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Development of shape memory and superelastic applications of some experimental alloys

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The paper presents the results obtained during the manufacturing and testing of experimental applications of some shape memory alloys (SMAs) belonging to CuZnAl and FeMnSiCr(Ni) alloys systems, respectively. CuZnAl actuators, manufactured as bending lamellas, were processed and trained for two way shape memory effect (TWSME). After up to 500 heating-cooling cycles under applied bending load, the actuators were used to develop thermal protection systems in hydraulic and electric circuits, as well as to build up composite mini-actuators. Constrained-recovery applications of FeMnSi-based SMAs were developed under the form of pipe couplings processed from powder metallurgy mechanically alloyed (PM-MA'd) FeMnSiCrNi and of FeMnSiCr truncated cone-shaped modules, for thermal expansion compensation, processed by high-speed high pressure torsion (HS-HPT).

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1. Introduction

Shape-memory alloys (SMAs) belong to the larger group of "intelligent/ smart materials" with typical properties, related to martensitic transformation induced by cooling-heating, mechanical loading-unloading or magnetic field application-removal [1]. The first SMA-related property was referred to as "rubberlike behavior" and was reported in 1932, in a 1-mm wire of Au–47.5 at.% Cd, by Arne Ölander [2]. Since then, the SMA family constantly increased with new members and commercial applications have been developed based on five alloy systems, namely: (i) TiNi, (ii) CuZnAl, (iii)CuAlNi, (iv) FeMnSi and (v) FeNiCo [3]. The first SMA-application, ever known, was presented at Brussels International Fair, in 1958 and comprised a cycling lifting device actuated by a AuCd sigle crystal rod, which lifted a load, fastened at its free end, when heated and lowered it, when cooled [4]. Since 1958, SMA applications have been constantly developed into four major groups designated as: (i) free-recovery; (ii) constrained recovery, (iii) work generating and (iv) superelastic applications [5] to which a fifth group, represented by magnetic SMA applications, was subsequently added [6].

Since the years seventies of the past century, the scientific world became more and more involved in SMA research-development both at fundamental and applicative levels. Consequently, scientific events were organized for the dissemination of research results, firstly in the so-called "Pacific Area". Thus an International Conference on Martensitic Transformation (ICOMAT) was firstly held in Kobe, Japan (May 10-12, 1976). The following editions were held in: 2. Kiev, Ukraine (May 14-21, 1977); 3. Boston, MA, USA (June 24-29, 1979); 4. Leuven, Belgium (August 8-12, 1982); 5. Nara, Japan (August 26-30, 1986); 6. Sydney, Australia (July 3-7, 1989); 7. Monterey, CA, USA (July 20-24, 1992); 8. Lausanne, Switzerland (August 20-25, 1995); 9. Bariloche, Argentina (December 7-11, 1998); 10. Helsinki, Finland (June 10-14, 2002); 11. Shanghai, P.R. China (June 14-17, 2005); 12. Santa Fe, NM, USA (June 29-July 5, 2008); 13. Osaka, Japan (September 4-9, 2011) [7]. At ICOMAT 14, held in Bilbao, Spain, (July, 6-11, 2014) Prof. Kaneaki Tsuzaki presented the world largest application of SMA, to present date, represented by 2 tons-anti-seismic dampers, made from Fe-Mn-Si, developed by the company Takenaka [8].

On the other hand, in Europe another series of events, firstly named European Symposium of Martensitic Transformation in Science and Technology (ESOMAT) have been organized starting with Bochum, Germany (May 9-10, 1989). Next editions were simply called European Symposium of Martensitic Transformation and were held in: IInd. Aussois, France (September 16-18, 1991); IIIrd. Barcelona, Spain (September 14-16 1994); IVth. Enschede, The Netherland (July 1-5, 1997); Vth. Como, Italy (September 4-8 2000); VIth. Cirencester, England (August 17-22, 2003); VIIth. Bochum, Germany (September 10-15, 2006); VIIIth. Prague, Czech Republic (September 7-11, 2009); IXth. Sankt Petersburg, Russia (September 9-16, 2012) [9]. The Xth ESOMAT conference will be held in Anwerp, Belgium, in September 14-18, 2015 [10].

