



METALLIC ALLOY WITH SHAPE MEMORY – SELECTED PROPERTIES AND ENGINEERING ASPECTS

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Abstract

In the case of shape memory alloys (SMA), a form to which a material is expected to return during heating can be repeatedly programmed, whereas other related properties can be individually adjusted. It was found that most producers of commercial assortment based on SMA as well as traders are seldom willing to lift the veil of secrecy on this topic. In the context of own experimental studies, the authors made a reference to the technical aspects of some post-treatments of a Ni-Ti alloy with a view to further practical application, e.g. the design and construction of machinery and structures with the involvement of SMA. For these purposes, high-temperature shape setting trials were carried out using various parameters of heat treatment with no secrecy surrounding the procedures applied. Some of the tested parameters proved effective, whereas some were less useful. Following the activation of the reverse transformation by heating, a somewhat different behaviour was observed, and simultaneously one of the crucial material temperatures was determined. The paper as a whole is reported from a specifically engineering/technical point of view, which is continuously emphasized in the content of the presented article.

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Introduction

In modern engineering shape memory materials (SMM) constitute the most important type of materials among the so-called intelligent materials, which in turn fall into a broader subgroup of active/multi-functional materials. It is noteworthy than in contrast to typical construction materials, the functional materials play specific roles. In this case, other than the ability to transfer mechanical loads and stresses. A material can only be considered as a SMART material if it changes its properties, parameters or behaviour under the influence of a specific of external, non-mechanical factors (KAMILA 2013, KAUSHAL et al. 2016). The reaction inside the material is reversible.

It has been found that functional materials happen to be very advanced materials developed to provide a specific property or function. In some cases these materials exhibit a combination of different features within one structure. Metallic nickel-titanium (Ni-Ti) alloys with shape memory effect (SME) reveal the following main properties: free shape change associated with the one-way and two-way shape memory effect (OWSME and TWSME) and the phenomenon of pseudo-elasticity (PE). These phenomena can be revealed owing to different paths of thermo-mechanical loads that these materials are exposed to (VAN HUMBECK 2001, MOHD JANI et al. 2014, NARESH et al. 2016). Other related functional properties include: restrained shape recovery, shape recovery inhibited by an opposing force during heating, high damping capacity and fatigue resistance in the martensitic state, as well as biocompatibility (VAN HUMBECK 2001, KUCHARCZYK et al. 2011, MOHD JANI et al. 2014).

A vast and interesting array of their properties creates a platform for possible industrial applications. These materials available in a wide assortment (e.g. plates, wires, rods, tubes, films) are used, among others, in electronics, telecommunication, industry, security, sports, clothing, home technology and medicine. In some applications, such materials can act simultaneously as a sensor and an actuator or the actuator itself. The structure of SMM can be porous or nanometric. Furthermore, such materials are used to produce very small components applied in microscopic devices-mechanisms known as microelectromechanical systems. The manufacturing processes of products involving SMM are already based on 3D printing technologies.

An important thing to note is, especially from a practical perspective, that some characteristics related to the SME in shape memory alloys (SMA) can be adjustable (WANG et al. 2004, SADIQ et al. 2010, KUŚ, KŁYSZ 2012, BRAZ FERNANDES et al. 2013, VILLA 2015). Moreover, the shape to which the material is expected to return during its heating can be repeatedly programmed, depending on the application purposes/needs. For these purposes one of the so-called post-/final treatments can be applied to the SMA. An appropriate selection of material deformation parameters and subsequent annealing, in particular, give

the possibility to influence transformation temperatures and their sequences. It is of primary importance to understand the structure, as well as the properties of SMA, are additionally influenced by other factors like e.g. alloy composition, repeated cycling (DUERIG, PELTON 1994, KUŚ 2010, SADIQ et al. 2010, MOHD JANI et al. 2014).

Although various ready-made SMA based products are already commercially available, there is usually a need to change (or tune) certain material characteristics to a specific property or function, e.g. in the case of individual projects and construction of miscellaneous elements, devices or structures with the involvement of SMA. Unfortunately, most producers of SMA-assortment or traders are seldom willing to lift the veil of secrecy on this topic. The authors of the paper experienced this state of affairs on numerous occasions, not to mention the manufacturers keep the processing history in the materials sold undisclosed. Thus, it comes to the conclusion that some issues related to final processing remain unclear and deserve to be more systematically reported. The questions that pose themselves are as follows: how to fix the desired shape of the material – is it a matter of appropriate heat treatment, should the temperatures of structural transformations be obtained, should the sequences be altered? There are not many literature positions currently available, especially in the category of complete engineering technological information about the above-mentioned steps. A contribution to a different extent in this field was made by some researchers (SUZUKI 1998, LIU et al. 2008, RAO et al. 2015, HEIDARI et al. 2016, JAHANBAZI ASL et al. 2019). Because SMM are still classified as engineering materials with high innovation potential, the authors of this work imply that this sort of insightful data can be useful for machine designers, various examples of mechanism employing SMA in fields such as mechanics, mechatronics and robotics, as well as for students or enthusiasts.

