Article

Thermoelastic Properties and Elastocaloric Effect in Rapidly Quenched Ribbons of Ti_2NiCu Alloy in the Amorphous and Crystalline State

Evgeny Morozov *, Dmitry Kuznetsov , Vladimir Kalashnikov, Koledov Victor and Vladimir Shavrov

Kotel'nikov Institute of Radioengineering and Electronics (IRE) of Russian Academy of Sciences, 125009 Moscow, Russia; kuznetsov.dmitry89@gmail.com (D.K.); vladimir.kalashnikovS@gmail.com (V.K.); victor_koledov@mail.ru (K.V.); shavrov@cplire.ru (V.S.)

* Correspondence: evgvmorozov@gmail.com

Citation: Morozov, E.; Kuznetsov, D.; Kalashnikov, V.; Victor, K.; Shavrov, V. Thermoelastic Properties and Elastocaloric Effect in Rapidly Quenched Ribbons of Ti_2NiCu Alloy in the Amorphous and Crystalline State. *Crystals* **2021**, *11*, 949. <https://doi.org/10.3390/cryst11080949>

Academic Editors: Hongbin Bei and Sergio Brutti

Received: 21 June 2021

Accepted: 10 August 2021

Published: 15 August 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: The thermoelastic properties and the elastocaloric effect (ECE) were studied in rapidly quenched ribbons of the Ti_2NiCu alloy samples in amorphous and crystalline states under periodic mechanical tension with a frequency of up to 50 Hz. In the amorphous samples, elastic behavior is observed, described by Hooke's law, with a high coefficient of thermal expansion $\alpha = 1.7 \times 10^{-4} \text{ K}^{-1}$. Polycrystalline ribbons of the Ti_2NiCu alloy have the classical shape memory effect (SME), the temperatures of the forward and reverse thermoelastic martensitic transitions being $M_s = 345 \text{ K}$, $M_f = 325 \text{ K}$, $A_s = 332 \text{ K}$, and $A_f = 347 \text{ K}$ and the coefficient of the dependence of the transition temperature on mechanical stress being $\beta = 0.12 \text{ K/MPa}$. The experimentally measured value of the adiabatic temperature change under the action of mechanical stress (ECE) in the amorphous state of the alloy at room temperature ($T_r = 300 \text{ K}$) was $\Delta T = -2 \text{ K}$, with a relative elongation of $\varepsilon = 1.5\%$ and a mechanical stress of $\sigma = 243 \text{ MPa}$. For crystalline samples of Ti_2NiCu alloy ribbons, the ECE is maximum near the completion temperature of the reverse thermoelastic martensitic transformation A_f , and its value was 21 K and 7 K under cyclic mechanical loads of 300 and 100 MPa, respectively. It is shown that the ECE value does not depend on the frequency of external action in the range from 0 to 50 Hz. The specific power of the rapidly quenched ribbon was evaluated as a converter of thermal energy at an external mechanical stress of 100 MPa; its value was 175 W/g at a frequency of 50 Hz. The thermodynamic model based on the Landau theory of phase transitions well explains the properties of both amorphous ribbons (reverse ECE) and alloy ribbons with EPF (direct ECE).

Keywords: functional alloys; amorphous alloys; Ti_2NiCu ; shape memory effect; thermoelastic martensitic transition; elastocaloric effect; phase transition kinetics; specific power of energy conversion

1. Introduction

In recent years, the new solid-state functional materials and their properties have attracted great attention. They have found important applications in sensor and actuator technology. For example, intermetallic alloys with a shape memory effect (SME), which is caused by thermoelastic martensitic transition occurring in the solid phase of the alloy, have a remarkable property to restore their shape under significant deformation and perform mechanical work under the influence of temperature or magnetic fields [1]. At the end of the 20th century, the work [2] played an important role in the development of caloric effects. It increased the interest of the world scientific community in their study. In this work, a “giant” elastocaloric effect (ECE) during a phase transition in a solid-state alloy $\text{Fe}_{49}\text{Rh}_{51}$ is studied in a magnetic field and under tensile stress. In recent years, proposals have been made on the use of solid-state functional materials in alternative energy. To this end, new materials are being studied that demonstrate various caloric effects, such as magnetocaloric, elastocaloric, and electrocaloric, arising in samples of solid-state materials under the influence of external fields. The essence of the above effects is a strong change

in the entropy and temperature of these materials under the influence of external fields: magnetic, electric, and mechanical stress fields, which is maximum, respectively, near the phase transitions affecting the corresponding order parameters: magnetic moment, electric polarization, or structural order parameters.

