Viewpoint article

Elastocaloric effects in the extreme

H. Sehitoglu, Y. Wu, E. Ertekin

Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 1206 W. Green Street, Urbana, IL 61801, USA

A R T I C L E   I N F O

Article history:
Received 17 February 2017
Received in revised form 10 May 2017
Accepted 12 May 2017
Available online xxx

Keywords:
Shape memory alloys
Elastocaloric effect
Hysteresis
Fatigue
Entropy change

A B S T R A C T

There is a resurgence of interest in the elastocaloric (EC) effect of shape memory alloys (SMAs). The temperature change associated with the EC effect can be substantial, far exceeding those observed in well-known electrocaloric and magnetocaloric materials. The major driver of the EC effect is the entropy change of transformation. Historically the EC effect under superelasticity has been studied at mainly 25 °C. The current paper considers six SMAs across a variety of test temperatures, focusing not only on the EC cooling capability but also on three important factors for practical application: the role of stress/thermal hysteresis, M₅ temperature, and fatigue.

© 2017 Published by Elsevier Ltd.

1. Introduction

The SMAs are amongst the most fascinating materials that are now undergoing a resurgence in interest due to the possibility of utilizing them for their EC response. In this paper we provide an overview of several SMAs of interest for EC effect, focusing on elastocaloric cooling during reverse transformation. We explain the thermodynamic properties governing the transformation, and discuss how several mechanical factors influence their elastocaloric response [1–7]. While thermodynamic properties govern the theoretical temperature change achievable in EC cooling, mechanical properties such as stress hysteresis and fatigue will affect the usage of the EC effect in practical applications. We therefore highlight the need for combined assessments of both thermodynamic and mechanical properties, and present a comprehensive set of results spanning five different SMAs across wide temperature ranges.

The first factor that can affect the utilization of the EC effect is the presence of stress/thermal hysteresis in the martensitic transformation. Stress hysteresis is a type of irreversibility that results in energy dissipation that can have a detrimental effect on the EC temperature change. As the degree of hysteresis exhibited in the stress/strain response can vary in a complex manner with temperature, the EC performance and associated temperature change are also expected to be sensitive to the temperature. This can be important for applications that require operation across large temperature ranges.

The second factor is fatigue, which is particularly important in view of the fact that in real applications EC temperature changes will be exercised for many cycles. Stability under cycling is necessary for long lifetimes. Most metallic alloys exhibit excellent fatigue resistance and can undergo elasto-plastic deformation under strain cycling for many cycles. The rule of thumb that fatigue lives of 1000 cycles can be expected for applied strain amplitudes of 1% holds true for a remarkable number of metallic alloys. In comparison, SMAs exhibit exceptional fatigue resistance. For instance, the SMA NiTi can undergo a strain cycling of 1% over 10⁵ cycles [8]. The strain range of 10% can be utilized for 10⁶ cycles in the SMA Ni₅Fe₃Ga [9].

The third factor that influences the superelastic response, and hence the elastocaloric behavior, is the heterogeneity of the transformation. This is a topic that is not well understood and is influenced by the development of internal stresses, residual austenite and residual martensite phases [10,11]. To achieve superior SMA behavior, the transformation fronts should traverse across the matrix and then trace the same path upon return. If the strains localize in bands upon cycling, similar to persistent bands in metals, the temperature changes remain confined to such narrow zones, limiting the EC effect.

The aim of the present work is first to provide an overview of several SMAs previously considered in the literature and highlight the thermodynamic factors that govern their theoretical EC cooling capability. Then, we comprehensively assess five SMAs (NiTi, Ni₅Fe₃Ga, Ni₅Ti₃Cu, Ni₅Ti₃Hf, Ni₅Fe₃Ga) for their EC cooling capability under superelastic unloading at a wide variety of ambient test temperatures. To highlight the critical role of mechanical response, we show the dependence of the measured EC temperature change on stress hysteresis, demonstrate that the temperature span where the EC effect is exhibited is well-correlated to the M₅ temperature, and discuss the fatigue response of SMAs under tension and compression.
2. Introduction to phase transformations in shape memory alloys – the terminology