In the context of own experimental research, the authors made reference to technical aspects of some post-treatments of a Ni-Ti alloy with a view to further practical application, e.g. design and construction of machinery and structures with the involvement of SMM. For this purpose, attempts concerning the high-temperature shape setting were conducted using various parameters of annealing treatment. The paper as a whole is reported from a specifically engineering/technical point of view, which is continuously emphasized in the content of the presented article.

Materials and methods

Commercially available Ni-Ti arc wires were used throughout the experimental works (Fig. 1). It was determined that the temperature A_f , defined as the end of the reverse transformation from martensite to austenite, falls well below

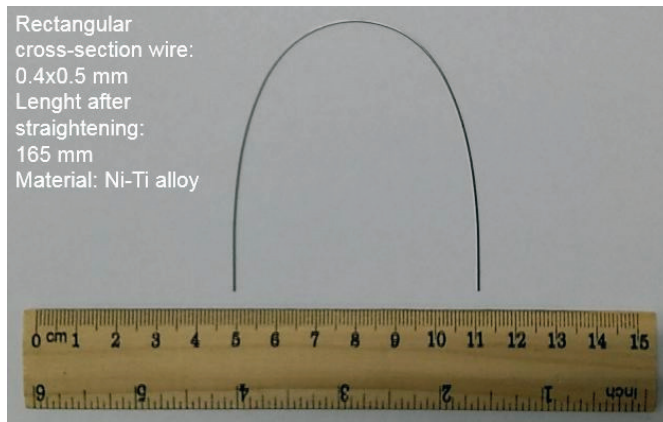


Fig. 1. Shape and as-received state (PE behaviour at room and lower temperature)

the ambient temperature. Thus, the materials in an as-received state exhibited PE at a room temperature and below.

As already mentioned above, the shape to which the material is expected to return during the SME can be programmed. Then, depending on the purpose, SMM may have different final shapes (e.g. straight elements, products in the form of springs or other profiles). The aforementioned information is the reason behind the implementation of annealing treatment, which applicable temperature range varies between 300 and 600°C, at adequate time intervals (SUZUKI 1998, LIU et al. 2008, RAO et al. 2015, STORTIERO 2015, HABERLAND, ELAHIMIA 2016, HEIDARI et al. 2016). The use of higher temperatures, during the heat treatment, is reported by JAHANBAZI ASL et al. (2019). Moreover, a contoured form-platform (either metallic or ceramic) is necessary to give shape that is to be desired. Apart from shaping up a material, the platform's main task is to block expanding or shrinking materials during heating from the martensitic state.

The shape setting form depicted in Figure 2 was used to perform the experiments. As shown in the picture, its circumference bears a resemblance to a fish, which was achieved by profiling a wire and then squeezing it between the nuts of the screws attached to a steel sheet. Then the hand-made platform was placed in a furnace.

The experiments consisted in carrying out heat treatment on SMA at six different temperatures over different periods of time. This paper presents the results obtained at two selected temperatures: $T=400$ and 475°C ; for times: $t=15$ and 45 min. For this purpose, a laboratory muffle furnace (produced by Czylok Company, Poland) was used. After the heat treatment processes were concluded, the authors proceeded to check the accuracy with which the shape was mapped in relation to the set shape of the platform. The wire samples were