As a recognition token of the international nature of the SMA industry, an additional series of conferences was later held, named Shape Memory and Superelastic Technology (SMST) and organized by a homonym professional organization, affiliated to American Society for Materials (ASM). SMST conferences have been organized on a different continent, every approximately 18 months, starting from 1994, in Asilomar, California;

Antwerp, Belgium (1999); China (2001); Baden-Baden, Germany (2004); Tsukuba, Japan (2007); Stresa, Italy (2008); Hong-Kong ; Prague, Czech Republic (2013). The next SMST conference will be held in Enstone Chipping Norton, UK (May 18-22, 2015) [11].

Romania was represented at a small part of these scientific events, by the present author and some colleagues, who participated to: ESOMAT 2006, 2009 and 2012, SMST 2008 and 2013 and ICOMAT 2014.

Based on a continuous activity, lasting for more than 20 years, SMA research-development took place at the Faculty of Materials Science and Engineering (MSE) of the Technical University of Iasi (TUI). Four of the most important SMA applications developed at MSE-TUI, will be described in the following.

2. Materials and methods

The different SMAs were obtained, belonging to CuZnAl, FeMnSiCrNi and FeMnSiCr systems, respectively.

Cu-15 Zn-6 Al (mass. %) SMA specimens of were produced by induction melting [12], cast into ingots and hot rolled [13]. Lamellar specimens were cut[14], which were heat treated [15] and trained in bending, by heating-cooling cycles, with a load fastened at their free-end [16]. During training, the specimens, which were martensitic at room temperature, were bent by the applied load. During heating they became austenitic and lifted the load by simple shape memory effect (SME). During cooling, the specimens became martensitic again (*i. e.* softer) and lowered the load, as explained in Fig.1 [17].

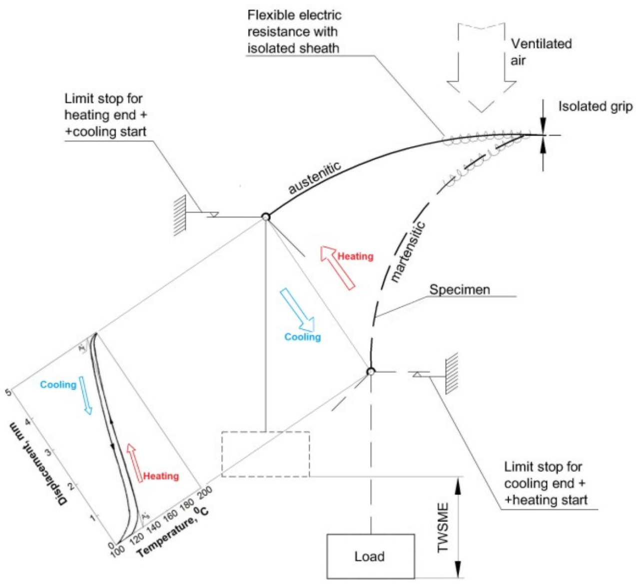

Fig. 1. Schematic illustration of TWSMA training in bending, of CuZnAl actuators, by heating-cooling cycles with a load fastened at their free-end, the displacement of which vs. temperature is shown in the lower left-side diagram

After repetitive heating-cooling, with applied bending load, the specimens were able to bend, during cooling, without any load. This spontaneous shape change, during heating and cooling, without the intervention of any external constraint, represents the two-way shape memory effect (TWSME) [18].

After TWSME-training, for up to 500 cycles, CuZnAl actuators were used to develop two types of SME applications: (i) thermal actuators and (ii) electrical actuators.

