UDK 539.3/.5:532.135:620.179.1

Materiali z oblikovnim spominom
Shape Memory Materials

BORUT BUNDARA

Predstavljeno je novo in hitro se razvijajoče področje materialov z oblikovnim spominom, ki sodijo k razumnim oziroma inteligentnim materialom. Razložene so osnovne mehanske lastnosti materialov z oblikovnim spominom: enosmerni oblikovni spomin, dvosmerni oblikovni spomin in superelastičnost. Opravljen je tudi kratek pregled stanja raziskav na tem področju v Sloveniji.

The new and extensively developing field of shape memory materials is introduced in the paper. Shape memory materials belong to the group of smart or intelligent materials. The basic mechanical properties of shape memory materials are introduced: one-way effect, two-way effect and superelasticity. In addition, a short overview is provided of research work in Slovenia in this field.

0 UVOD

Obdobja v zgodovini človeštva je mogoče razdeliti po materialih, ki jih je človek uporabljal v vsakdanjem življenju: kamena, bronasta in železna doba ter — v novejšem času — doba sintetičnih materialov. Vlogo materialov, ki so se uporabljali v obdobju od začetka zgodovine človeštva do vključno dobe sintetičnih materialov, bi lahko opisali kot pasivno, ne glede na vloženo znanje v njihovo izdelavo. Raziskave in razvoj materialov v zadnjem desetletju so usmerjeni k izdelavi materialov, ki imajo take lastnosti, da lahko iz njih izdelani elementi prevzamejo tudi aktivno vlogo kot sestavni deli naprav oziroma konstrukcij. V osnovi se ti materiali razlikujejo od pasivnih v tem, da so se zmožni aktivno odzvati na zunanji vpliv in pri tem opraviti tudi delo. Za te materiale se uveljavlja izraz razumni oziroma inteligentni materiali. Za razvoj na področju inteligentnih materialov je mogoče trditi, da je še v zametkih, vendar nekateri že napovedujejo, da se je začela nova doba v zgodovini človeštva — doba inteligentnih materialov [1].

V skupino razumnih oziroma inteligentnih materialov spadajo tudi materiali z oblikovnim spominom, ki so dobili ime po svoji značilni lastnosti, da si lahko zapomnijo svojo izvirno obliko, v katero se v določenih razmerah povrnejo tudi po navidez trajni deformaciji.

0 INTRODUCTION

Time periods in the history of humankind can be defined by the materials that people of the relevant age used in his everyday life: Stone Age, Bronze Age, Iron Age, and in the most recent history - Synthetic Materials Age. The role of materials that have been used in the mentioned ages could be described as a passive one, in spite of the knowledge needed for their fabrication. In the past decade, research and development have been devoted to materials whose properties enable them to be an active part of the mechanism or the structure. The main difference between these materials and passive ones is their ability to respond actively to some external influence and to perform some activity during their response. Because of their active role, the term smart materials or intelligent materials has been established in literature for these materials. It could be said that development in the field of intelligent materials is in the early stage. However, some scientists are announcing the beginning of a new Age in the history of humankind — the Smart Materials Age [1].

To the group of smart or intelligent materials, respectively, belong also Shape Memory Materials. The name of these materials — Shape Memory — expresses the capability to memorise their initial shape. Under certain circumstances they return to this initial shape in spite of the permanent like deformation.

1 ZGODOVINSKI PREGLED MATERIALOV Z OBLIKOVNIM SPOMINOM

Vsi avtorji si niso povsem enotni, kateri dogodek bi veljalo določiti kot začetek zgodovine materialov z oblikovnim spominom. V literaturi je mogoče najti različne letnice – 1932 [2], 1938 [3], 1951 [4], ki jih različni avtorji navajajo kot prva poročanja o takrat nerazumljivih pojavih, ki jih dandanes imenujemo: oblikovni spomin. Letnica začetka sicer ni prav posebej pomembna. Če že, je kot začetek verjetno najprimernejši dogodek, ko je bil pojav razumljen kot oblikovni spomin. S tega vidika se zdi še najprimernejša letnica 1951, ko je bilo prvič poročano o odkritju lastnosti oblikovnega spomina pri zlitini Au-Cd, kmalu za tem, leta 1953, pa je bila lastnost oblikovnega spomina ugotovljena še pri zlitini In-Ti. Za uporabo v praksi in s tem tudi za pospešen razvoj na področju materialov z oblikovnim spominom, je pomembno odkritje lastnosti oblikovnega spomina pri zlitini Ni-Ti, leta 1963 [5]. Zanimivo je, da je za temeljno razumevanje pojava oblikovnega spomina pomembna zlitina Cu-Al-Ni, katere lastnost oblikovnega spomina je bila ugotovljena leta 1964 [6] in podrobneje raziskana v sedemdesetih letih.

Prva odkritja lastnosti oblikovnega spomina so vzpodbudila pospešene raziskave, katerih cilj je bil:

— razumevanje mehanizmov pri oblikovnem spominu,

— izboljšanje oblikovno-spominskih lastnosti znanih zlitin,

— odkritje novih zlitin,

— uporaba materialov z oblikovnim spominom v praksi.

Danes je znanih že precej zlitin z oblikovnim spominom: Ag-Cd, Au-Cd, Cu-Zn, Cu-Zn-X (X = Si, Sn, Al, Ga), Cu-Al-Ni, Cu-Sn, Cu-Au-Zn, Ni-Al, Ni-Ti, In-Ti, In-Cd, Mn-Cu, Fe-Pt, Fe-Pd, Fe-Ni-Co-Ti, Fe-Ni-C, Fe-Mn-Si, Fe-Cr-Ni-Mn-Si-Co.

Med naštetimi zlitinami je za uporabo v praksi daleč najbolj zanimiva zlitina Ni-Ti. Poleg izjemnih oblikovno-spominskih lastnosti odlikujejo to zlitino še: velika duktilnost, visoka napetost tečenja, velika trdnost v primerjavi z lastno težo, izvrstna korozijska odpornost in relativno nizka cena. Kolikor je znano, je ta zlitina sploh prva, katere oblikovno-spominska lastnost je bila uporabljena v praksi. Kakor je to že običaj pri pomembnih novih odkritjih, je tudi v tem primeru prva uporaba povezana z vojsko [7]. Pri popravilu cevnih sistemov podmornic, so se stiku cevi z varjenjem izognili tako, da so za stik uporabili objemke iz zlitine Ni-Ti. Ob uporabi v vojaški in nato tudi vesoljski tehniki se je uporaba zlitine

1 HISTORICAL OVERVIEW OF THE SHAPE MEMORY MATERIALS

Authors of relevant papers are not of the same opinion which event could be recognised as the beginning of shape memory history. The following years could be found in the literature: 1932 [2], 1938 [3], 1951 [4]. All these years are based on the first reports on some material properties that were not understandable at that time and are known today as shape memory. Actually, the year of the beginning is not very important. It would perhaps be most convenient to assume for the beginning the event when the property was understood as shape memory. From this point of view, the most appropriate would be 1951, when the shape memory property of the Au-Cd alloy was reported for the first time. Not much later, in 1953, the property of shape memory was reported for the In-Ti alloy. However, discovery of the shape memory property of the Ni-Ti alloy, in 1963 [5], seems to be the most important event for the extensive development and for the implementation of the shape memory property in practice. For a basic understanding of the shape memory property of alloys, the Cu-Al-Ni alloy is important. The shape memory of this alloy is reported in 1964 [6], with detailed researched in the seventies.