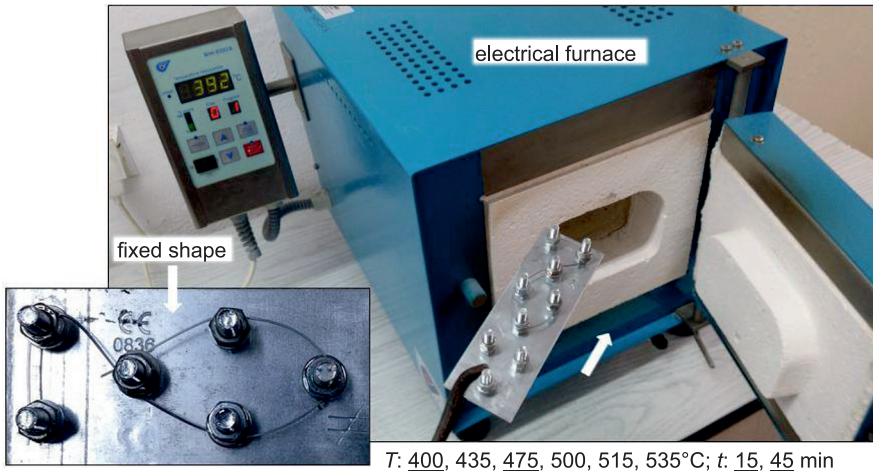


Fig. 2. Shape setting form used in experiments

allowed to cool in the open air of the laboratory, once removed from the chamber of the furnace. The assortment had been prepared accordingly, so a new wire was always available for a new heat treatment regime. The simultaneous stage of the experiments conducted involved the implementation of SME as the result of preliminary cooling of the wire material, then deformation and finally its heating. It was an attempt to determine the range of crucial temperatures, in which the tested material behaved differently (displaying OWSME, PE and TWSME). The shape recovery process was of primary interest, hence thoroughly monitored and an attempt was made to establish A_f .

There are obviously more advanced laboratory methods for assessing the properties of SMM, most notably their metallic subgroup (MOHD JANI et al. 2014, TURABI et al. 2016). Differential scanning calorimetry (DSC) is extensively used to characterize the thermal features of SMA. Currently access to this type of apparatus is rather wide enough, and cost performance measurement – not that high. Thermal properties, including the phase transformation temperatures, play a crucial role in determining the areas, in which basic SMA phenomena occur. During controlled heating up or cooling down of a material sample in DSC method the heat flow is measured. In our study, phase transformation from the low-temperature martensite to high-temperature austenite was complementary analyzed by DSC on the device Netzsch DSC 204 F1 Phoenix. In this case, for comparison purposes, determination of the A_f temperature was of interest. A small piece of sample, namely 3.5 mg in mass, was prepared for DSC testing, whereas the typical heating and cooling rates were 10 K/min.

Results and discussion

Figures 3 and 4 show the state and behaviour of the material after annealing at 400°C for 15 min. As seen below, after removing from the experimental platform the fixed shape of the material differs from the one set initially. It follows that the heat treatment parameters used proved to be inappropriate for the purposes of preserving the shape defined by the platform. Nonetheless, the high-temperature shape obtained was further employed to characterize the material during the implementation of the SME.

