformation) and stress (for thermally induced transformations. Determining the start and finish temperatures as well as start and finish stresses in the martensite transformations as a function of temperature and stress, and the effect of the contribution of the elastic energy on these parameters;
- Studying the stress and temperature dependence of the dissipative and elastic energies;
- Studding the effects of the thermal and mechanical cycling on the elastic and dissipative energies.

Conclusions

1. From the measurements of elongation-temperature (ε-T) and the elongation- stress (ε-σ) hysteresis curves in CuAl(11.5wt%)Ni(5.0wt%) single crystalline shape memory alloy, the stress and the temperature dependences of the transformation strain (ε^{tr}) was determined [3]:

   The transformation strain, determined from the σ-ε loops, depends on the temperature showing a saturation value of about 6.1%. As it is expected the same saturation value was obtained from the ε-T loops. The stress and temperature dependence of $\boldsymbol{\varepsilon^{tr}}$ is interpreted by the gradual change of the martensite structure: at higher uniaxial stress values more oriented martensite variant structure develops with higher resultant strain.

2. Derivatives of the non-chemical free energy contributions, by the martesite volume fraction, ξ, to the phase transformation at fixed temperatures as well as at fixed stresses have been studied in CuAl(11.5wt%)Ni(5.0wt%) single crystal shame memory alloys. These contributions were calculated form the ξ-σ and ξ-T hysteresis loops [3].
   a) The derivatives of the elastic energy by the martensite volume fraction, ξ, have strong temperature and stress dependence
   b) The derivatives of the dissipative energy were practically constant, or the changes were almost within the experimental errors.
   c) The ξ-T hysteresis curve at zero stress was obtained from the DSC curve. The elastic energy, calculated from the start and finish temperatures of it, fits very well to the straight lines obtained from the start and finish temperatures of the ξ-T hystersis curves at different $\sigma\neq 0$ levels.
   d) The slopes of the start and finish stresses versus temperature as well as the start and finish temperatures versus stress functions are different from the slopes of the equilibrium transformation stress versus temperature, $\sigma_o(T)$, as well as of the equilibrium transformation temperature versus stress, $T_o(\sigma)$, functions, respectively. It is shown that this is due to the temperature as well as stress dependence of the elastic energy contributions.

3. The total dissipative and elastic energy contributions were calculated from the integrals of their derivatives [2,6]

   Both the stress and temperature dependence of the total elastic energy per cycle shows a linear dependence in the investigated range with slopes -1.30 J/molMpa and -1.04 J/molK, respectively. The total elastic energy, E, decreases both with increasing stress and temperature, in accordance with the increasing volume fraction of the well oriented single variant structure.

4. Effect of the number of thermal and mechanical cycling, N, on the dissipative and the elastic energies has been studied in CuAl(11.5wt%)Ni(5.0wt%) single crystal shame memory alloy [5]. Both the dissipative and elastic energy show a definite dependence on the number of cycles in the first few cycles and then a saturation values is reached with increasing N. i.e. the stress-strain and strain-temperature responses stabilize.

   In thermal cycling the elastic energy, *E*, as well as the dissipative energy, *D* per one cycle increases as well as decreases, respectively with increasing number of cycles, while in mechanical cycling there is an opposite tendency. These changes are inevitably related to the change in the martensite variant structure during cycling.

5. It was obtained in the CuAl(11,6w%)Be(0.36w%) polycrystalline shape memory alloy that
   i. The elastic energy decreases with increasing applied uniaxial stress and it reaches a saturation value at high enough stresses. On other hand the dissipative energy increases and saturates at high stresses.
   ii. No thermal cycling effect has been detected on the DSC curves measured at zero σ.