The first discoveries of shape memory properties initiated extensive research with the following objectives:

— understanding of the shape memory mechanisms,

— improvement of the shape memory properties of already known alloys,

— searching for new alloys,

— implementation of the shape memory materials in practice.

The results of research work in recent years are the following shape memory alloys: Ag-Cd, Au-Cd, Cu-Zn, Cu-Zn-X (X = Si, Sn, Al, Ga), Cu-Al-Ni, Cu-Sn, Cu-Au-Zn, Ni-Al, Ni-Ti, In-Ti, In-Cd, Mn-Cu, Fe-Pt, Fe-Pd, Fe-Ni-Co-Ti, Fe-Ni-C, Fe-Mn-Si, Fe-Cr-Ni-Mn-Si-Co.

The alloy Ni-Ti is the most important shape memory alloy for implementation in practice. The shape memory characteristics of Ni-Ti alloy exceed any of the alloys known today. In addition, Ni-Ti alloy has: high ductility and yield strength, high strength to weight ratio, excellent corrosion resistance and a relatively low price. As far as is known, Ni-Ti is the first alloy which shape memory property has been used in practice. And, as is often the case with important discoveries, the shape memory property was used for the first time in the army [7]. To avoid welding, pipe

Ni-Ti razširila še na druga, za vsakdanje življenje bolj pomembna področja [8], [9]. Tu velja posebej omeniti zelo pomembno lastnost zlitine Ni-Ti, to je njeno biološko združljivost, zaradi česar se je njena uporaba izredno razširila tudi v medicini [10], [11].

V zadnjih letih je v literaturi mogoče opaziti prve objave o raziskavah oblikovnega spomina pri polimerih [12], [13]. Iz dostopne literature je mogoče sklepati, da je fazna premena osnova oblikovno spominskega mehanizma tudi v primeru polimerov. Vendar je v tem primeru premena povezana s temperaturo steklastega prehoda Tg, ki je pri polimerih značilna temperaturna točka premene iz steklastega v gumijasto stanje in nasprotno.

2 FIZIKALNO OZADJE OBLIKOVNEGA SPOMINA PRI ZLITINAH

Skoraj vsa spoznanja, povezana z materiali z oblikovnim spominom, slonijo na rezultatih raziskav zlitin z oblikovnim spominom. Temelj oblikovnega spomina pri zlitinah je fazna premena iz martenzita v avstenit in nasprotno. V izogib morebitnemu nesporazumu velja navesti, da se v ustrezni literaturi izraza »martenzit« in »avstenit« uporabljata posplošeno za poimenovanje »nižje« oziroma »višje« temperaturne faze in v splošnem ne določata oblike kristalne rešetke.

Pri snoveh sta znana dva osnovna načina premene: difuzijska in nedifuzijska. Fazne premene, povezane s pojavom oblikovnega spomina, so nedifuzijske. Značilnost nedifuzijske premene je, da poteka v obliki pomika oziroma povezane preureditve atomov v neko novo, bolj stabilno kristalno strukturo. Pri tem se kemijska sestava materiala ne spremeni. Nedifuzijska premena v splošnem napreduje neodvisno od časa in je hitrost pomika mejnih ploskev med dvema fazama omejena le s hitrostjo zvoka. To so atermalne transformacije, saj je količina nove faze običajno odvisna le od temperature in ne od tega, koliko časa je material izpostavljen določeni temperaturi.

Z vidika kristalografije je martenzitna premena sestavljena iz naslednjih treh procesov:

— mrežnega popačenja, pri katerem martenzitna struktura nastaja iz izvirne faze;

— mrežno invariantnega striga (dvojčenje in zdrs);

— mrežne rotacije (zasuki mreže).

Pri mrežnem popačenju poteka sprememba iz ene v drugo mrežo z raztezanjem ali s krčenjem vzdolž kristalografskih smeri. Mrežno popačenje je torej prva stopnja martenzitne premene, ki

couplings of shape memory Ni-Ti alloy were used to assemble pipes during ordinary maintenance of the pipe system of a submarine. Later, the shape memory property of Ni-Ti alloy was also used in the space program and finally, it has spread to areas that are more important for everyday life [8], [9]. It must here be stressed, that the Ni-Ti alloy has a very important property, biocompatibility which enables the extensive use in medicine [10], [11].

In recent years, there have been first reports on the shape memory properties of polymers [12], [13]. It could be concluded from the available literature that also in relation to polymers, phase transition is the basis of the shape memory property. However, the transition in polymers is related to the glass transition temperature, Tg, which is a characteristic temperature related to the transition between a glass like and a rubbery like states.

2 PHYSICAL BACKGROUND OF SHAPE MEMORY EFFECT IN ALLOYS

Nearly all knowledge related to shape memory materials is based on the results of studies on shape memory alloys. The basis of the shape memory effect of alloys is phase transition from martensite to austenite and the reverse. To avoid misunderstanding, it should be stressed that in the relevant literature, the terms »martensite« and »austenite« are used to define phase at lower or higher temperature, respectively. In general, these two terms do not define the form of crystal lattice.

Two forms of the phase transition process are known for materials: diffusion and diffusionless. Phase transitions related to shape memory are diffusionless. The basic property of diffusionless transition is that it takes place in the form of a shift or continuous rearrangement of atoms to a new, more stable crystal structure. The chemical composition of the material remains. In general, diffusionless transition is time independent and the moving velocity of boundaries between two phases is limited to the velocity of sound only. Diffusionless transformations are athermal and the quantity of the new phase depends only on temperature and not on the time the material is exposed to this temperature.

From the crystallography point of view, martensitic transition consists of the following three phases:

— lattice distortion - the martensitic structure is formed from the parent phase;

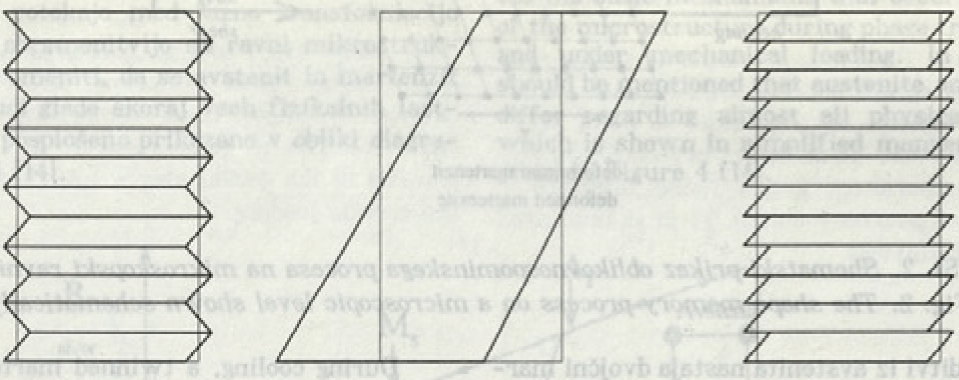
— lattice invariant shear (twining and slip);

— lattice rotation.