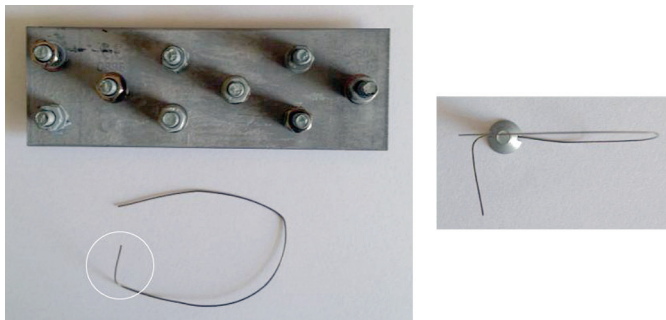


Fig. 3. Material shape fixed after annealing at 400°C for 15 min

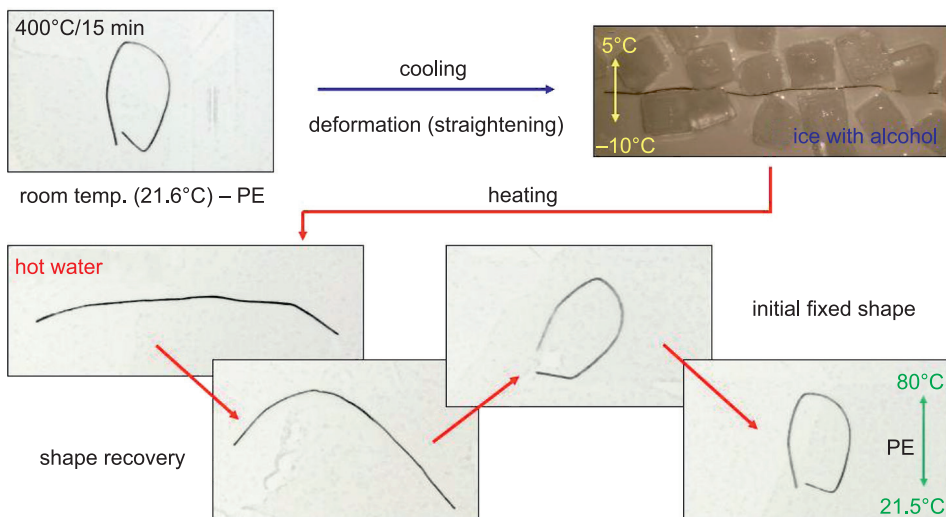


Fig. 4. Material behaviour after annealing at 400°C for 15 min

Note that when a new shape is prepared for fixation, an Ni-Ti alloy should initially consist of low-temperature martensite phase. Then it gets easily-deformable, owing to the presence of martensite – its state resembles plasticine or a soft solder wire. In the opposite case (austenite as the starting phase in a material), it is still possible to shape a material on the form. However, it becomes more difficult.

The experiments have shown that in the cooling temperature range from +5 to -10°C the material is in a martensitic state, which makes it highly ductile. The heating range through the temperature (80÷21.5°C) revealed full recovery of the preserved shape (OWSME). The dynamics of the recovery reaction significantly dropped above the threshold of 24°C, while it was found that the material exhibited PE at ambient temperature.

Figures 5, 6 and 7 show the shape and behaviour of the material after annealing at 475°C for 15 min. As can be seen below, after removing from the experimental form the shape of the material is compatible with the one previously set.

The experiments have shown that in the cooling temperature range from +20 to -5°C the material is in a martensitic state. The heating rate through the temperature (75÷35°C) revealed full recovery of the fixed shape. Below the threshold of 34°C only partial recovery of the preserved shape was observed, whereas the temperatures below roughly 27°C inhibited the material from returning to its high-temperature shape (Fig. 7).