The phase transformations in SMAs occur in a reversible manner from a high symmetry austenitic phase to a low symmetry martensitic phase upon application of stress or upon cooling below the transformation temperature. The transformation is diffusionless, but first-order and thus temperature-dependent, and occurs via nucleation and growth of a new phase [12]. It typically involves a large deviatoric component, and since it is a result of shear-dominated strain, can be triggered under tension, compression, and shear loading. In some SMAs, the strains exhibited can reach up to 14% upon application and removal of stress cycle after cycle. This behavior defies conventional metals such as steels, where failure would occur within a few cycles at such high strains. Since the dilatational strains are negligible, the application of hydrostatic stress does not induce a shape change in SMAs. The transformation occurs at stress levels well below the slip stress and can be measured in mechanical experiments at different test temperatures. As deformation temperatures approach a characteristic temperature \( T_0 \), the transformation can no longer be induced by stress. The EC effect arises from the latent heat of the first order martensitic transformation. Several thermodynamic and mechanical quantities are used to characterize the phase transformation and associated EC effect. Large temperature changes arise when the entropy change of transformation itself is large. The entropy change associated with the transformation can be measured from the slope of the Clausius-Clapeyron (transformation stress versus temperature) curves or from differential scanning calorimetry (heat flow measurement). Alternatively the entropy change can be obtained from first-principles calculations of phonon spectra although this can be challenging in practice. However, while the entropy change of transformation can be readily related to the adiabatic temperature change, i.e. the theoretical temperature change achievable under ideal conditions, there are several mechanical parameters that result in a deviation from the idealized response. The current paper aims to document the role of mechanical properties on measured temperature changes.

To explain the terms relevant to EC effects and superelasticity in SMAs, it is worthwhile to study the schematic given in Fig. 1. The flow stress is plotted as a function of temperature, displaying the austenite to martensite transformation regime at temperatures below \( M_s \) and austenite slip at temperatures above \( M_s \). The transformation temperature is denoted as \( T_0 \). In the insets in Fig. 1, the superelastic response including hysteresis (stress vs. strain) and the elastocaloric temperature change under unloading (temperature vs. time) are given. For superelastic response, three important parameters are the transformation stress, the stress hysteresis, and the transformation strain. For elastocaloric cooling the key parameter is the temperature change obtained upon rapid unloading. This can be measured directly by infrared thermography. Finally, we note the importance of the functional behavior of the SMAs on the use of the EC effect. Physical damage mechanisms can contribute to fatigue and fracture. The propensity for strain localization in certain classes of SMAs may accelerate the accumulation of damage [11].

Thermal measurements of stress-induced martensitic transformations in NiTi have been reported in the literature since the 1970s, which largely focused on characterizing the temperature change upon transformation [13–16]. Since then, more SMAs have been identified that exhibit good EC potential. A comprehensive review paper that documents EC effects in several different shape memory alloys has appeared recently [17]. This previous review provides an excellent comparison of physical properties of EC alloys in comparison with magnetocaloric and elastocaloric alloys. In the present work, our aim is to review the role of mechanical response and functional properties as they influence elastocaloric performance. Such an assessment, illustrating a better understanding of the mechanical properties, is vital in evaluation and development of SMAs with superior elastocaloric characteristics for practical application.