In the first case, trained actuators were subjected to thermal cycling within a hydraulic installation, where oil is the heat-transfer agent. The details of this experiment are shown in Fig.2

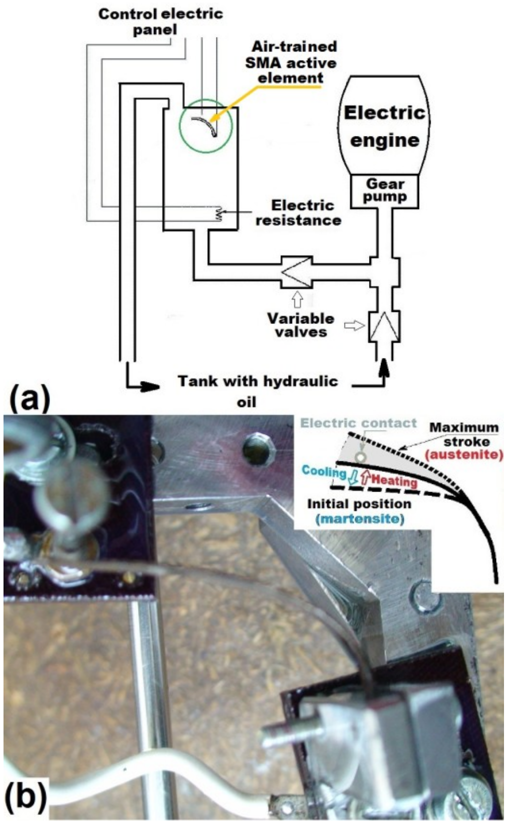

Fig. 2. Details of TWSME thermal cycling of CuZnAl trained actuators: (a) scheme of the hydraulic installation: (b) position of the actuator at room temperature (martensitic) and magnified detail about its functioning principle

The hydraulic installation, from Fig. 2(a), comprises a tank with oil, an electric engine, a pump, and a thermal exchange chamber. The oil, sent by the pump to the thermal exchange chamber, is heated above 90^0C by means of an electric resistance. The trained SMA element, shown in Fig. 2(b) in its bent (martensitic) state, is heated by oil and develops SME by touching an electric contact, thus turning off the electric resistance [19]. The variations of both oil pressure and temperature with time are recorded in the case of SMA active elements trained for different number of cycles.

The second application developed by means of CuZnAl trained elements represents a micro-actuator with active elements of SMA/ polysiloxane composite [20]. Fig.3 contains constructive details of the device.

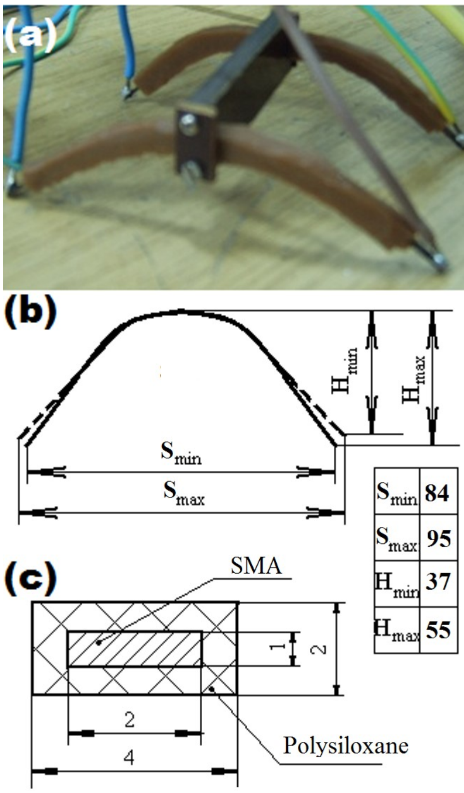

Fig. 3. Constructive details of the micro-actuator with four SMA/ polysiloxane composite arms: (a) perspective view of the device, without any applied load; (b) illustrations of the limit dimension of the arms; (c) cross-section of one composite arm, with dimensions of component elements

The two arms are alternatively actuated by electric currents between 15-20 A. When heated, SMA elements deflect, partially straiten and its dimensions vary, in such a way that the span (S) increases and the height decreases. At the limit, the dimensions S_{max} and H_{min} are attained, as listed in Fig.3(c). The variations of the span (S) and the height (H), as a function of temperature, can be monitored by cinematographic analysis [21], while the micro-actuator is subjected to different loads, of 20, 50 and 100 g, placed on its central beam.