The ECE, that is, a change in the temperature of solids during adiabatic deformation, has been known for a long time [3]. Recently, a lot of work has been devoted to the study of ECE [4–13]. It was shown in [4] that Ti–Ni alloy with a thermoelastic martensitic transition and SME has a significant ECE (more than 20 K). This is not surprising, since ECE is, in fact, the inverse SME effect, and the Ti–Ni alloy is a recognized record holder for SME parameters among functional intermetallic compounds. However, in [5–7], it was noted that, despite the giant ECE, this alloy actively accumulates fatigue defects, which reduce its value with repeated periodic loading. The authors of [4] proposed the study of ECE in other materials, such as intermetallic compounds with SME: Ni₂FeGa, Ni₂TiCu, CuZnAl, and CoNiAl, which are also recognized as promising for elastocaloric cooling due to their high thermomechanical characteristics. A colossal value of the ECE was recorded in the Ni–Mn–Ti alloy, up to 31.5 K [9]. The disadvantages of this and other works include measurements of the ECE at a single deformation or at low frequencies (of the order or less than 1 Hz). As a result, the important questions about the maximal attainable energy flow rate induced by mechanical stress, at the thermoelastic martensitic transition, and the ultimate specific power of thermal energy conversion by a working fluid based on a solid-state material with ECE remains unanswered.

The rapidly quenched Ti₂NiCu alloy, which is obtained in the form of ribbons by the spinning method, attracts much attention due to its manufacturability and high values of the functional properties of SME [14–17]. The thermoelastic martensitic transition and SME in this alloy were demonstrated on nanoscale size of samples [18], and composites based on it were found to be very convenient for creating actuators with reversible thermoinduced deformation, which are recorded in miniature size and frequency performance [19]. It was proposed to use composite nano-instruments with SME for technologies of the bot. 73 tom-up to nanomanipulation and nano-assembling [20].

The ECE under tensile stress in the Ti₂NiCu alloy was very convenient to be studied, since the alloy was obtained in the form of thin ribbons with a thickness of the order of 30–40 µm with high strength, up to hundreds of MPa, and a convenient temperature range of the martensitic phase transition in the range of 40–60 °C. In addition, the Ti₂NiCu alloy obtained by ultrafast quenching on a rotating copper wheel immediately after preparation turned out to be amorphous or layered amorphous-crystalline. The presence of alloy samples in a polycrystalline state, in which a thermoelastic martensitic transition of the 1st order and SME were present, and in amorphous state in which there was no long-range crystalline order and, therefore, a thermoelastic phase transition was not observed, makes this alloy very convenient for a comparative study of the role of the phase transition to nature SME and ECE.

The aim of this work is the experimental and theoretical study of the thermoelastic properties and ECE in the rapidly quenched ribbons of the Ti₂NiCu alloy in amorphous and crystalline states at different values of the frequency of the external tensile stress. Additionally, the aim is to estimate the maximum specific power of heat conversion by a working body made of a rapidly quenched Ti₂NiCu ribbon.

2. Materials and Methods

Samples of the Ti₂NiCu alloy were obtained by ultrafast quenching at a speed of 10⁷ K/s in the form of a ribbon with 30–40 µm thickness and 1.5 mm wide. After quenching, the alloy was mainly in the amorphous state [14].