3. Review of the elastocaloric response

Fig. 2(a) summarizes the adiabatic (theoretically achievable) temperature change \( \Delta T_{th} \) as a function of the entropy change of transformation \( \Delta S \). We have incorporated many of the key shape memory alloys that exhibit considerable elastocaloric potential; the results summarized are for Ni50.5Ti49.2 (at.%) single crystals [18], Ni50.2Ti49.8 (at.%) wire [19], Ni50.2Ti49.8Cu2.6 (at.%) thin film [20], Ni52.5Ti50.4Cu2.6 (at.%) thin film [21], NiFeCuCo [6], and NiTiCuV [7], CuZnAl [22–24], Ni2FeGa [18], NiFeGaCo [25], NiAl [18], FePd [26], NiMnInCo [27], NiMnIn [28], and NiMnSn [29]. The quantity \( \Delta T_{th} \) is related to \( \Delta S \) by the relationship \( \Delta T_{th} = \frac{T \Delta S}{C_p} \), where \( T \) is the deformation temperature and \( C_p \) is the heat capacity [30,31]. The NiTi-based SMAs have the largest \( \Delta S \) and also exhibit the highest \( \Delta T_{th} \). The NiTi-based SMAs have the largest \( \Delta S \) and also exhibit the highest \( \Delta T_{th} \), exceeding 40 °C. Related alloys such as NiTiCu and CuZnAl are very promising, but exhibit a lower \( \Delta S \) compared to NiTi. Meanwhile Ni2FeGa, a relatively new shape memory alloy, also has a lower \( \Delta S \) but has added the advantage of extending the operational temperature of the EC effect. On the other hand, Fe- based SMAs exhibit a rather small entropy change.

In Fig. 2(b), the actual temperature change \( \Delta T_{EC} \) measured in our experiments is shown, now plotted as a function of \( \Delta \sigma/\varepsilon \), the measured stress hysteresis (the difference between forward and reverse transformation stress) normalized by the forward transformation stress. Such a normalization allows comparison of different SMAs with different transformation stresses and is consistent with previous derivations of stress hysteresis [32]. The specific compositions in Fig. 2(b) are Cu59.1Zn27Al13.8, Ni50Fe9Ga27, Ni50.5Ti49.8Hf3.3, Ni50Ti50Cu10, Ni50Ti49.2Co4, Ni33.2Al16.9. The corresponding lattice changes are L21, J18R, L21 to 14M to L10, B2 to B19′, B2 to B19. B2 to B19′ and B2 to L10 respectively. The temperature changes are
measured with infrared thermal imaging, the stresses are measured with a load cell, and the strains are measured using digital image correlation [5]. The figure shows that, in addition to $\Delta T_{th}$, NiTi alloys exhibit superior performance in $\Delta T_{EC}$ as well. Most interestingly, we observe an inverse relationship between $\Delta T_{EC}$ and $\Delta \sigma/\sigma_{T\approx A_{f}}$. This suggests that larger temperature changes are achieved in practice when less stress hysteresis is present, and that a given SMA may exhibit an ideal operating temperature that minimizes the hysteresis and results in larger $\Delta T_{EC}$. For each alloy, our results were collected over a range of test temperatures. Since for a given alloy different test tempera-
tures can give rise to different $\Delta \sigma/\sigma_{T\approx A_{f}}$ in some SMAs such as CuZnAl for which the superelastic window is large, the span of the ellipsoids in Fig. 2(b) are wide.

To gain insight into the role of deformation temperature on the measured temperature change $\Delta T_{EC}$, the maximum temperature at which EC cooling upon superelastic unloading can still occur is plotted versus the $M_d$ temperature in Fig. 3(a). As expected, larger $M_d$ enables extension of EC response to higher temperatures. The results show that Ni$_3$FeGa and CuZnAl can be highly effective for elevated temperature EC operation due to delayed onset of austenite slip. Fig. 3(b) shows how $\Delta T_{EC}/\Delta T_{th}$, the ratio of the measured EC temperature change to the theoretically achievable temperature change, varies with the degree of temperature hysteresis (the difference between for-

![Fig. 2. Adiabatic temperature change and effect of stress hysteresis.](image)

![Fig. 3. The maximum operating temperature of the EC effect versus the $M_d$ temperature.](image)
ward and reverse transformation temperature normalized by the equilibrium temperature) exhibited by each material. Interestingly, there is a reasonable correlation between $\Delta T_{tr}/\Delta T_{tr}$ and the temperature hysteresis. These observations illustrate that measured temperature changes can better approach the theoretical maximum value when the thermal hysteresis is low. For example, NiTi exhibits a large relative thermal hysteresis while Ni$_2$FeGa does not. Even though the theoretical EC temperature drop for Ni$_2$FeGa is 8 °C it is close to the theoretical value of 12 °C, while the measured change in NiTi is 20 °C compared to the theoretical value of 50 °C.