During lattice distortion, transition from one to another lattice consists of stretching or contracting along the crystallographic directions.

ustvari potrebno kristalno strukturo, ne zadošča pa za nastanek nepopačene habitusne ravnine, kar je prva od štirih karakteristik martenzitne premene. Da bi ostala stična ravnina med avstenitom in martenzitom makroskopsko koherentna tudi po mrežnem popačenju, se mora pojaviti še druga stopnja martenzitne premene, tj. mrežno invariantna strižna deformacija. Mrežno invariantna strižna deformacija je neke vrste prilagoditveni del martenzitne premene, ki spremeni obliko transformiranega področja, ne spremeni pa oblike novo nastale kristalne mreže. Mrežno invariantna deformacija torej deloma izravna makroskopsko popačenje, ki bi nastalo, če bi se proces martenzitne premene končal le s prvo stopnjo – mrežnim popačenjem. Naslednja kristalografska značilnost martenzitnih transformacij je podstruktura, ki nastane s strižno deformacijo na enega od dveh mogočih načinov: dvojčenje ali drsenje. Na sliki 1 je prikazano, kako se na makroskopski ravni izravna sprememba oblike, zaradi mrežnega popačenja, z eno ali drugo obliko mrežno invariantne strižne deformacije.

Lattice distortion is the first stage of the martensitic transition that forms the necessary crystal structure, but it is not sufficient for the formation of the undistorted Habitus plane that is the first of four characteristics of a martensitic transition. In order to obtain macroscopical coherency of the contact plane between the austenite and martensite, the second stage of the transition, i.e. lattice invariant shear deformation, has to take place. Lattice invariant shear deformation is somehow an accommodation part of martensitic transition that changes the form of the transformed area but not the form of the new crystal lattice. Actually, lattice invariant deformation compensates for the macroscopic distortion that would appear if the martensitic transition process were to conclude with the first stage – lattice distortion. An important crystallographic property of martensitic transformation is a substructure that is formed by shear deformation in one of two modes: twinning or slip. Figure 1 shows schematically how the change of the form is compensated on the macroscopic level by one of two modes of lattice invariant shear deformation.



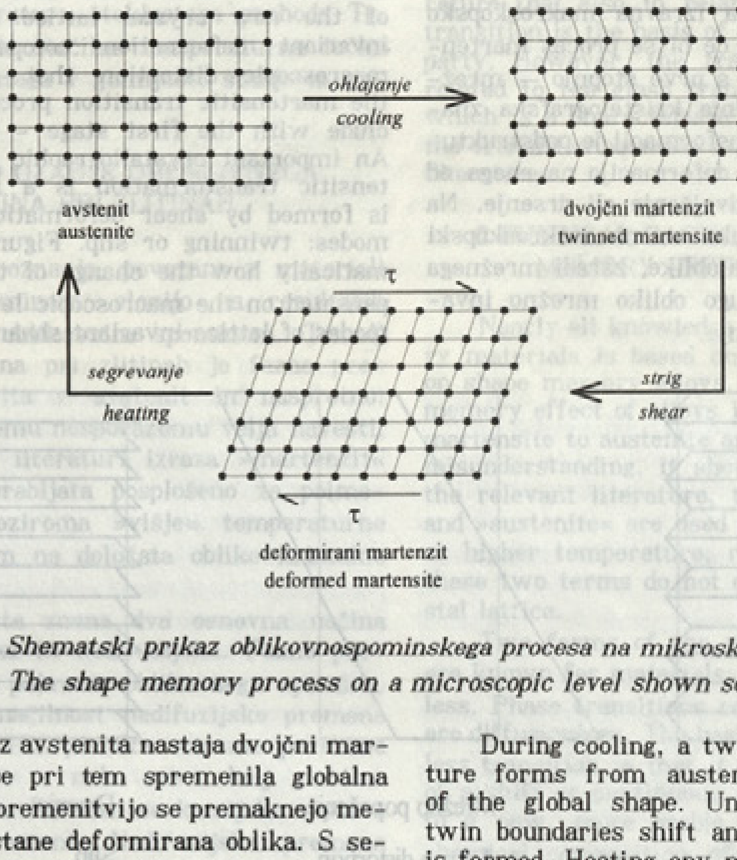
Sl. 1. *Shematski prikaz dveh načinov kompenzacije mrežnega popačenja: z dvojčenjem oziroma z drsenjem (zdrsom)*

Fig. 1. *Compensation for lattice distortion by twinning or by slip shown schematically*

Za oblikovnospominski mehanizem pri zlitinah je pomembno dvojčenje, ker omogoča spremembo oblike tudi v nasprotni smeri. Če ima material, po transformaciji iz avstenita v martenzit, strukturo dvojčnega martenzita, ostaneta oblika in prostornina nespremenjena. Ob strižni obremenitvi dvojčnega martenzita se pomikajo dvojčne meje v smeri obremenitve, ne da bi se pri tem trgale atomske vezi. Posledica obremenitve je deformacija, ki se na makroskopski ravni kaže v spremembi oblike, na mikroskopski ravni pa se kaže v nastanku deformiranega martenzita. Ob razbremenitvi ostane kristalna struktura v deformirani

Compensation by twinning is important for the shape memory mechanisms in alloys because it enables change of shape also in the reverse direction. The transition from austenite to martensite, when the structure of the material has the form of twinned martensite, does not result in a change of shape and volume. Under shear loading, the twin boundaries move in the direction of loading, without tearing the atom bonds. The result of the loading is deformation that manifests itself in a change of shape on the macroscopic level and in the formation of deformed martensite on the microscopic level. After unloading, the structure obliki, ki ustreza obliki pri mrežnem popačenju. S segretjem nad ustrezno temperaturo se deformirani martenzit preoblikuje v avstenit. Na mikroskopski ravni se nasprotna transformacija v avstenit kaže v spremembi kristalne rešetke, na makroskopski ravni pa se kaže v povrnitvi v obliko, kakršna je bila pred deformacijo. Na mikroskopski ravni in v poenostavljeni obliki je osnova oblikovnospominskega pojava pri zlitinah prikazana na sliki 2 [14].

retains the deformed shape that corresponds to the shape of lattice distortion. When heated above the adequate temperature, deformed martensite transforms to austenite. On the microscopic level, reverse transformation to austenite results in change of the crystal lattice and, on the macroscopic level, it results in a return to the original shape before deformation. The basis of the shape memory effect in alloys on the macroscopic level is shown in a simplified form in Figure 2 [14].



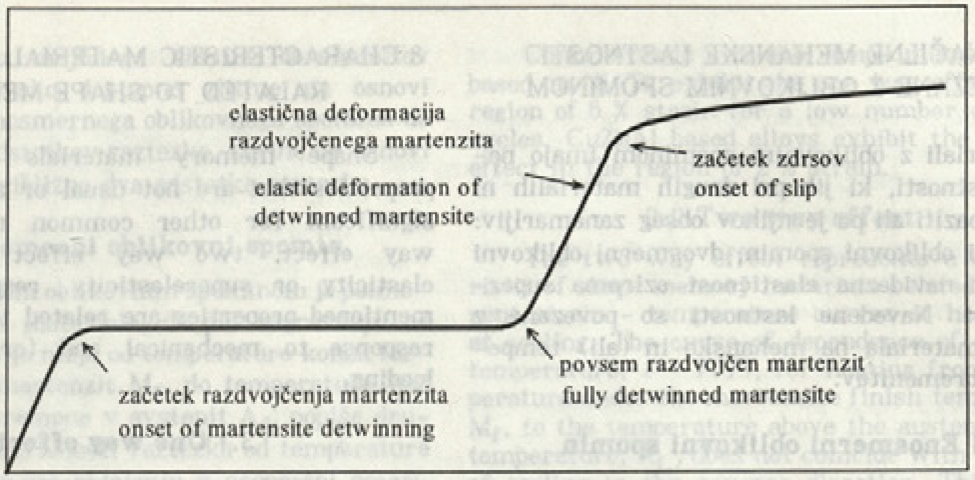
Sl. 2. *Shematski prikaz oblikovnospominskega procesa na mikroskopski ravni.*
Fig. 2. *The shape memory process on a microscopic level shown schematically.*

Pri ohladitvi iz avstenita nastaja dvojčni martenzit, ne da bi se pri tem spremenila globalna oblika. S strižno obremenitvijo se premaknejo meje dvojčkov in nastane deformirana oblika. S segretjem ene ali druge martenzitne oblike se material povrne v avstenitno strukturo [14].