To study the thermoelastic properties and ECE, we selected samples of rapidly quenched ribbons of Ti₂NiCu alloy approximately 10–12 cm long, 1.5 mm wide, and 36 µm thick [21]. Afterwards, rapid quenching samples were in amorphous state. Ribbons were annealed at T = 450 °C for 2 h with cooling in air to gain a crystalline state and study

the SME and ECE. Figure 1 shows the results of study of the structural phase transition by differential scanning calorimetry (DSC). The characteristic temperatures of the start and finish of the direct and reverse martensitic transitions of the samples were $M_s = 62.0\text{ }^{\circ}\text{C}$, $M_f = 51.1\text{ }^{\circ}\text{C}$, $A_s = 59.8\text{ }^{\circ}\text{C}$, and $A_f = 67.5\text{ }^{\circ}\text{C}$, and the latent phase transition energy was $\lambda = 11.5\text{ J/g}$.

Figure 1. DSC data (blue line—cooling, red line—heating) for rapidly quenched Ti_2NiCu ribbon annealed for 2 h at a temperature of $450\text{ }^{\circ}\text{C}$.

The setup described in [22] was used to determine the thermomechanical properties. The principle of operation of the experimental setup is based on the stretching of an alloy specimen of an alloy with SME under constant load at a variable temperature.

An original experimental setup was constructed to study the ECE in rapidly quenched Ti_2NiCu alloy ribbons at a frequency up to 50 Hz. It consisted of the actuator (asynchronous electric motor with a crank mechanism and a spring) rigidly fixed to the platform and connected to a variable voltage source. The actuator provided periodic deformation of the test sample, rigidly fixed from one end, with the other end attached to the spring, which, in turn, was attached to the actuator connecting rod. The temperature of the sample was changed by passing an electric current through it. A sweep current generator was used as a source, providing gradual heating and cooling of the ribbon through the martensitic transition range, with a peak current value of about 1 A. The surface temperature of the sample was measured remotely using an infrared camera brand Flir SC-7000 with a frame frequency of up to 400 Hz. To increase the accuracy of thermal measurements, the region of the ribbon on which the camera was focused was blackened. A personal computer was used to collect and process high speed thermograms recorded by camera and measured data.

3. Results

3.1. Thermoelastic Properties of Ti_2NiCu Melt Spun Ribbon

Figure 2 shows the dependencies of the deformation of the ribbon annealed at a temperature of $450\text{ }^{\circ}\text{C}$ for 2 h under the action of different constant mechanical stresses.

Figure 2. Temperature dependences of sample deformation at various constant mechanical loads (indicated in the inset of the graph, MPa) for an annealed strip (up arrow—direct transformation upon cooling, down arrow—reverse transformation upon heating).

The amorphous ribbon sample did not exhibit a thermoelastic martensitic transformation, which was pronounced in the annealed sample (Figure 2). The maximum reversible deformation of the annealed ribbon sample was 2.5% at a load of 405 MPa.

Contrary to the amorphous ribbon, the polycrystalline ribbon, with an increase of temperature, was compressed in the vicinity of thermoelastic martensitic transition. At the higher external stretching load, thermal cycling was carried out at the higher compression. This behavior indicates a clear SME due to two-stage thermoelastic martensitic transformation in the temperature range 325–360 K, depending on the stress applied. The average value of the coefficient of dependence of the temperature A_f of the end of the transformation from martensite to austenite on mechanical stress was found: $\beta = 0.12 \text{ K/MPa}$. The calculated value of the coefficient of thermal expansion for the annealed ribbon in the low temperature martensitic state well below M_f was approximately $4.2 \times 10^{-7} \text{ K}^{-1}$.

3.2. ECE in Rapidly Quenched Ribbons

3.2.1. ECE in Amorphous Rapidly Quenched Ti_2NiCu Ribbons

As a result of the measurements of ECE, IR thermograms were obtained and processed. An example of images obtained by a high-speed IR camera from an unstretched and stretched amorphous ribbon of a Ti_2NiCu alloy is shown in Figure 3a,b. When stretched, the tape cools were reflected by the color change of the image elements (pixels). For quantitative measurement of the ECE, temperature distribution diagrams of the number of pixels were constructed (Figure 3c,d). In each of the diagrams, a background peak with a room temperature of 300 K (shown in black) and a peak corresponding to the temperature of the sample are highlighted.