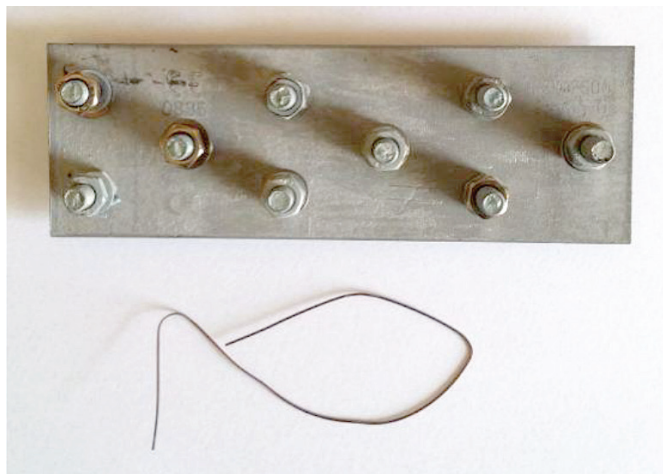


Fig. 5. Material shape fixed after annealing at 475°C for 15 min

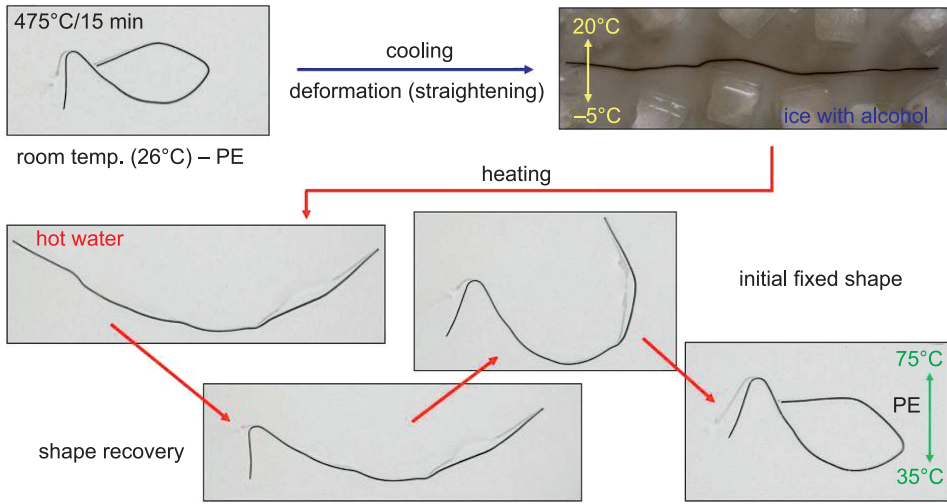


Fig. 6. Material behaviour after annealing 475°C for 15 min

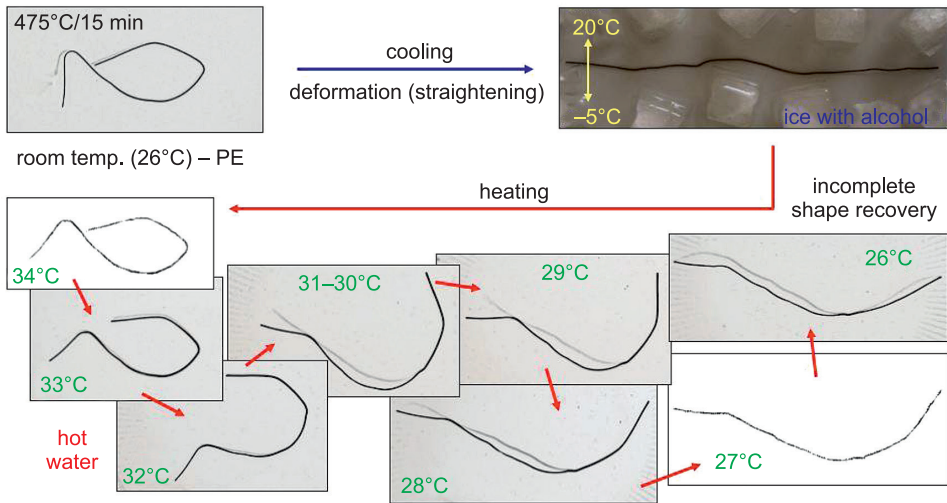


Fig. 7. Detailed views in material behaviour after annealing at 475°C for 15 min

While annealing at 400°C for 15 minutes may be inefficient to fully preserve the desired shape, an increase by 45 minutes may be sufficient to facilitate this. Figures 8, 9, 10 show the state and behaviour of the material after annealing at 400°C for an extended period of time. As evidenced, after its removal from the platform, the shape of the material seems to be much more compatible with what was intended, especially in direct comparison with what was observed during 15 minutes of heating (Fig. 3).