Fe-14Mn-6 Si-9Cr-5Ni (mass. %) SMA specimens were produced from pure elemental powders, at Istanbul Technical University [22]. In order to increase the compactness and homogeneity degree, 10 to 50 % of the powder volume was mechanically alloyed (MA'd) [23]. After analysing the MA effects on the thermal behaviour of the powders [24], the particles were subjected to a complete powder metallurgy (PM) processing, by pressing and sintering as previously detailed [25], before being hot rolled [26] and heat treated [27]. The resulting lamellar specimens were gradually heated and rounded, by means of calibres, in order to obtain pipe-coupling rings [28]. The rings were trained by repetitively expanding their diameter at room temperature and by heating them to 300^0C, in order to develop free-recovery SME. The evolutions of rings diameter and free-end displacement with temperature are monitored by cinematographic analysis [29]. Details of the entire ring processing flow are shown in Fig.4.

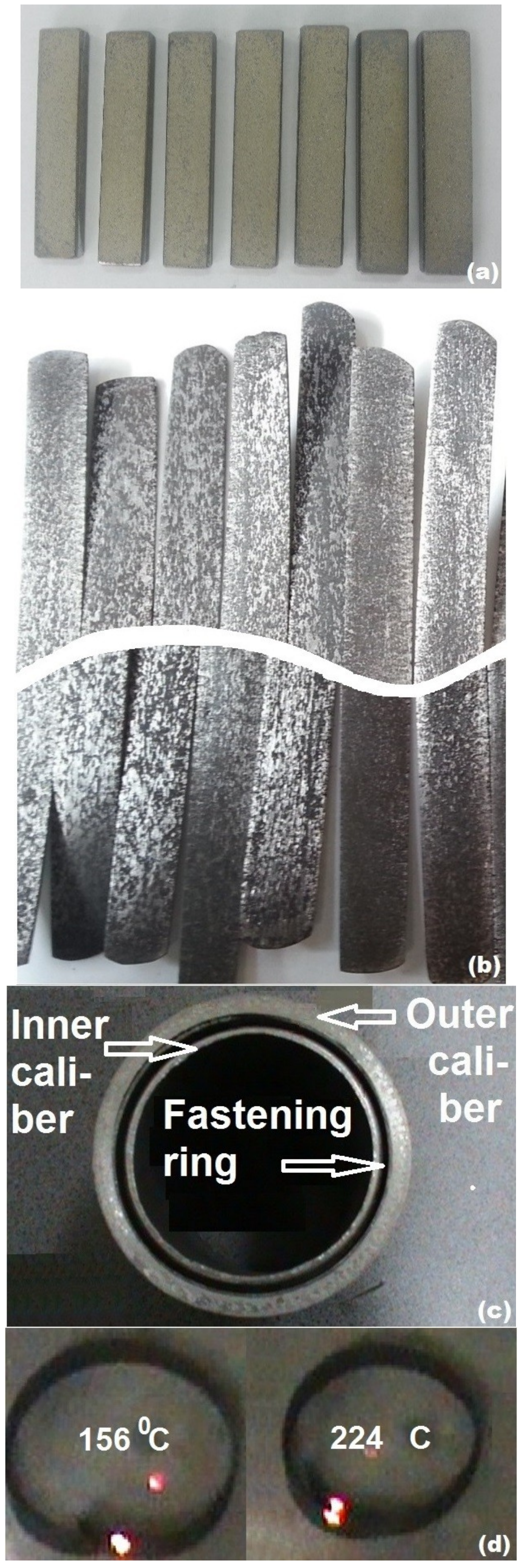

Fig. 4. Processing flow of FeMnSiCrNi PM specimens: (a) sintered specimens; (b) hot rolled specimens; (c) ring-shape setting with calibres; (d) training stages

Fe-28Mn-6Si-5Cr (mass. %) SMA ingots, obtained by cold crucible induction melting [30] were axially drilled and cut into circular crown slices. These billets were further processed by an original technology of High-Speed High Pressure Torsion (HS-HPT) [30], being transformed into multifunctional modules with coned disk spring-shape [31]. The main stages of HS-HPT modules processing are illustrated in Fig.5.