It can be seen that this peak moved to the region of lower temperatures during ribbon stretching deformation, which occurred due to the inverse ECE in the elastic ribbon. No pronounced effect of the change to the frequency of the external force cycles up to 10 Hz on the value of the ECE was observed, indicating that, in this range, the ECE does not depend on the frequency.

Figure 3. IR thermograms for studying ECE in an amorphous Ti_2NiCu ribbon. (a) The undeformed tape, (b) the stretched tape, (c) a temperature distribution diagram in the undeformed ribbon, and (d) a temperature distribution diagram in the stretched ribbon.

3.2.2. ECE in the Polycrystalline Ti_2NiCu Ribbons

Thermograms are shown on Figure 4, which shows the crystalline samples of Ti_2NiCu alloy ribbons. The thermograms record the spatial distribution of the sample temperature under periodic exposure to tensile stress with increasing and decreasing average ribbon temperature in the region of the martensitic transition. Photographs from the thermal imager screen of a strip sample in a stretched and undeformed state, which are shown in Figure 4a,b, respectively, demonstrate uneven heating and cooling during cyclic loads.

As a result of processing the thermograms, the dependences of the sample temperature on time during heating and back cooling were obtained. An example of such a dependence is shown in Figure 5 at a cyclic load with the amplitude of 100 MPa with an exposure frequency of 10 Hz. The rate of gradual heating of the sample (for measuring the ECE over the entire range of the phase transition and near it) is 4 K/s, and the rate of back cooling is 3.5 K/s. It was experimentally shown that, with a frequency of tension-compression cycles of more than 1 Hz, the process was adiabatic and external heating/cooling did not contribute to the ECE. As can be seen in Figure 5, at a periodic load with an amplitude of 100 MPa and a frequency of 10 Hz, and an increase and then a decrease of the current through the sample, the heating rate of the sample was 4 K/s and the maximum value of the ECE was 7 K.

Figure 4. Thermograms of a polycrystalline tape made of Ti_2NiCu alloy deformed at a frequency of 6 Hz: a—a tape under load, b—a tape without a load. Dependences of the sample temperature on time (c) and (d) at the time point corresponding to the recording of thermograms (a) and (b), respectively.

Figure 5. The dependence of the temperature of the sample on time during heating and cooling at a cycle frequency of the driving force of 10 Hz. The maximum load of 100 MPa.

Analyzing the thermograms obtained at different parameters of external influences on the Ti_2NiCu ribbons, it was found that the maximum value of the ECE at cyclic loads was 21 K (Figure 6) at a load of 300 MPa and the frequency of the loading cycles was 3 Hz.

Figure 6. The dependence of the temperature of the sample on time during gradual heating under the influence of external periodic mechanical stress with a frequency of 3 Hz, with a maximum value of 300 MPa.

During the experiments, it was shown that the value of the ECE did not depend on the frequency of the external driving force (Figure 7).

Figure 7. Dependence of ECE on the frequency of tensile and compression cycles of the sample at a maximum mechanical stress of 100 MPa at a temperature of Af.

To assess the possibility of using rapidly quenched Ti_2NiCu ribbons as a working fluid in elastocaloric heat pumps, in Figure 8, the plot of the specific power versus the frequency of the external periodic force on the studied tapes is given.

To get the formula of the specific power, we use the relation of the thermal energy of the sample:

$$Q = c_M \cdot m \cdot \Delta T \quad (1)$$

where c_M is the specific heat of the sample in martensitic state, since the ECE is due to the induction of overheated martensite under the action of an external load, m is the mass of the sample, and ΔT is the change in the temperature of the sample (ECE).

Figure 8. Dependence of the specific power of a working fluid based on a Ti_2NiCu polycrystalline ribbon on the frequency of external mechanical stress.