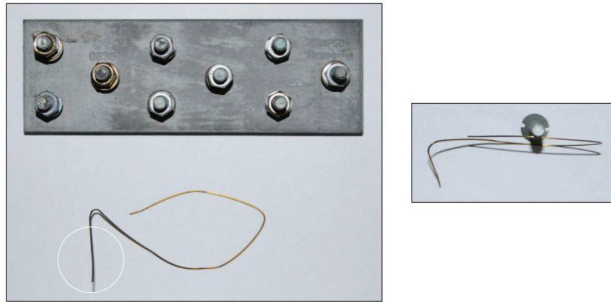


Fig. 8. Material shape fixed after annealing at 400°C for 45 min

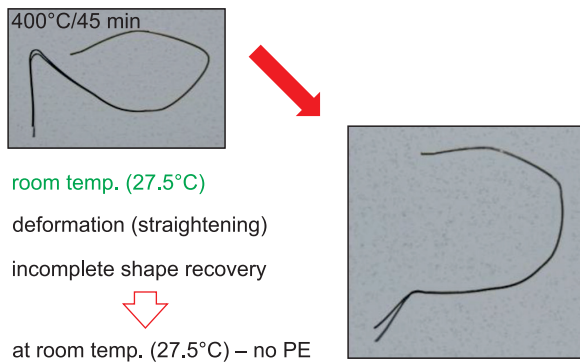


Fig. 9. Material behaviour after annealing at 400°C for 45 min

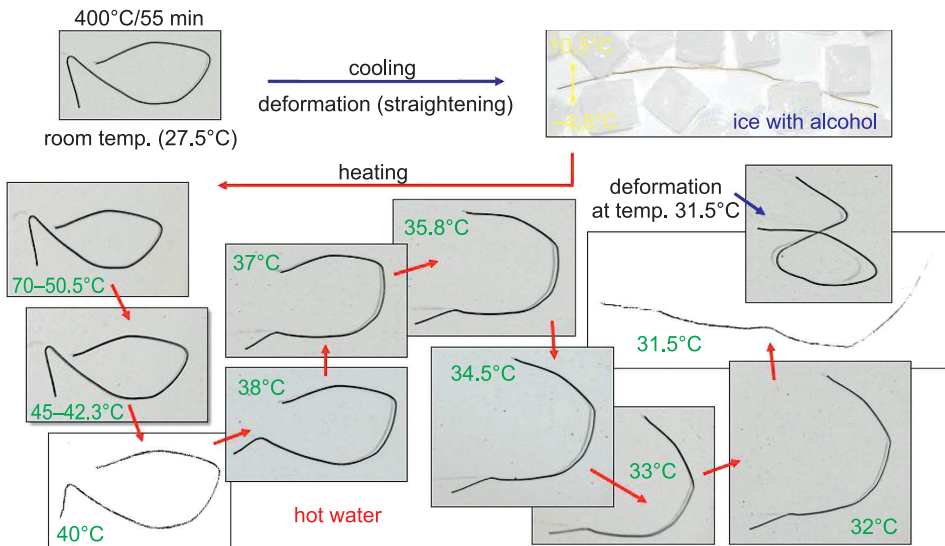


Fig. 10. Detailed views in material behaviour after annealing at 400°C for 45 min

Analogically, the high-temperature shape obtained was further employed to characterize the material during the implementation of the SME. Unlike the previous case, the material no longer displayed PE behaviour at room temperature (in this case estimated at 27.5°C). Following the deformation at this temperature, only partial (incomplete) recovery of shape memory can be observed (Fig. 9).

Figure 10 shows in detail the behaviour of the material in the context of the implementation of SME. The experiments have shown that in the cooling temperature range from +10.5 to -4.5°C the material is in a martensitic state. The heating rate through the temperature (70÷42.3°C) revealed full recovery of the fixed shape. Around the threshold of 40°C only partial recovery of the preserved shape was observed, whereas the temperatures below roughly 31.5°C inhibited the material from returning to its high-temperature shape.

While carrying out the experiments related to the phenomenon of shape recovery at 400°C over the course of 45 min, the authors noticed that upon completion of several full cycles of transformations, the material began to show the first symptoms of the TWSME (Fig. 11). This scientific phenomenon is predicated upon the fact that the changes in the shape of the material (which in this case are less noticeable than for the OWSME) can be observed both during heating and cooling. The literature sources available to the authors link the above-mentioned observation with the introduction of well-thought-out modifications to the material microstructure during the SME cycles.

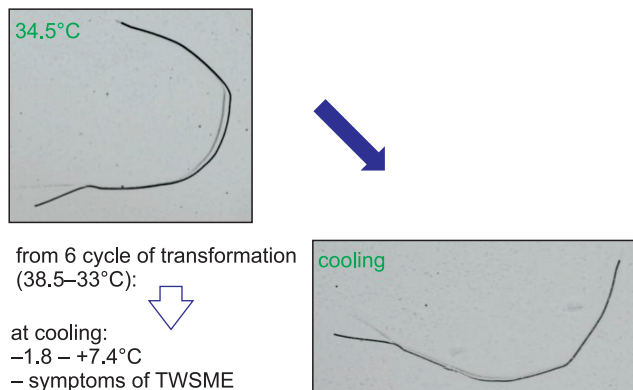


Fig. 11. Material behaviour after annealing at 400°C for 45 min. It shows symptoms of TWSME

In reference to the behaviour of SMA during SME, the phenomenon of phase transformation temperature hysteresis occurs and should be taken into consideration. The experiments proved that it is possible to modify the reaction temperatures of a material to suit its specific purpose (in a controlled manner). This is the reason why fairly simple heat treatment is carried out with

different parameters. The work presents the results obtained for two selected temperatures, 400 and 475°C; for times, 15 and 45 min, whereas it is important to note that the heat treatment processes were carried out for other values of temperature between 400 and 535°C. Some of the tested parameters proved effective, whereas some were less useful. The microstructure of the material examined changed in the aftermath, especially if pre-deformed.

As was mentioned earlier, phase transformation from the low-temperature martensite to high-temperature austenite was analyzed by DSC method. Thus, for confirmation purposes, determination of the A_f temperature was of interest. Figure 12 presents the data received from the calorimetric measurement for a sample during its heating cycle, which was previously annealed at 475°C for 15 min.