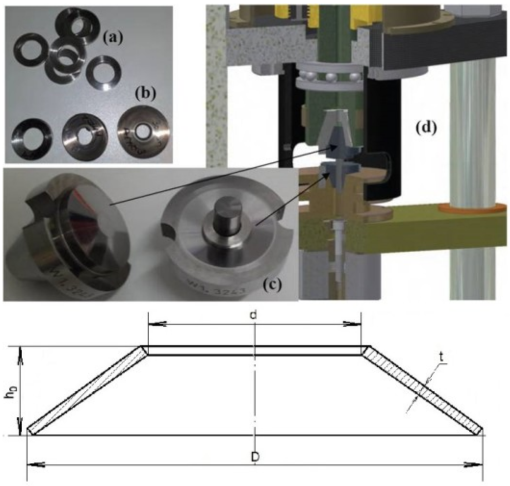

Fig. 5. Details of HS-HPT processing: (a) SMA samples; (b) SMA modules; (c) upper and lower HPT anvils, (d) deformation zone; (e) geometry of modules

The modules revealed, in initial state, the presence of a hardness gradient of approx. 16 HV/ mm, along truncated cone generator, increasing from inner to outer areas, due to different deformation degrees in these zones [32]. The modules were subjected to static compression tests, with a deformation rate of 0.5 mm/ min, applied between flat surfaces, in two different conditions: (i) dry condition (without lubrication), on an INSTRON 3382 testing machine with thermal chamber and (ii) wet condition (with lubrication), on an INSTRON 8801 testing machine. Compression load variations *vs.* stroke were recorded in both cases. At the end, a series of compressed modules were heated in constrained state, within the heating chamber of INSTRON 3382 testing machine, and the variations of constrained recovery forces *vs.* temperature were recorded.

3. Results and discussion

3.1 TWSME functioning of CuZnAl thermal actuators

Five CuZnAl thermal actuators, trained in bending, under load, for 100, 200, …, 500 cycles were subjected to thermal cycles within the hydraulic installation. After obtaining a stabilized behaviour, five consecutive cycles were selected for each differently-trained actuator. The durations of each of these five cycles are summarized in Fig. 6

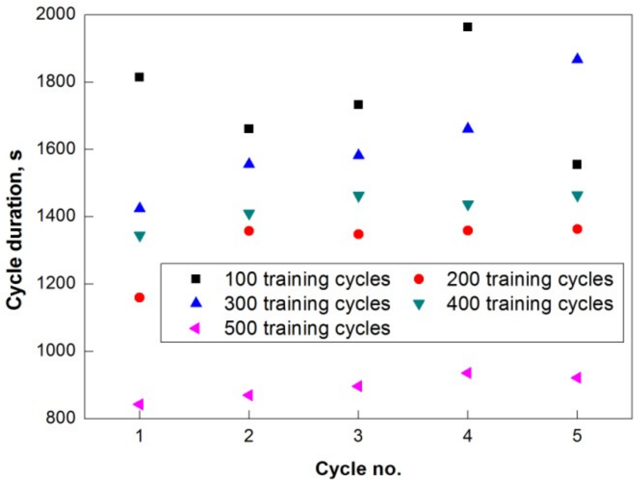

Fig. 6 Summary of cycle durations for five consecutive TWSME cycles performed by differently trained CuZnAl actuators

Two tendencies are noticeable, for cycle duration evolution: (i) to slightly increase during thermal cycling and (ii) to markedly decrease with the number of training cycle. Thus, from the 1st to the 5th thermal cycle, the duration increased from 1160 to 1363 s, for the actoators trained for 200 cycles and from 843 to 922 s, for the actuators trained for 500 cycles. Conversely, excepting for the actuators trained for 200 cycles, the durations of the other differently trained actuators experienced an obvious decreasing tendency. Accordingly, the decreasing order of the average cycle durations was: 1745 s, after 100 training cycles; 1618 s, after 300 training cycles; 1424 s, after 400 training cycles and finally 894 s, after 500 cycles [19].