By definition, the specific power (power per 1 g of mass) for one period of oscillation (τ) is:

$$W = \frac{Q}{m \cdot \tau} \quad (2)$$

Thus, substituting (1) expression into (2) and taking into account that $\tau = 1/f$ (f —frequency of oscillations), we obtain:

$$W = c_M \cdot f \cdot \Delta T \quad (3)$$

where c_M is the specific heat of the sample in martensitic state, f is the frequency of cycles of exposure to external mechanical stresses, and ΔT is the ECE. At $f = 50$ Hz (the maximum frequency provided by the experimental setup) and a mechanical stress of 100 MPa ($\Delta T = 7$ K), we obtain $W = 175$ W/g.

4. Discussion

In this work, we studied the ECE in rapidly quenched ribbons of the Ti_2NiCu alloy in various structural states. ECE in an amorphous and polycrystalline alloy at a temperature corresponding to the temperature A_f of the polycrystalline Ti_2NiCu alloy has a different sign, which is in qualitative agreement with estimations that were done based on the measurement data of their thermoelastic properties.

The very derivation of the formula for calculating the dependence of deformation on temperature in classical solids is theoretically described in [19], using the expansion of the Helmholtz free energy function to the second order in deflation and temperature. The calculated ECE value of the amorphous Ti_2NiCu alloy ($\Delta T = 2$ K) can be obtained from the equation:

$$\frac{\Delta T}{T} = -\frac{\alpha K}{c_p} \cdot \frac{\Delta l}{l}, \quad (4)$$

where ΔT is the ECE value, T is the initial temperature of the sample ($\Delta T \ll T$), α is the coefficient of thermal expansion, K is the coefficient of volume elasticity ($K = E/(3(1-2\nu))$, E is Young's modulus, ν is Poisson's ratio), c is the specific heat of the sample (without martensitic transition), ρ is the specific density of the sample, and $\Delta l/l$ is the relative strain of the sample under tension (l is the length of the sample, Δl is the linear deformation of the sample). It corresponds very well to the experimentally obtained value of the ECE.

In a polycrystalline alloy, the greatest effect is observed at a temperature A_f . This is explained by the formation of a low temperature structural phase under the influence of

mechanical stress and, in article [9], is obtained and theoretically described in detail using the Gibbs thermodynamic potential for materials with shape memory:

$$\Delta T(S, O \rightarrow f = p, \sigma) \simeq \frac{T\Delta S(Ti, O \rightarrow f = p, \sigma)}{c_M} \quad (5)$$

where T is the sample temperature, ΔS is the entropy change, and c_M is the specific heat of the sample in martensitic state. We substitute the values ($\lambda = 1.15 \times 10^4$ J/kg, $c_M \approx 500$ J/(kg K)), and taking into account that $T\Delta S = \lambda$ (λ is the latent energy of phase transition), we obtain $\Delta T \approx 20$ K. In the present work, the experimentally measured maximum value of the ECE is $\Delta T = 21$ K. Given the measurement error, we can conclude that the entire high temperature phase under the influence of a mechanical stress of 300 MPa completely passes into the low temperature phase. It follows that, in the experiment, the maximum possible value of the ECE for this alloy was achieved with the used methods of sample preparation.

The obtained maximum value of the ECE is in good agreement with the theoretical estimate of the ECE described in [9].

It is also shown that the ECE value does not depend on the frequency of the external driving force. From this we can conclude that the limit speed of the phase transition has not been reached. Dependence-specific power on frequency shows linear character.

5. Theory

A first-order structural phase transition takes place in the material with SME. Proceeding from this, we can say that the dependence $\sigma(\epsilon)$ is nonlinear [22].

For the theoretical description of the ECE at a structural phase transition, we use the expansion of the Helmholtz free energy function up to the fourth order in deformation and up to the second order in temperature.

$$F = \frac{a}{2}\epsilon^2 + \frac{b}{3}\epsilon^3 + \frac{c}{4}\epsilon^4 - \frac{A}{2}\Delta T^2 \quad (6)$$

where $a = a_0^*(T - T_c)$; but b , c , and A are temperature-independent constants. T_c is the phase transition temperature.