Finally, we illustrate our results on the fatigue response of several important SMAs in Fig. 4. Fig. 4(a) shows the cycling strain range $\Delta \varepsilon_{cr}$ versus fatigue life $N_f$, and indicates that longer fatigue lives can be achieved for smaller $\Delta \varepsilon_{cr}$, i.e., the strain difference during cycling, and $\varepsilon_{tr}$, the transformation strain. The $\Delta \varepsilon_{cr}/\varepsilon_{tr}$ vs. $N_f$ curves of polycrystalline CuZnAl alloys were replotted based on the data reported by Melton and Mercier [33] and Oshima and Yoshida [34]. Similar results have been shown by Sakamoto et al. [35] and Siredey et al. [36] for CuNiAl and CuAlBe alloys, respectively. A comprehensive study on the fatigue response of Ni$_2$FeGa single crystals has been undertaken by Efthathiou et al. [9]. In the case of NiTi-based SMAs, many papers have been published regarding the fatigue lives of NiTi [8,33,37–41] and polycrystalline NiTiCu [41]. For practical usage EC operation must exceed millions of cycles, and (as expected) in Fig. 4(a), longer fatigue lives are obtained for smaller $\Delta \varepsilon_{cr}$. Amongst the alloys considered Ni$_2$FeGa can achieve such long lives in tension for strain levels exceeding 10%, which makes it rather promising. On the other hand, the NiTi (both polycrystalline and single crystal) alloys exhibit shorter lifetimes, especially when cycled near the maximum transformation range $\Delta \varepsilon_{cr} \approx 1$. Meanwhile in Fig. 4(b) the dependence of the EC temperature change $\Delta T_{tr}$ on $\Delta \varepsilon_{cr}$ is illustrated for three major SMAs, which shows that to achieve the largest temperature changes the strain ranges need to close to the transformation strain $\varepsilon_{tr}$. Cycling with large $\Delta \varepsilon_{cr}$ ensures that more of the austenite domain can be converted to martensite and vice versa. Under such conditions, a given alloy's performance in practice can be limited by fatigue life. These results highlight the need and potential benefits to considering compression-compression cyclic loadings for achieving long term operation. The results summarized in Fig. 4(c) attest to the benefits of compression loadings where fatigue damage may not affect lifetimes in practical applications. Fig. 4(c) shows the EC temperature change under tension and compression for five alloys studied in our work. The results underscore the significant benefits of exploring compression loadings. Note that the temperature changes observed for NiTiHf$_{33}$ are small because of the severe localization effects during deformation.

4. Discussion of results

The NiTi has been the most widely studied SMA due to its superb functional properties such as superelasticity and shape memory effect under thermal cycling. It possesses the largest levels of entropy

![Figure 4](image-url)
change that makes it an excellent candidate for elastocaloric applications. In this study, we draw close attention to NiTi, and also bring to light some of our results on CuZnAI, Ni$_3$FeGa, NiTiCu and NiTiHf. For these alloys, elastocaloric cooling temperature change upon reverse transformation was assessed as a function of test temperature. Our analysis focuses on the strong sensitivity of the temperature change to stress hysteresis, the relationship between the temperature for the forward transition with respect to the $M_s$ temperature, and the possibility of cyclic degradation due to fatigue. A comparison of the measured vs. adiabatic temperature change is presented and we find that the largest temperature changes are obtained when stress/thermal hysteresis is minimized. The results underscore the benefits of Ni$_3$FeGa as an EC alloy even though its entropy change is smaller than NiTi.