List of Publications:

1- D.L. Beke, **T.Y. El Rasasi,** L. Daróczi, *"On the temperature and stress dependence of transformation strain in single crystalline Cu-Al-Ni shape memory alloys"* **ESOMAT 2009**, 02002 (2009) DOI:10.1051/esomat/200902002 ©

2- **T.Y. El Rasasi,** L. Daróczi, D.L. Beke, *"On the relation between the martensite start stress and the temperature in single crystalline Cu-11.5wt%Al-5.0wt%Ni shape memory alloy"*, **Materials Science Forum**, 659 (2010) 399. (IF.: 0.000)

3- **T.Y. El Rasasi**, L. Daróczi, D.L. Beke, *"Investigation of thermal and stress induced hysteresis curves in CuAl(11.5wt%)Ni(5.0wt%) single crystalline shape memory alloy" ,* **Intermetalics***,* 81 (2010) 1137. (IF.: 2.333).

4- **T.Y. El Rasasi**, L. Daróczi, D.L. Beke, *"On the Chemical and Non Chemical Free Energies in the martensite transformation in Cu Al-Ni shape memory alloy"* ,**ACTA PHYSICA DEBRECINA,** TOMUS XLIV **(2010)** 149. (IF.: 0.000)

5- **T.Y. El Rasasi**, M.M. Dobróka, L. Daróczi, D.L. Beke *"Effect of thermal and mechanical cycling on the elastic and dissipative energy in CuAl(11,6wt%)Be(0.36wt%) shape memory alloy"* in print in **Journal of Alloys and Compounds.** (IF. 2.134)

6- **T.Y. El Rasasi**, L. Daróczi, D.L. Beke *"Calculation of elastic energy contributions in single crystalline Cu-11.5wt%Al-5.0wt%Ni shape memory alloy" submitted to* **Materials Science Forum** (IF.: 0.000)

7- D.L. Beke, L. Daróczi, **T.Y. El Rasasi,** *"Determination of the elastic and dissipative energy contributions to the martensitic phase transformation in shape memory alloys "*accepted as a chapter in the book **"Shape memory Alloy"** *book editor* **F.M.B. Fernandes, IN TECH, 2012**

Citations:

[1] M. Fischlschweiger, E.R. Oberaigner, "Kinetics and rates of martensitic phase transformation based on statistical physics", **Computational Materials Science** 52 (1) (2012) 189

[2] Oberaigner, E.R., Fischlschweiger, M. *"A statistical mechanics approach describing martensitic phase transformation"* **Mechanics of Materials** 43 (9) (2012) 467

Posters:

[P1] Poster in the ***ESOMAT 2009,***

"On the temperature and stress dependence of transformation strain in single crystalline Cu-Al-Ni shape memory alloys".

D.L. Beke, T.Y. El Rasasi, L. Daróczi,

[P2] Poster in the ***VII Hungarian Conference on Material Science 2009*,**

"On the relation between the martensite start stress and the temperature in single crystalline Cu-11.5wt%Al-5.0wt%Ni shape memory alloy".

T.Y. El Rasasi, L. Daróczi, D.L. Beke

[P3] Poster and oral presentation in ***The 1st Egyptian Scientific workshop, Vienna 2011***

"On the Chemical and Non Chemical Free Energies in the martensite transformation in Cu Al-Ni shape memory alloy".

T.Y. El Rasasi, L. Daróczi, D.L. Beke

[P4] Poster in the ***ICOMAT 2011 Osaka, Japan 2011***

"Effect of thermal and mechanical cycling on the elastic and dissipative energy in CuAl(11,6wt%)Be(0.36wt%) shape memory alloy".

T.Y. El Rasasi, M.M. Dobróka, L. Daróczi, D.L. Beke

[P5] Poster in the ***VIII Hungarian Conference on Materials Science 2011*** *"Calculation of elastic energy contributions as the function of the martensite volume fraction in single crystalline Cu-11.5wt%Al-5.0wt%Ni shape memory alloy".*

T.Y. El Rasasi, L. Daróczi, D.L. Beke

[P6] Oral presentation in ***The 2ed Egyptian Scientific workshop, Prague 2012***

"On the elastic and dissipative energy contributions to the phase transformations in Cu-based shape memory alloys".

T.Y. El Rasasi, L. Daróczi, D.L. Beke