A-priory:

$$dF = -pdV - SdT \quad (7)$$

Since the studied effect implies only uniaxial deformations in the phase transition region, and considering that $\sigma = -p$, we obtain:

$$dF = \sigma\epsilon - SdT \quad (8)$$

From (8), we can conclude:

$$\frac{\partial F}{\partial(\epsilon)} = \sigma \quad (9)$$

$$\frac{\partial F}{\partial(\Delta T)} = -S \quad (10)$$

Substituting expression (6) into (9), we obtain the thermal equation of state (11). The graph of this expression is sketched in Figure 9. The coefficients describing a cubic relationship, are taken as follow: $a = 1.4 \times 10^{10}$ Pa, $b = -1.5 \times 10^{12}$ Pa and $c = 5.3 \times 10^{13}$ Pa. This property possessed in alloys with SME is called superelasticity. The characteristic points of maximum and minimum on the red curve are points of phase stability loss. The curve between them has no physical meaning and will not be observed in the experiment. The blue curve gives a qualitative image of the experimental dependence corresponding to a first-order phase transition with specific hysteresis.

$$\sigma = a \cdot \epsilon + b \cdot \epsilon^2 + c \cdot \epsilon^3 \quad (11)$$

Figure 9. The effect of superelasticity: the red line is the theoretical curve, the blue line is the expected experimental curve (arrows show the directions of the stress change).

For solids, in contrast to gas, the change in entropy occurs in the vicinity of the temperature point $T \neq 0$; therefore, the concept of entropy S in a solid makes sense as a change in entropy ΔS . Then (10) has a form:

$$\frac{\partial F}{\partial(\Delta T)} = -\Delta S \quad (12)$$

Substituting expression (6) into (12), we obtain the caloric equation of the state:

$$\Delta S = A\Delta T - \frac{1}{2}a_0\epsilon^2 \quad (13)$$

Since deformation occurs under adiabatic conditions ($\Delta S = 0$), we obtain:

$$\Delta T = \frac{a_0\epsilon^2}{2A} \quad (14)$$

The resulting expression for the ECE (14) shows a quadratic dependence on deformation during the phase transition. To estimate the ΔT value, we take $a_0 = \frac{a}{T-T_c}$, $A = \frac{c_M \cdot \rho}{T}$. Where $a = 1.4 \times 10^{10}$ Pa; $(T - T_c) = 5$ K—half the width of the hysteresis, $c_M = 500$ J/(kg·K)—specific heat capacity in martensitic state; $\rho = 7 \times 10^3$ kg/m³—density; $T = Af = 340$ K—sample temperature. Then $a_0 = 2.8 \times 10^9$ Pa/K; $\epsilon = 1.2 \times 10^{-2}$; $A = 10^4$ J/(m³·K²). As a result $\Delta T = 20.1$ K, which is well confirmed by the experiment (Figure 6).

6. Conclusions

We conclude that a comparative study of amorphous and polycrystalline melt spun ribbons of Ti₂NiCu alloy clearly revealed the drastic effect of thermoelastic martensitic transition. The ECE in amorphous and polycrystalline alloy at a temperature corresponding to the temperature A_f of the polycrystalline Ti₂NiCu alloy has a different sign, which is in qualitative agreement with the measurement data of thermoelastic properties.

It is shown that the maximum value of the ECE is achieved at the point corresponding to the completion of the inverse thermoelastic martensitic phase transition $T = 67.5$ °C. The

maximum ECE value in the Ti₂NiCu alloy is 21 K at a load of 300 MPa and a frequency of deformation cycles of up to 3 Hz.

The value of the ECE does not depend on the frequency of tensile cycles up to 50 Hz. The maximum specific heat transfer power calculated for a elastocaloric heat pump was estimated as $W = 175 \text{ W/g}$, with an applied external mechanical periodic stress of 100 MPa and a frequency of 50 Hz and ECE as high as 7 K.