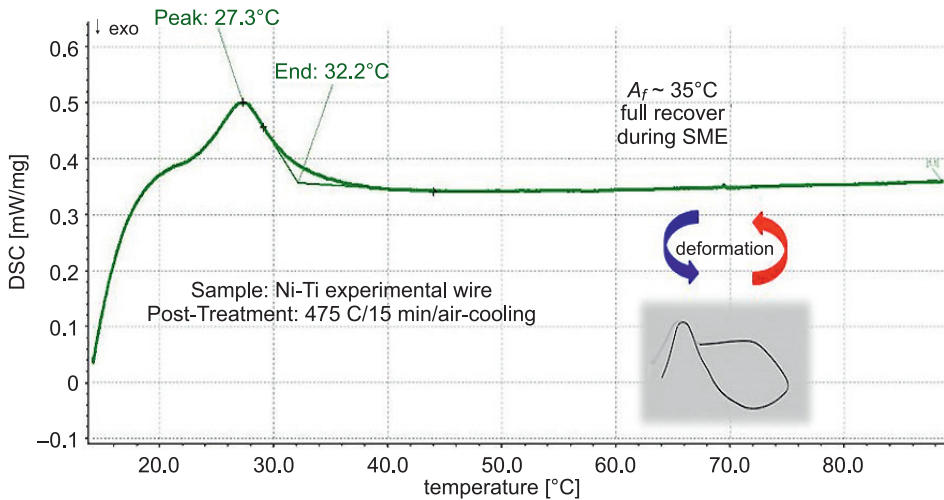


Fig. 12. DSC heating curve obtained for material after annealing at 475°C for 15 min

As shown in above figure, one endothermic peak was recorded after heating regime what clearly means that during heating the reverse transformation from martensite to austenite occurred. From the obtained DSC profile the phase transformation temperatures can be deduced – by means of the method of tangent lines and their intersections. This approach is generally accepted in the scientific community dealing with SMA as being sufficiently accurate. The discrepancy between the values of temperature A_f in relation to its previous behavior during the implementation of the SME can be explained by the lack of external load as the calorimetric measurements were done (Memry Corporation).

Summary

SMM, including metals and their alloys, fall into the category of SMART materials. According to one of the available definitions, these materials are featured by the ability to change their properties, parameters or behaviour under the influence of external factors. Among many SMA, binary Ni-Ti present an interesting set of functional properties. They create big possibilities for new and creative practical applications.

Seemingly uncomplicated heat treatment of Ni-Ti based SMA gives an opportunity to influence selected characteristics associated with the SME and the shape to which the material is expected to return. In the context of own experimental research, the authors made reference to selected technical aspects of some final treatments of a Ni-Ti alloy with a view to further practical application, e.g. design and construction of machinery and structures with the involvement of SMM. In this case, usually there is a need to regulate (or modify) certain material characteristics to a specific function and SMM make it possible. This interesting feature distinguishes such materials from conventional structural materials with precisely predefined properties, to which the engineers must adapt to. It is important to note that while it is desirable for the above-mentioned needs, instability of SMA functional properties (e.g. transformation temperatures) in some cases can prove to be a problem.

The authors of the paper are convinced that the available literature sources providing data on the above-mentioned topics are insufficient, especially regarding the access to engineering technological information, including procedures in details, practical advices and tips from measurements, or observations. Also, there are rather not many reports that contribute to this field. On the downside, these articles are sometimes heavy-going for an ordinary person interested in SMM. Furthermore, such people hardly every have expertise in the topic and expect more professional guidance. The authors believe the information they provided could prove to be useful for machine designers, various examples of mechanism employing SMA in fields such as mechanics, mechatronics and robotics, as well as enthusiasts.

It turns out that there are already many sources commercially offering SMART materials including SMA. For the moment, the most accessible way to purchase such materials is via foreign online platforms (and then process them on one's own). Their offer usually includes wires or springs of different sizes. Therefore, if a reader takes an interest in the topic discussed, our work could serve as guidance, which justifies the purpose of this research. Finally, it is worth to emphasize that the popularity of SMM is not in decline, despite being on the market for many years, considering both research and utilization potential (MOHD JANI et al. 2014, NARESH et al. 2016).