Dogajanje na makroskopski ravni je shematsko prikazano na sliki 3 [14] na primeru nateznega preizkusa zlitine z oblikovnim spominom. Preizkus poteka pri temperaturi, pri kateri ima zlitina strukturo dvojčnega martenzita. V začetku obremenjevanja je deformacija posledica elastične deformacije dvojčnega martenzita. Ko obremenitev doseže ustrezno velikost, se sproži mehanizem razdvojčenja martenzita. Med procesom razdvojčenja martenzita ima napetost konstantno vrednost, raztezek pa se močno zveča. Po končanem procesu razdvojčenja se deformacija nadaljuje z elastično deformacijo razdvojčenega martenzita, do stopnje, ko se deformacijski mehanizem nadaljuje z zdrsi. Posledica zdrsov so trajne, nepovratne deformacije.

During cooling, a twinned martensite structure forms from austenite, without a change of the global shape. Under shear loading, the twin boundaries shift and a deformed structure is formed. Heating any martensitic form results in reverse transformation of the structure to austenite [14].

How the deformation process in a shape memory alloy is manifested on the macroscopic level is shown schematically in Figure 3 [14] for the example of a tensile test. A tensile test is performed at the temperature of the twinned martensitic structure. At the beginning of the test, deformation is the result of elastic deformation of twinned martensite. At an appropriate level of loading, the mechanism of detwinning of martensite starts. During the detwinning process, the stress is constant and strain increases significantly. At the end of the detwinning process, deformation continues with elastic deformation of detwinned martensite, until a limit, when the deformation process continues with slips. Permanent, irreversible deformation occurs due to slips.



Sl. 3. *Shematski prikaz tipične krivulje napetost — raztezek, $\sigma - \varepsilon$, za dvojčno martenzitni material*

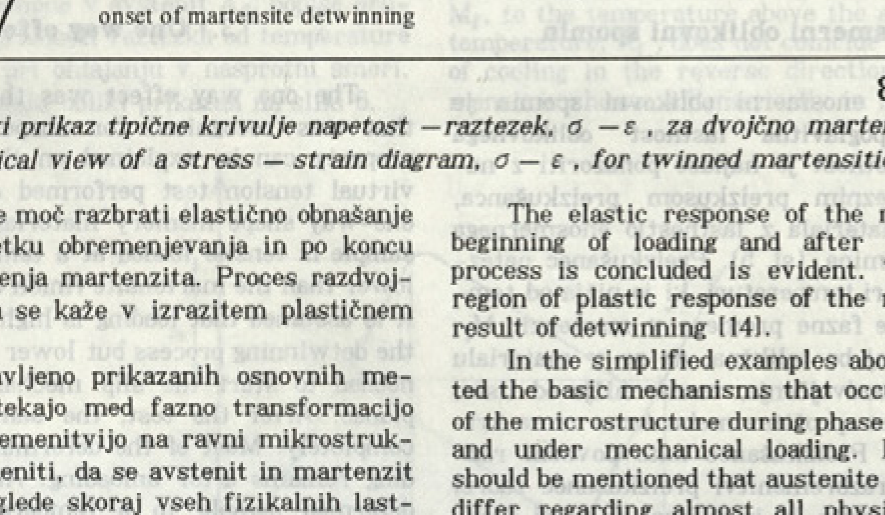
Fig. 3. *Typical view of a stress — strain diagram, $\sigma - \varepsilon$, for twinned martensitic material*

Iz krivulje je moč razbrati elastično obnašanje materiala v začetku obremenjevanja in po koncu procesa razdvojčenja martenzita. Proces razdvojčenja martenzita se kaže v izrazitem plastičnem platoju [14].

Ob poenostavljeno prikazanih osnovnih mehanizmih, ki potekajo med fazno transformacijo in mehansko obremenitvijo na ravni mikrostrukture, velja še omeniti, da se avstenit in martenzit razlikujeta tudi glede skoraj vseh fizikalnih lastnosti, kar je posplošeno prikazano v obliki diagrama na sliki 4 [14].

The elastic response of the material at the beginning of loading and after the detwinned process is concluded is evident. The significant region of plastic response of the material is the result of detwinning [14].

In the simplified examples above are presented the basic mechanisms that occur on the level of the microstructure during phase transformation and under mechanical loading. In addition, it should be mentioned that austenite and martensite differ regarding almost all physical properties, which is shown in simplified manner in the diagram in Figure 4 [14].



Sl. 4. *Shematski prikaz spreminjanja lastnosti materiala z oblikovnim spominom ob faznih premenah iz avstenita v martenzit in nasprotno [14]*

Fig. 4. *The dependence of some selected properties of shape memory material on phase transition from austenite to martensite and the reverse [14]*

V diagramu pomenijo: R — električno upornost, ΔL — spremembo dolžine in ΔV — spremembo prostornine.

Symbols in the diagram represent: R — electrical resistance, ΔL — length change and ΔV — volume change.

3 ZNAČILNE MEHANSKE LASTNOSTI POVEZANE Z OBLIKOVNIM SPOMINOM

Materiali z oblikovnim spominom imajo nekatere lastnosti, ki jih pri drugih materialih ni mogoče opaziti ali pa je njihov obseg zanemarljiv: enosmerni oblikovni spomin, dvosmerni oblikovni spomin in navidezna elastičnost oziroma superelastičnost. Navedene lastnosti so povezane z odzivom materiala na mehansko in (ali) temperaturno obremenitev.

3.1 Enosmerni oblikovni spomin

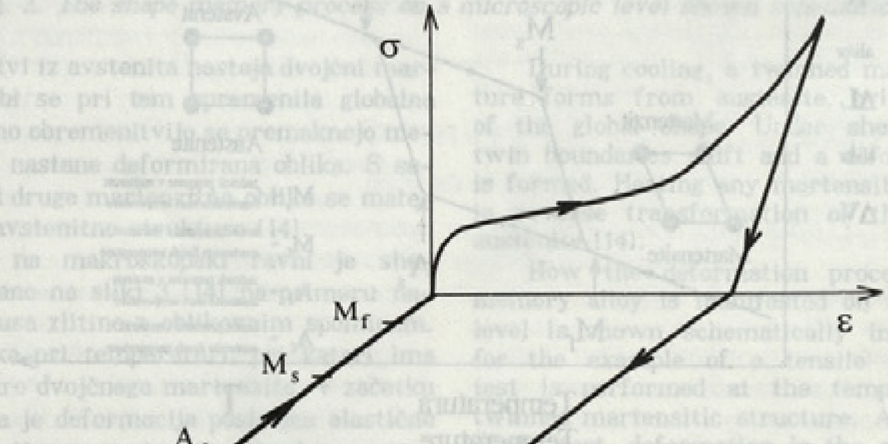
Z izrazom enosmerni oblikovni spomin je poimenovana poglavitna lastnost oblikovnega spomina. To lastnost je najlaže ponazoriti z namišljenim nateznim preizkusom preizkušanca, izdelanega iz materiala z lastnostjo enosmernega oblikovnega spomina, (sl. 5). Preizkušanec natezno obremenijo pri temperaturi, ki je nižja od temperature končne fazne premene v martenzit M_f. Obremenitev naj bo tolikšna, da se v materialu sproži proces razdvojčenja, vendar nižja od tiste, ki je potrebna za sprožitev mehanizma zdrsa kristalnih ravnin. Preizkušanec nato povsem razbremenijo. Po razbremenitvi preizkušanec zadrži večji del deformacije, ki jo je imel ob polni obremenitvi. Če se tako deformirani preizkušanec segreje nad temperaturo konca fazne premene v avstenit A_f, se povrne v obliko, ki jo je imel pred natezno obremenitvijo.