Theoretical calculations, according to thermodynamical model of the ECE for amorphous ribbons, showed good agreement with experimental results. The formula for ECE for polycrystalline ribbons predicts the maximum value of the ECE near martensitic transition and monotonic dependence of the adiabatic temperature change versus tensile stress until complete transition martensite-austenite has also been experimentally verified and confirmed.

Author Contributions: Conceptualization, E.M.; Data curation, D.K. and V.K.; Formal analysis, K.V.; Methodology, V.S. All authors have read and agreed to the published version of the manuscript.

Funding: The work was performed as part of the state assignment of Kotelnikov Institute of Radio Engineering and Electronics of the Russian Academy of Sciences (Kotelnikov IRE RAS).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Moya, X.; Kar-Narayan, S.; Mathur, N.D. Caloric materials near ferroic phase transitions. *Nat. Mater.* **2014**, *13*, 439–450. [[CrossRef](#)] [[PubMed](#)]
2. Nikitin, S.A.; Myalikgulyev, G.; Annarazov, M.P.; Tyurin, A.L.; Myndyev, R.W.; Akopyan, S.A. Giant elastocaloric effect in FeRh alloy. *Phys. Lett. A* **1992**, *171*, 234–236. [[CrossRef](#)]
3. Liang, X.; Xiao, F.; Jin, M.; Jin, X.; Fukuda, T.; Kakeshita, T. Elastocaloric effect induced by the rubber-like behavior of nanocrystalline wires of a Ti-50.8 Ni (at.%) alloy. *Scr. Mater.* **2017**, *134*, 42–46. [[CrossRef](#)]
4. Sehitoglu, H.; Wu, Y.; Ertekin, E. Elastocaloric effects in the extreme. *Scr. Mater.* **2018**, *148*, 122–126. [[CrossRef](#)]
5. Zhou, M.; Li, Y.; Zhang, C.; Li, S.; Wu, E.; Li, W.; Li, L. The elastocaloric effect of Ni_{50.8}Ti_{49.2} shape memory alloys. *J. Phys. D Appl. Phys.* **2018**, *51*, 132018. [[CrossRef](#)]
6. Ossmer, H.; Chluba, C.; Kauffmann-Weiss, S.; Quandt, E.; Kohl, M. TiNi-based films for elastocaloric microcooling—Fatigue life and device performance. *APL Mater.* **2016**, *4*, 62. [[CrossRef](#)]
7. Bechtold, C.; Chluba, C.; Lima de Miranda, R.; Quandt, E. High cyclic stability of the elastocaloric effect in sputtered TiNiCu shape memory films. *APL Mater.* **2012**, *101*, 9. [[CrossRef](#)]
8. Cong, D.; Xiong, W.; Planes, A.; Ren, Y.; Mañosa, L.; Cao, P.; Nie, Z.; Sun, X.; Yang, Z.; Hong, X.; et al. Colossal Elastocaloric Effect in Ferroelastic Ni-Mn-Ti Alloys. *Phys. Rev. Lett.* **2019**, *122*, 252019. [[CrossRef](#)] [[PubMed](#)]
9. Mañosa, L.; Planes, A. Materials with Giant Mechanocaloric Effects: Cooling by Strength. *Adv. Mater.* **2017**, *29*, 1603607. [[CrossRef](#)] [[PubMed](#)]
10. Li, Y.; Zhao, D.; Liu, J. Giant and reversible room-temperature elastocaloric effect in a single-crystalline Ni-Fe-Ga magnetic shape memory alloy. *Sci. Rep.* **2016**, *6*, 25500. [[CrossRef](#)] [[PubMed](#)]
11. Schmidt, M.; Schütze, A.; Seelecke, S. Elastocaloric cooling processes: The influence of material strain and strain rate on efficiency and temperature span. *APL Mater.* **2016**, *4*, 064107. [[CrossRef](#)]
12. Xie, Z.; Sebald, G.; Guyomar, D. Temperature dependence of the elastocaloric effect in natural rubber. *Phys. Lett. A* **2017**, *381*, 2112–2116. [[CrossRef](#)]
13. Lu, B.; Liu, J. Elastocaloric effect and superelastic stability in Ni-Mn-In-Co polycrystalline Heusler alloys: Hysteresis and strain-rate effects. *Sci. Rep.* **2017**, *7*, 2084. [[CrossRef](#)] [[PubMed](#)]
14. Kareev, S.I.; Glezer, A.M.; Shelyakov, A.V. Shape memory effect in Ti-Ni-Cu alloy caused by Joule heating. *Bull. Russ. Acad. Sci. Phys.* **2009**, *73*, 1293–1295.
15. Kourov, N.I.; Korolev, A.V.; Pushin, V.G.; Koledov, V.V.; Shavrov, V.G.; Khovailo, V.V. Electrical and magnetic properties of the rapidly quenched Ni_{2.16}Mn_{0.84}Ga alloy with the shape-memory effect. *Phys. Metal. Metallograf.* **2005**, *99*, 4, 376.
16. Pushin, V.G.; Kourov, N.I.; Korolev, A.V.; Kazantsev, V.A.; Yurchenko, L.I.; Koledov, V.V.; Shavrov, V.G.; Khovailo, V.V. Effect of rapid quenching on the physical properties of the Ni₅₄Mn₂₁Ga₂₅ alloy. *Phys. Metal. Metallograf.* **2005**, *99*, 401–410.