3.2 TWSME functioning of CuZnAl electrical actuators

The variations with temperature of the span (S) and the height (H) of one of the composite arms of the micro-actuator, described in previous section, were determined by cinematographic analysis, during an electrical actuation heating-cooling cycle. Span and height variations, without load and with three applied loads, are illustrated in Fig.7.

It is obvious that the spans tend to increase with temperature and with applied load, while the heights experience an opposite tendency: to decrease with temperature and applied load. At the end of the heating cooling cycle, spans values are always larger than in initial state, in Fig.7(a). When comparing initial and final height values, at the beginning and the end of the heating-cooling cycles, respectively, Fig.7(b) shows that final values are lower than initial one, in the case of load application. Nevertheless, in the absence of applied load, the final height value is larger than the initial one. This response suggests that the bias force, developed by the polysiloxane matrix, was stronger than the shape recovery associated with reverse martensitic transformation [33].

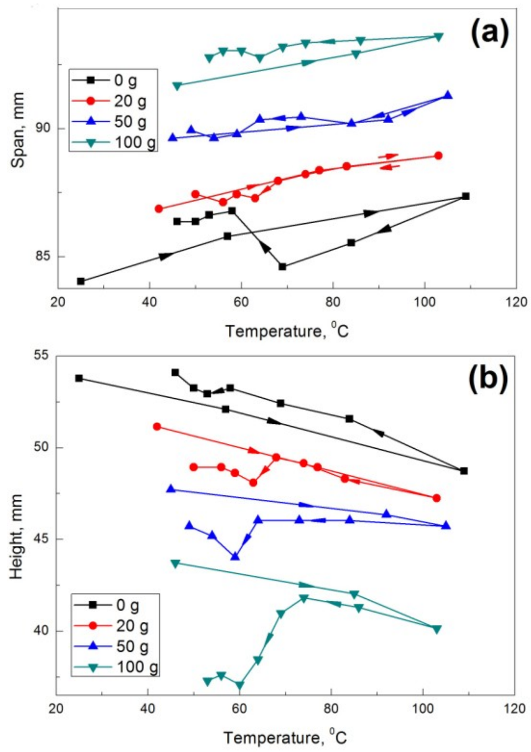

Fig. 7. Dimensional changes of the geometry of one composite arm of the micro-actuator, for different applied loads, during electrically actuated heating-cooling cycles: (a) span variations; (b) height variations

3.3 Free-recovery SME of PM-MA FeMnSiCrNi pipe-coupling rings

After ten deformation-heating-cooling cycles, PM-MA FeMnSiCrNi pipe-coupling rings are considered as fully trained, since this thermomechanical treatment is effective in improving SME magnitude [34]. In the specific case of o trained pipe-coupling, manufactured from PM-50 %MA'd FeMnSiCrNi, the variations of diameter and free-end displacement were determined by cinematographic analysis, as illustrated in Fig.8.

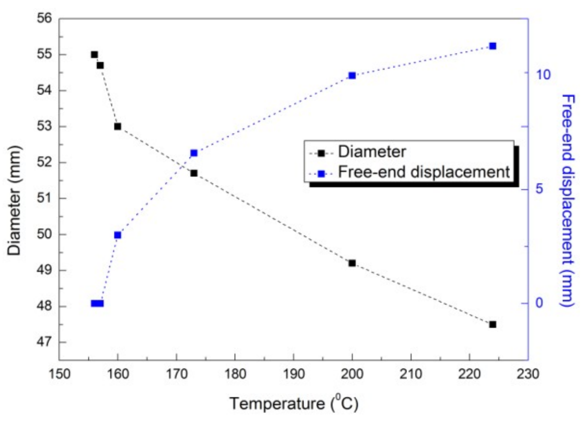

Fig. 8. Dimensional changes of the geometry of trained PM-50 % MA'd FeMnSiCrNi pipe-couplings during free-recovery heating to 230^{0}C.