3 CHARACTERISTIC MATERIAL PROPERTIES RALATED TO SHAPE MEMORY

Shape memory materials exhibit some properties that are not usual or at least not so significant for other common materials: one way effect, two way effect and pseudo-elasticity or superelasticity, respectively. The mentioned properties are related to the material response to mechanical and (or) temperature loading.

3.1 One way effect

The one way effect was the first property that was recognised for shape memory. This property can be explained on the example of a virtual tension test performed on a sample of one-way shape memory material, Figure 5. The sample is tensile loaded at a temperature that is lower than the martensite finish temperature, M_f. It is assumed that loading is high enough to start the detwinning process but lower than the loading needed to start the slip mechanism in crystal planes. After the test, the sample is unloaded completely. Most of the deformation at full loading remains after unloading. After heating the deformed sample to a temperature above the austenite finish temperature, A_f, the sample returns to the initial shape, i.e. the shape before the tensile loading.



Sl. 5. *Shematski prikaz enosmernega oblikovnega spomina v trirazsežnem prostoru: napetost — raztezek — temperatura, $\sigma - \varepsilon - T$*

Fig. 5. *One way effect shown schematically in the form of 3 D diagram: stress — strain — temperature, $\sigma - \varepsilon - T$*

V primeru majhnega števila obremenitev izkazujejo trgovsko dostopne zlitine na osnovi NiTi lastnost enosmernega oblikovnega spomina do približno šest odstotkov raztezka, zlitine na osnovi CuZnAl pa do približno dva odstotka raztezka.

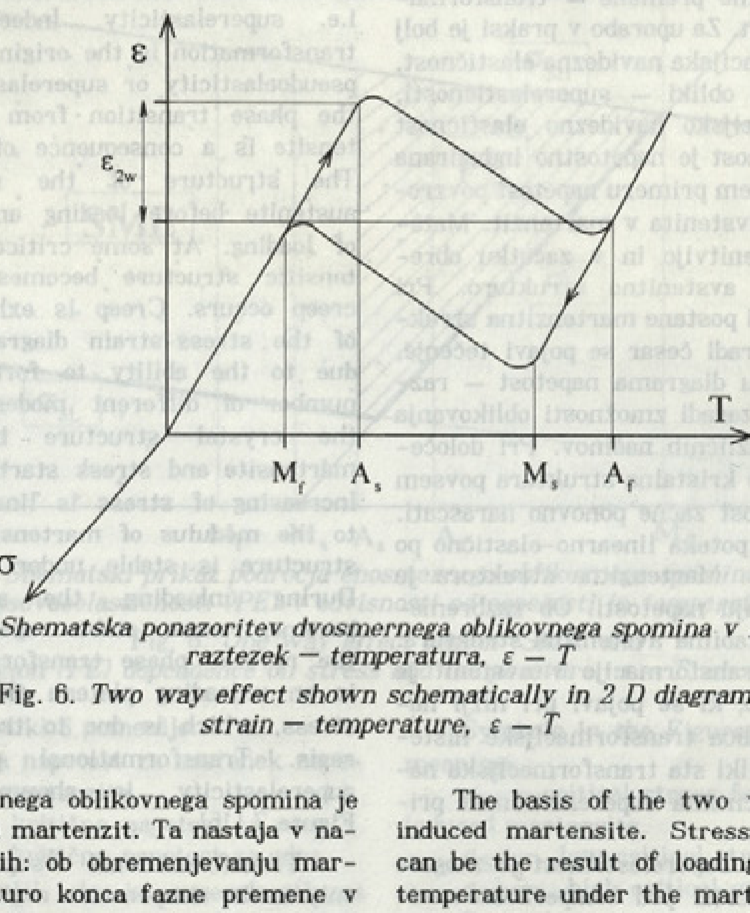
Commercially available shape memory alloys based on Ni-Ti, exhibit the one way effect in the region of 6 % strain for a low number of loading cycles. CuZnAl based alloys exhibit the one way effect in the region of 2 % strain.

3.2 Dvosmerni oblikovni spomin

Z dvosmernim oblikovnim spominom je poimenovana lastnost materiala, da pri segrevanju od temperature, ki je nižja od temperature konca fazne premene v martenzit M_f, do temperature nad koncem fazne premene v avstenit A_f, popiše drugačno krivuljo odvisnosti raztezka od temperature $\varepsilon = f(T)$, kakor pri ohlajanju v nasprotni smeri. Pojav je v shematski obliki prikazan na sliki 6.

3.2 Two way effect

The two way effect represents a characteristic of shape memory materials related to different strain - temperature curves at heating and at cooling. The curve of dependence of strain on temperature, $\varepsilon = f(T)$, for heating from a temperature under the martensite finish temperature, M_f, to the temperature above the austenite finish temperature, A_f, does not coincide with the curve of cooling in the reverse direction. This phenomenon is shown schematically in Figure 6.



Sl. 6. *Shematska ponazoritev dvosmernega oblikovnega spomina v ravnini raztezek — temperatura,* $\varepsilon - T$

Fig. 6. *Two way effect shown schematically in 2 D diagram: strain — temperature,* $\varepsilon - T$

Osnova dvosmernega oblikovnega spomina je napetostno inducirani martenzit. Ta nastaja v naslednjih dveh primerih: ob obremenjevanju martenzita pod temperaturo konca fazne premene v martenzit, M_f, ali ob obremenjevanju avstenita pri temperaturi blizu, a nad temperaturo konca fazne premene v avstenit A_f. Posledica obremenitve je sprememba oblike posameznih zrn v martenzitni strukturi.

V zvezi z dvosmernim oblikovnim spominom velja navesti, da je ta lastnost izražena v območju občutno manjših raztezkov, kakor pri enosmernem oblikovnem spominu istih zlitin. Zmožnost dvosmernega oblikovnega spomina ni naravna lastnost zlitine, temveč »naučena« lastnost, ki jo zlitina pridobi med posebno termomehansko obdelavo.

The basis of the two way effect is stress induced martensite. Stress induced martensite can be the result of loading of martensite at a temperature under the martensite finish temperature, M_f, or of the loading of austenite at a temperature close to, but above the austenite finish temperature, A_f. Loading results in a change of the shape of some grains in the martensitic structure.

In relation to the two way effect it should be mentioned that this property is limited to the lower range of strains compared to the one way effect of the same alloys. Actually, the two way effect is not an original property of the alloy. It is a »learned« property that is obtained by special thermo-mechanical training.

3.3 Navidezna elastičnost in superelastičnost

Navidezna elastičnost je pogost pojav, ki ni značilen le za materiale z oblikovnim spominom. V splošnem pomenu je z izrazom navidezna elastičnost poimenovana kakršnakoli nelinearnost krivulje napetost — raztezek v območju razbremenitve. Nekateri materiali se v določenih razmerah obnašajo izrazito navidezno elastično, kar se kaže v izraziti spremembi nagiba tangente na krivuljo napetost — raztezek ob razbremenjevanju. V izrazitih primerih ima krivulja razbremenitve celo plato. V takem primeru govorimo o superelastičnosti.