17. Kamantsev, A.P.; Koledov, V.V.; Mashirov, A.V.; Dilmieva, E.T.; Shavrov, V.G.; Cwik, J.; Los, A.S.; Nizhankovskii, V.I.; Rogacki, K.; Tereshina, I.S.; et al. Magnetocaloric and thermomagnetic properties of Ni_{2.18}Mn_{0.82}Ga Heusler alloy in high magnetic fields up to 140 kOe. *J. Appl. Physics* **2015**, *117*, 163903.
18. Irzhak, A.V.; Lega, P.V.; Zhikharev, A.M.; Koledov, V.V.; Orlov, A.P.; Kuchin, D.S.; Tabachkova, N.Y.; Dikan, V.A.; Shelyakov, A.V.; Berezin, M.Y.; et al. Shape memory effect in nanosized Ti₂NiCu alloy-based composites. *Rep. Acad. Sci.* **2017**, *472*, 139. [[CrossRef](#)]
19. Lega, P.; Koledov, V.; Orlov, A.; Kuchin, D.; Frolov, A.; Shavrov, V.; Khovaylo, V. Composite Materials Based on Shape-Memory Ti₂NiCu Alloy for Frontier Micro- and Nanomechanical Applications. *Adv. Eng. Mater.* **2017**, *19*, 1700154. [[CrossRef](#)]
20. von Gratoski, S.V.; Koledov, V.V.; Shavrov, V.G.; Petrenko, S.F.; Irzhak, A.V.; Shelyakov, A.V.; Jede, R. Advanced System for Nanofabrication and Nanomanipulation Based on Shape Memory Alloy. In *Frontiers in Materials Processing, Applications, Research and Technology*; Springer: Singapore, 2018; pp. 135–154. [[CrossRef](#)]
21. Belyaev, S.P.; Istomin-Kastrovsky, V.V.; Koledov, V.V.; Kuchin, D.S.; Resnina, N.N.; Tabachkova, N.Y.; Shavrov, V.G.; Shelyakov, A.V.; Ivanov, S.E. Structure and functional properties of rapidly quenched ribbons of Ti₂NiCu alloy with different fractions of the crystalline phase. *Bull. Russ. Acad. Sci. Phys.* **2011**, *75*, 1078. [[CrossRef](#)]
22. Landau, L.D.; Lifshitz, E.M. *Course of Theoretical Physics Vol 7: Theory and Elasticity*; Pergamon Press: Oxford, UK, 1959.