It is worth noting that the operational range of elastocaloric effect in Ni$_3$FeGa is the highest while the CuZnAl (in compression) also exhibits a very large temperature range. Since at high temperatures the critical resolved shear stress for slip will limit superelasticity, the temperature span of the EC effect can benefit from alloys with a large $M_s$ temperature. The $M_s$ temperature of Ni$_3$FeGa is rather high reaching 350 °C. Along the same lines, we expected possible operation of CoNiAl at high temperatures but the entropy change is lower compared to Ni$_3$FeGa [5]. Further studies can be conducted to identify materials with higher $M_s$ temperatures. One possibility is to introduce HF as a ternary addition to NiTi, unfortunately in our case we observed strain localization during superelastic deformation, high stress hysteresis, and rapid deterioration of the superelastic effect. The NiTiCu provides benefits by stabilizing the transformation temperatures of NiTi, but unfortunately it results in a lower entropy change and a smaller EC temperature change.

To obtain the largest elastocaloric response on a given alloy, we note that the deformation (applied strain) must be high enough to convert the entire austenite domain to martensite and vice versa. Under such large strain cycling to ensure transformation of the entire domain, fatigue damage may limit the lifetime of the alloy in practice. To circumvent the problems arising from fatigue, the use of compression loadings can be proved to be beneficial. The transformation strains in compression are lower (5%) for NiTi compared to tension (10%), whereas the adiabatic temperature change remains very similar. In terms of fatigue performance, in tension CuZnAl and Ni$_3$FeGa display superior characteristics to NiTi and NiTiCu, while all four alloys exhibit exceptional fatigue characteristics in compression. For example, for NiTi the cycles to failure was 150 in tension while in compression failure is not observed in excess of $10^4$ cycles.

To summarize our observations for the materials considered in this study, we undertook a closer evaluation of several promising SMAs to assess their EC behavior. We note that especially in tension the magnitude of stresses for transformation are rather small for Ni$_3$FeGa, CuZnAl and NiTiCu alloys, which could be advantageous to generate an EC response under small loadings. The transformation strain in Ni$_3$FeGa is higher than NiTi, The CuZnAl transformation strain is comparable to NiTi while the NiTiCu is lower than the other three. Amongst these four promising alloys the fatigue response in tension is superior in Ni$_3$FeGa. If higher loads can be generated, compressive loading is far more advantageous resulting in similar or better temperature change compared to tension while not being compromised by damage accumulation.

5. Viewpoint conclusions

The work emphasizes the need to understand mechanical properties such as the stress hysteresis and the fatigue response to optimize the EC capacity of SMAs. We summarize the conclusions in capsule form below:

1. The research on elastocaloric effects coupled with mechanical response in SMAs is still in its infancy. The potential for practical application is intimately tied to stress hysteresis and fatigue performance. The fatigue performance is especially critical because to maximize the EC effect the SMAs should be cycled close to their maximum transformation strain, potentially accelerating the accumulation of damage. The lower stress hysteresis results in smaller dissipation, and we find that it is correlated to larger measured temperature changes. Lowering the temperature hysteresis associated with the transformation also allows the measured temperature change to approach the theoretically possible adiabatic value.

2. Searching for alloys that exhibit higher entropy changes continues as a promising line of research. For example, the NiTi alloys with additions of HF possess higher entropy changes, yet fall short on mechanical properties for long-term operation. Heat treatments and texturing may modify and possibly improve the results.

3. By considering SMAs with higher $M_s$ temperatures so that the temperature range of superelasticity can be widened, the operating temperature range for systems that use the EC effect can correspondingly be extended as well.

4. The results underscore the potential of compressive cycling as a possible avenue to extend the lifetime of systems that utilize the EC effect in practice. Upon comparison of tension and compression cycling, the adiabatic temperature changes (obtained from the measured entropy change) in both cases are of the same magnitude.

Acknowledgements

The work is supported by the National Science Foundation, DMR-REF grant # 1437106. The EBSD analysis was carried out in the Frederick Seitz Materials Research Laboratory Central Research Facilities, University of Illinois. The single crystals were grown by Prof. Yurii Chumlyakov of Tomsk State University, Russia.

References