Navidezna elastičnost je lahko posledica dvojčenja — dvojčna navidezna elastičnost ali napetostno inducirane fazne premene — transformacijska superelastičnost. Za uporabo v praksi je bolj pomembna transformacijska navidezna elastičnost, še posebej v skrajni obliki — superelastičnosti. Pogoj za transformacijsko navidezno elastičnost oziroma superelastičnost je napetostno inducirana transformacija. V takem primeru napetost povzroči fazno premeno iz avstenita v martenzit. Material ima pred obremenitvijo in v začetku obremenjevanja stabilno avstenitno strukturo. Pri neki kritični napetosti postane martenzitna struktura bolj stabilna, zaradi česar se pojavi tečenje, ki se izrazi v platoju diagrama napetost — raztezek. Plato nastane zaradi zmožnosti oblikovanja martenzita na več različnih načinov. Pri določenem raztezku postane kristalna struktura povsem martenzitna in napetost začne ponovno naraščati. Naraščanje napetosti poteka linearno-elastično po modulu za martenzit. Martenzitna struktura je stabilna le ob delovanju napetosti. Ob razbremenitvi postane zopet stabilna avstenitna struktura. Posledica povratne transformacije v avstenit je razbremenitveni plato, ki se pojavi pri nižji napetosti, kar je posledica transformacijske histereze. V shematski obliki sta transformacijska navidezna elastičnost oziroma superelastičnost prikazani na sliki 7 [15].

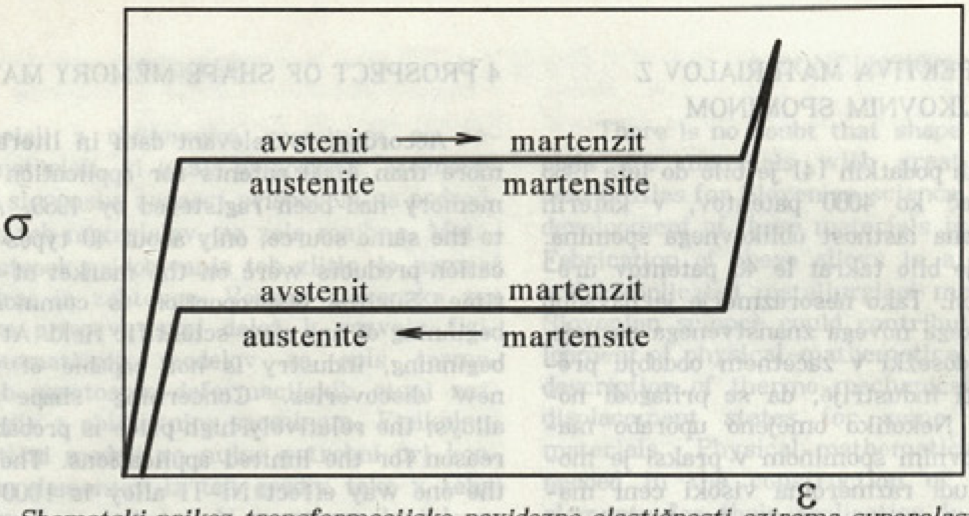
Transformacijsko superelastičnost je mogoče opaziti le, če je material pod temperaturo navidezno elastičnega obnašanja materiala M_d in nad temperaturo konca fazne premene v avstenit A_f. Če temperatura presega temperaturo navidezno elastičnega obnašanja materiala M_d, napetostni martenzit ne more nastati. Če je temperatura nižja od temperature konca fazne premene v avstenit A_f, ostane napetostni martenzit stabilen tudi med razbremenitvijo, zato ni razbremenitvenega platoja. Odvisnost obnašanja materiala z oblikovnim spominom od temperature je prikazana v shematski obliki na diagramu na sliki 8 [4].

3.3 Pseudoelasticity and superelasticity

Pseudoelasticity is not a phenomenon that is characteristic of shape memory materials only. The term, pseudoelasticity, in general expresses any nonlinearity of the stress-strain curve in the region of unloading. Some materials exhibit extreme pseudoelasticity in certain circumstances. The result is a significant change of the slope of the tangent of the unloading stress-strain curve. In extreme cases, the unloading curve even has a plateau. Such a property is expressed by the term superelasticity.

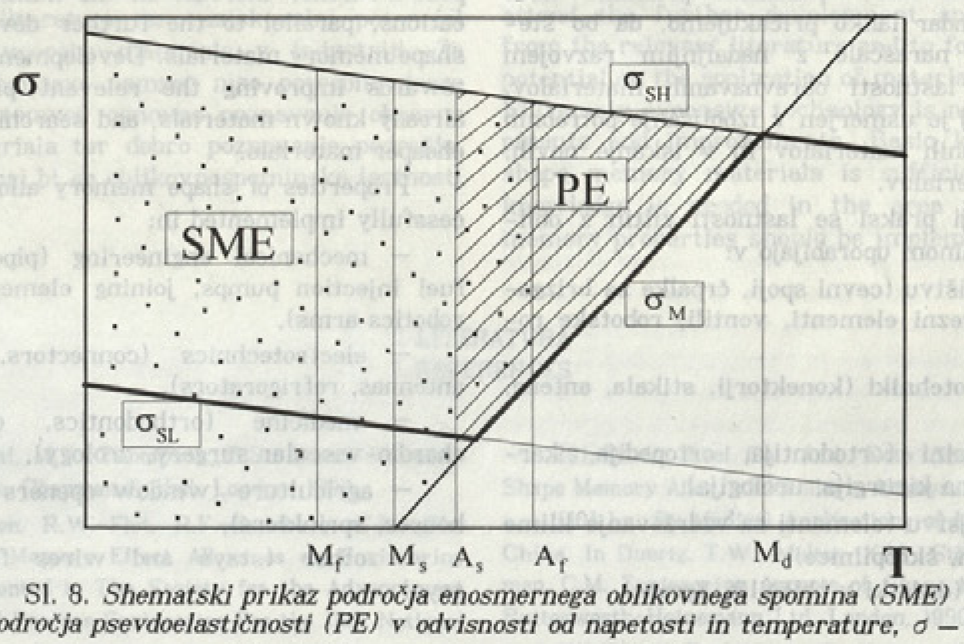
Superelasticity can be result of twinning — twin pseudoelasticity, or stress induced phase transition — transformational pseudoelasticity, i.e. superelasticity. Indeed, stress induced transformation is the origin of transformational pseudoelasticity or superelasticity. In this case, the phase transition from austenite to martensite is a consequence of the acting stress. The structure of the material is stable austenite before loading and at the beginning of loading. At some critical stress, the martensitic structure becomes more stable and creep occurs. Creep is exhibited in a plateau of the stress-strain diagram. The plateau is due to the ability to form martensite in a number of different modes. At some strain, the crystal structure becomes completely martensite and stress starts to increase again. Increasing of stress is linear-elastic according to the modulus of martensite. The martensitic structure is stable under acting stress only. During unloading, the austenitic structure becomes more stable again. The effect of the reverse phase transformation to austenite is an unloading plateau that occurs at lower stress, which is due to transformation hysteresis. Transformational pseudoelasticity, or superelasticity, is shown schematically in Figure 7 [15].

Transformational superelasticity occurs only in the temperature region under the pseudoelastic behaviour of the material, M_d, and above the austenite finish temperature, A_f. If the temperature exceeds the temperature of pseudoelastic behaviour of the material, M_d, stress induced martensite cannot be formed. If the temperature is lower than the austenite finish temperature, A_f, the stress induced martensite remains stable during unloading, and an unloading plateau does not appear. The behaviour of the shape memory material related to dependence on temperature is schematically shown in Figure 8 [4].