References

- BRAZ FERNANDES F.M., MAHESH K.K., PAULA A.S. 2013. *Thermomechanical Treatments for Ni-Ti Alloys*. In: *Shape Memory Alloys – Processing, Characterization and Applications*. Ed. F.M.B. Fernandes. InTech., p. 3-26.
- DUERIG T., PELTON A. 1994. *TiNi Shape Memory Alloys*. In: *Materials Properties Handbook: Titanium Alloys*. ASM International, p. 1035-1048.
- HABERLAND C.H., ELAHINIA M.H. 2016. *Fabricating NiTi SMA Components*. In: *Shape Memory Alloy Actuators: Design, Fabrication, and Experimental Evaluation*. Ed. M.H. Elahinia. First Edition. John Wiley & Sons, Ltd., p. 191-238.
- HEIDARI B., KADKHODAEI M., BARATI M., KARIMZADEH F. 2016. *Fabrication and modeling of shape memory alloy springs*. *Smart Materials and Structures*, 25: 125003.
- HUMBEECK J. VAN. 2001. *Shape Memory Alloys: A Material and a Technology*. *Advanced Engineering Materials*, 3(11): 837-850.
- JAHANBAZI ASL F., KADKHODAEI M., KARIMZADEH F. 2019. *The effects of shape-setting on transformation temperatures of pseudoelastic shape memory alloy springs*. *Journal of Science: Advanced Materials and Devices*, 4(4): 568-576. <https://doi.org/10.1016/j.jsamd.2019.10.005> (access: 5.12.2019).
- KAMILA S. 2013. *Introduction, classification and applications of smart materials: an overview*. *American Journal of Applied Sciences*, 10(8): 876-880.
- KAUSHAL A., VARDHAN A., RAWAT R.S.S. 2016. *Intelligent Material For Modern Age: A Review*. *IOSR Journal of Mechanical and Civil Engineering*, 13(3): 10-15. <http://www.iosrjournals.org/iosr-jmce/papers/vol13-issue3/Version6/B13030-61015.pdf> (access 8.08.2019).
- KUCHARCZYK W., MAZURKIEWICZ A., ŻUROWSKI W. 2011. *Nowoczesne materiały konstrukcyjne – wybrane zagadnienia*. Wyd. Politechnika Radomska, Radom., p. 429-454.
- KUŚ K. 2010. *The Influence of Repeated Heating and Cooling Process on the Transformation Characteristics in Ni-Ti Alloy*. *Technical Sciences*, 13: 203-211.
- KUŚ K., KLYSZ S. 2012. *Investigation of thermal transformation properties under different annealing conditions of Ni-Ti shape memory alloy*. *Bulletin of the Military University of Technology in Warsaw*, LXI(2): 245-255.
- LIU X., WANG Y., YANG D., QI M. 2008. *The effect of ageing treatment on shape-setting and superelasticity of a nitinol stent*. *Materials Characterization*, 59: 402-406.
- Memry Corporation. *Inspections. Testing*. <https://www.memry.com/inspections-testing> (access 15.09.2019).
- MOHD JANI J., LEARY M., SUBIC A., GIBSON M.A. 2014. *A review of shape memory alloy research, applications and opportunities*. *Materials and Design*, 56: 1078-1113.
- NARESH C., BOSE P.S.C., RAO P.S.C. 2016. *Shape memory alloys: a state of art review*. *IOP Conf. Series: Materials Science and Engineering*, 149: 012054. <https://iopscience.iop.org/article/10.1088/1757-899X/149/1/012054/pdf> (access 10.06 2019).
- RAO A., SRINIVASA A.R., REDDY J.N. 2015. *Design of Shape Memory Alloy (SMA) Actuators*. *Springer Briefs in Computational Mechanics*, Springer.
- SADIQ H., WONG M.B., AL-MAHAIDI R., ZHAO X.L. 2010. *The effects of heat treatment on the recovery stresses of shape memory alloys*. *Smart Materials and Structures*, 19: 035021.
- STORTIERO F. 2015. *Design and Industrial Manufacturing of SMA Components*. In: *Shape Memory Alloy Engineering: For Aerospace, Structural and Biomedical Applications*. Eds. L. Lecce, A. Concilio. Butterworth-Heinemann. Elsevier Ltd., p. 215-244.
- SUZUKI Y. 1998. *Fabrication of shape memory alloys*. In: *Shape Memory Materials*. Eds. K. Otsuka, C.M. Wayman. Cambridge University Press, p. 133-148.
- TURABI A.S., SAEDI S., SAGHAIAN S.M., KARACA H.E., ELAHINIA M.H. 2016. *Fabricating NiTi SMA Components*. In: *Shape Memory Alloy Actuators: Design, Fabrication, and Experimental Evaluation*. First Edition. Ed. M.H. Elahinia. John Wiley & Sons, Ltd., p. 239-277.

- VILLA E. 2015. *Manufacturing of Shape Memory Alloys*. In: *Shape Memory Alloy Engineering: For Aerospace, Structural and Biomedical Applications*. Eds. L. Lecce, A. Concilio. Butterworth-Heinemann. Elsevier Ltd., p. 79-96.
- WANG Z.G., ZU X.T., FENG X.D., ZHU S., ZHOU J.M., WANG L.M. 2004. *Annealing-induced evolution of transformation characteristics in TiNi shape memory alloys*. *Physica B.*, 353: 9-14.