Sl. 7. *Shematski prikaz transformacijske navidezne elastičnosti oziroma superelastičnosti [15]*

Fig. 7. *Schematic view of transformational pseudoelasticity, or superelasticity [15]*



Sl. 8. *Shematski prikaz področja enosmernega oblikovnega spomina (SME) in področja psevdoelastičnosti (PE) v odvisnosti od napetosti in temperature, σ – T [4]*

Fig. 8. *One way effect region (SME) and pseudoelasticity region (PE) dependence on stress and temperature, σ – T, shown schematically [4]*

V diagramu na sliki 8 pomenijo:

σ_M – kritična napetost za nastanek napetostno induciranega martenzita,

σ_{SL} – spodnja kritična napetost za zdrs,

σ_{SH} – zgornja kritična napetost za zdrs.

Mogoče je oceniti, da je superelastičnost lastnost, ki je zelo zanimiva za uporabo v praksi. V primeru statične obremenitve oziroma deformacije je ta lastnost ugodna, ko je potrebna konstantna obremenitev pri razmeroma velikih tolerancah glede deformacije oziroma geometrijske oblike, npr. robotika, ortodontija, torni spoji. V primeru dinamične obremenitve je ta lastnost uporabna za dušenje nihanj oziroma blažitev udarnih obremenitev (absorpcija energije). Trgovsko dostopne zlitine na osnovi Ni-Ti imajo lastnost superelastičnosti v območju raztezka do približno šest odstotkov.

Symbols in the Figure 8 have the following meaning:

σ_M – critical stress for formation of stress induced martensite,

σ_{SL} – low critical stress for slip,

σ_{SH} – high critical stress for slip.

Superelasticity is a property of a great interest for application in practice. In relation to static loading or deformation, the advantage of superelasticity is constant loading at relatively high tolerances. High tolerances of deformation or geometry are demanded in: robotics, orthodontics, friction joints. In the case of dynamic loading, superelasticity is applicable in the damping of oscillations and the absorption of impact loading (energy absorption). Commercially available alloys on the Ni-Ti base, exhibit superelasticity to approximately six percent strain.

4 PERSPEKTIVA MATERIALOV Z OBLIKOVNIM SPOMINOM

Po dostopnih podatkih [4] je bilo do leta 1988 registriranih več ko 4000 patentov, v katerih je bila uporabljena lastnost oblikovnega spomina. Po istem viru je bilo takrat le 40 patentov uresničenih v praksi. Tako nesorazmerje je navadno na začetku vsakega novega znanstvenega razvoja, saj znanstveni dosežki v začetnem obdobju presegajo zmožnosti industrije, da se prilagodi novim odkritjem. Nekoliko omejeno uporabo materialov z oblikovnim spominom v praksi je mogoče pripisati tudi razmeroma visoki ceni materiala, ki je v primeru zlitine Ni-Ti z enosmernim oblikovnim spominom približno tisoč USD/kg. Vendar lahko pričakujemo, da bo število uporab naraščalo z nadaljnjim razvojem na področju lastnosti obravnavanih materialov. Njihov razvoj je usmerjen v izboljšanje potrebnih lastnosti znanih materialov in v iskanje novih, cenejših materialov.

V sedanji praksi se lastnosti zlitin z oblikovnim spominom uporabljajo v:

— strojništvu (cevni spoji, črpalke za brizganje goriva, vezni elementi, ventili, robotske roke),

— elektrotehniki (konektorji, stikala, antene, hladilniki),

— medicini (ortodontija, ortopedija, kardio-vaskularna kirurgija, urologija),

— kmetijstvu (elementi za vzdrževanje klime v rastlinjakih, škropilnice),

— drugo (dodatki v oblačilih, igrače).

5 RAZISKAVE NA PODROČJU MATERIALOV Z OBLIKOVNIM SPOMINOM V SLOVENIJI

Raziskovalni dosežki na področju materialov z oblikovnim spominom v Sloveniji so rezultat dela treh raziskovalnih skupin, ki so jih vodili: prof. Kosec [16], [17], prof. Kosel [18] do [25] in prof. Križman [26] do [28]. Prva skupina je bila usmerjena predvsem v metalurške raziskave na področju zlitin z oblikovnim spominom, druga v problematiko matematičnega modeliranja zlitin z vidika nelinearne mehanike in tretja predvsem v probleme litja. Glede na objave s tega področja je mogoče sklepati, da so raziskave najbolj intenzivne na področju matematičnega modeliranja reoloških lastnosti gradiv z oblikovnim spominom in analiz nelinearnih mehanskih stanj enoosnih konstrukcijskih elementov.

4 PROSPECT OF SHAPE MEMORY MATERIALS

According to relevant data in literature [4], more than 4000 patents for application of shape memory had been registered by 1988. According to the same source, only about 40 types of application products were on the market at the same time. Such a disproportion is common at the beginning of any new scientific field. At the very beginning, industry is not capable of following new discoveries. Concerning shape memory alloys, the relatively high price is probably also a reason for the limited applications. The price of, the one way effect Ni-Ti alloy is 1000 USD/kg approximately. However, it is reasonable to expect a further increase in the number of applications, parallel to the further development of shape memory materials. Development is oriented towards improving the relevant properties of already known materials, and searching for new, cheaper materials.

Properties of shape memory alloys are successfully implemented in:

— mechanical engineering (pipe couplings, fuel injection pumps, joining elements, valves, robotics arms),

— electrotechnics (connectors, switches, antennas, refrigerators),

— medicine (orthodontics, orthopaedics, chardio-vascular surgery, urology),

— agriculture (window openers for greenhouses, sprinklers),

— other (stays and wires for lingerie, toys).

5 OVERVIEW OF THE RESEARCH WORK ON SHAPE MOMORY MATERIALS IN SLOVENIA

Research achievements in the field of shape memory materials in Slovenia are the result of the research work of groups working at three institutions. These three groups are leaded by: Prof. Kosec [16], [17], Prof. Kosel [18] to [25] and Prof. Križman [26] to [28]. The studies of the first group have been focused on the metallurgical background of shape memory alloys. The attention of the second group is focused on mathematical modelling from the point of view of nonlinear mechanics. The third group has been mainly oriented to the problem of casting. Concerning published papers, it seems that the most intensive studies are in the field of mathematical modelling of the rheological properties of shape memory materials and the analysis of the nonlinear states of uniaxial structural elements.

6 SKLEP

Materiali z oblikovnim spominom so nedvomno materiali, ki imajo prihodnost. Možnosti, da bi tudi slovenska znanost prispevala na področju razvoja teh materialov, so zelo majhne. Metalurški postopek pridobivanja teh zlitin je namreč izredno drag in zahteven. Vendar slovenska znanost lahko prispeva svoj delež k razvoju fizikalno-matematičnih modelov za opis termomehanskih napetostno-deformacijskih stanj različnih gradiv z oblikovnim spominom. Fizikalno-matematični modeli so nujno potrebni pri konstruiranju elementov iz teh gradiv tako v tehniki kakor tudi v medicini. V ta namen bi bilo pametno spremljati razvoj in prevzemati znanje iz objav v literaturi ter raziskovalni potencial usmeriti v uporabo materiala v industriji. Za izume in izboljšave namreč niso potrebne drage tehnologije, temveč osnovno poznavanje obravnavanega materiala ter dobro poznavanje področja, na katerem naj bi se oblikovnospominske lastnosti uporabljale.

6 CONCLUSION

There is no doubt that shape memory materials are materials with great prospect. The possibilities for Slovenian science to contribute to development of these materials is rather limited. Fabrication of these alloys is a very expensive and complicated metallurgical method. However, Slovenian science could contribute to the development of physical-mathematical models for the description of thermo-mechanical stress-strain-displacement states for some shape memory materials. Physical-mathematical models are needed in the construction of shape memory elements for their application in techniques and medicine. It would therefore, be reasonable to attend the further development and knowledge from the relevant literature and to focus research potential on the application of material in industry. Extremely expensive technology is not needed for patents and improvements. Basic knowledge on shape memory materials is sufficient and good knowledge is needed in the area where shape memory properties should be implemented.

7 LITERATURA
7 REFERENCES

[1] Gandhi, M.V.–Thompson, B.S.: Smart Materials and Structures. Chapman & Hall, London, 1992.

[2] Benson, R.W.–Flot, R.F.–Sandburg, C.L.: The Use of Shape Memory Effect Alloys as an Engineering Material. Presented to The Society for the Advancement of Material and Process Engineering For the 15th National SAMPE Technical Conference, October 1983, Cincinnati, Ohio.

[3] Schetky, L.M.: Shape-Memory Alloys. Scientific American, Vol. 241, 1979.

[4] Miyazaki, S.–Otsuka, K.: Development of Shape Memory Alloys. ISIJ International, Vol. 29, 1989, No. 5.

[5] Beuhler, W.J.–Gilfrich, J.V.–Wiley, R.C.: Effect of Low-Temperature Phase Changes on the Mechanical Properties of Alloys Near Composition TiNi. Journal of Applied Physics, Vol. 34, May 1963, No. 5.

[6] Arbuzova, I.A.–Handros, L.G.: Anomal'noe udlinenie i umen'šenie soprotivlenija plastičeskoj deformacii pri martensitnom prevraščenii v splave Cu-Al-Ni. Fizika metallov i metallovedenie, Vol. 17, 1964, No. 3.

[7] Liberatore, D.J.–Baskerville, E.: The Introduction of Heat Recoverable Couplings to Ship Repair and Maintenance. Naval Engineers Journal, December 1982.

[8] Stöckel, D.: Superelastische Nickel-Titan-Legierungen. Eigenschaften und Anwendung. Metallwissenschaft und Technik, Vo. 47, August 1993, No. 8.

[9] Daido Steel Co., Ltd. Data Sheets of Ni-Ti Shape Memory Alloy, »Kiokalloy«, Nagoya, 1994.

[10] Lu, S.: Medical Applications of Ni-Ti Alloys in China. In Duerig, T.W., Melton, K.N., Stöckel, D., Wayman, C.M. Engineering Aspects of Shape Memory Alloys. Butterworth-Heinemann Ltd, London, 1990.

[11] Ming, Z.–Jinfang, G.–Xujun, M.–Guansen, Y.: Medical Applications of SMA in Beijing General Research Institute for Non-ferrous Metals. In Chu, Y. and Tu, H. Shape Memory Materials '94. Proceedings of the International Symposium on Shape Memory Materials. International Academic Publishers, Bejing, 1994.

[12] Tobushi, H.–Hayashi, S.–Kojima, S.: Cyclic Deformation of Shape Memory Polymer of Polyurethane Series Subjected to Loading at Low Temperature. Transactions of the Japan Society of Mechanical Engineers, Vol. 58, 1992, No. 10.

[13] Tobushi, H.–Hayashi, S.–Kojima, S.: Mechanical Properties of Shape Memory Polymer of Polyurethane Series. Proceedings of the 1993 SEM »50th Anniversary« Spring Conference on Experimental Mechanics, Dearborn, June 1993.

[14] Wayman, C.M.–Duerig, T.W.: An Introduction to Martensite and Shape Memory. In Duerig, T.W., Melton, K.N., Stöckel, D., Wayman, C.M. Engineering Aspects of Shape Memory Alloys. Butterworth-Heinemann Ltd, London, 1990.

[15] Duerig, T.W.–Zadno, R.: An Engineer's Perspective of Pseudoelasticity. In Duerig, T.W., Melton, K.N., Stöckel, D., Wayman, C.M. Engineering Aspects of Shape Memory Alloys. Butterworth-Heinemann Ltd, London, 1990.

[16] Bezjak, J.: Raziskave martenzitne transformacije v zlitinah CuZnAl z oblikovnim spominom. Magisterij, Fakulteta za naravoslovje in tehnologijo Univerze v Ljubljani, 1990.

[17] Breže, B.: Izdelava predoblik iz zlitine CuZnAl z oblikovnim spominom. Magisterij, Fakulteta za naravoslovje in tehnologijo Univerze v Ljubljani, 1992.

[18] Hrovat, B.–Kosel, F.: Vzmet kot pogonski element nizkotemperaturnih oblikovno spominskih toplotnih strojev. Kuhljevi dnevi 92, Portorož 1992.

[19] Hrovat, B.–Kosel, F.: Springs as Power Element of Low Temperature Shape Memory Heat Units. GAMM, Wissenschaftliche Jahrestagung '93, Dresden, 1993.

[20] Kosel, F.–Velej, M.: Displacements of Shape Memory Alloy Cantilever Beam. The International Symposium on Shape Memory Materials, Shape Memory Materials '94, International Academic Publishers, Beijing, 1994.

[21] Velej, M.: Določitev napetostno-deformacijskega stanja in premičnega stanja v konstrukcijskih elementih iz gradiva z oblikovnim spominom. Magisterij, Fakulteta za strojništvo Univerze v Ljubljani, 1992.

[22] Velej, M.–Kosel, F.: Analiza mehanskega stanja v enoosnih elementih iz gradiv z oblikovnim spominom. Kuhljevi dnevi '92, Portorož 1992.

[23] Velej, M.–Kosel, F.: Rheology and Displacements of Structural Shape Memory Alloy Elements. GAMM, Wissenschaftliche Jahrestagung '93, Dresden, 1993, 124.

[24] Velej, M.–Kosel, F.: Reologija in premiki konstrukcijskih elementov iz zlitin z oblikovnim spominom. Kovine, zlitine, tehnologije, Vol. 28, 1994.

[25] Velej, M.–Kosel, F.: Rheology and Displacements of Structural Shape Memory Alloy Elements. ZAMM, Z. Angew. Math. und Mech., 74, 4, 1994, T 327-328.

[26] Breže–B., Križman, A.: Martenzit v polkristalnih Cu-Zn-Al zlitinah. Posvet o metalurgiji in kovinskih gradivih, 41., Portorož 1990.

[27] Križman, A.–Breže, B.–Klančar, Z.–Anžel, I.: Raziskave faznih transformacij v zlitini Cu-Zn-Al. Posvet o metalurgiji in kovinskih gradivih, 40, Portorož 1989.

[28] Križman, A.–Breže, B.–Anžel, I.–Križman, D.: Raziskave termomehanske obdelave Cu-Zn-Al zlitine z oblikovnim spominom. Posvet o metalurgiji in kovinskih gradivih, 41., Portorož 1990.

Avtorjev naslov: mag. Borut Bundara, dipl. inž.
Tržaška 49
61000 Ljubljana

Author's Address: Mag. Borut Bundara, Dipl. Ing.
Tržaška 49
61000 Ljubljana, Slovenia

Prejeto:
Received: 6.4.1995

Sprejeto:
Accepted: 22.11.1995