Considering that the coupling was previously expanded at room temperature, it is expectable the free-recovery SME would cause diameter decrease, so as to recover its initial reduced value. In the present case, the diameter decreased from 55 mm, at 156^{0}C, to 47.5 mm, at 224^{0}C. In the same time the displacement of one of the coupling's free ends was registered with a magnitude of 11.3 mm, for the same temperature increase.

3.4 Superelastic-like and constrained-recovery responses of HS-HPT'd FeMnSiCr modules

HS-HPT modules were machined, so as to correct eventual processing non-uniformities caused by severe plastic deformation, before being subjected to dry and lubricated compression tests, respectively, performed between flat surfaces. The variations of compression load as a function of displacement (stroke) are illustrated, in the two cases, in Fig. 9. In both cases, the presence of horizontal or almost horizontal load (force) plateaus is noticeable, both during loading and unloading, thus justifying the attribute of "superelastic-like" response of force-displacement variations [35].

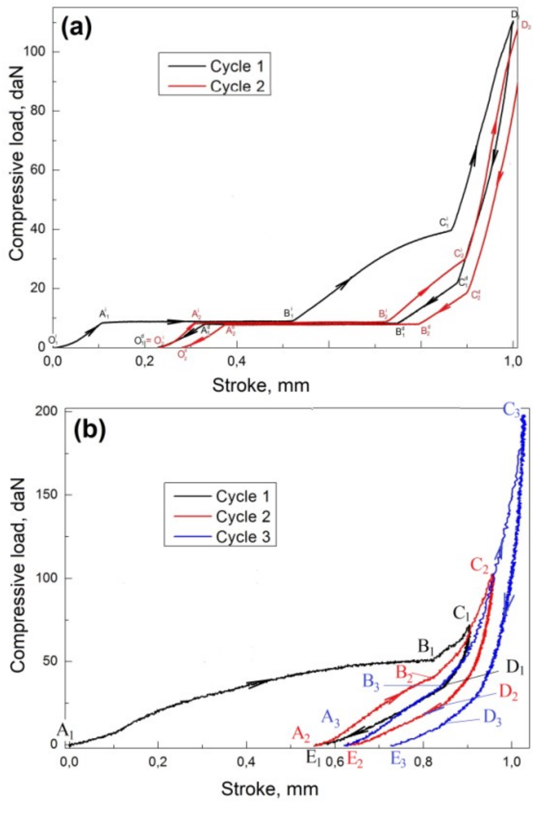

Fig. 9. Force-deformation "superelastic-like" responses of HS-HPT modules subjected to compression loading-unloading tests, between flat surfaces: (a) without lubrication; (b) with lubrication

The force (load) plateaus can be associated with the presence of the hardness gradient, especially in the case of dry compression response, illustrated in Fig.9(a). At the beginning of dry compression, $0A_i$ corresponds to the elastic deformation of the zone close to the small diameter of the module. On the portion A_iB_i the gradual elastic bending of cone's generator occurred and on B_iC_i the module became flattened, with a strong plastic component. Further deformation caused the occurrence of hydrostatic compression on C_iD_i. The same portions occur during unloading, being reproducible in the second cycle.

During lubricated compression, the force-deformation response has a typical two-slope shape, comprising: (i) an initial low-slope region, corresponding to module flattening and (ii) a final high-slope region corresponding to material compression. Because the module was allowed to slip, with regards to the flat compression surface, no gradual deformation occurred, as in the case of dry compression test. During lubricated compression cycling, load variation experienced the following tendencies: (i) initial slow increase during module flattening, suggesting cross-section rotation, as in the case of disk springs; (ii) final fast increase during hydrostatic compression and (iii) obvious pseudoelastic behaviour (additional spring-back, during unloading). Therefore, in both cases a superelastic-like force-deformation response, during compression, was developed by the HS-HPT modules.

In order to emphasize the behaviour of HS-HPT modules during constrained recovery test, the evolution of recovery force was illustrated in Fig.10.

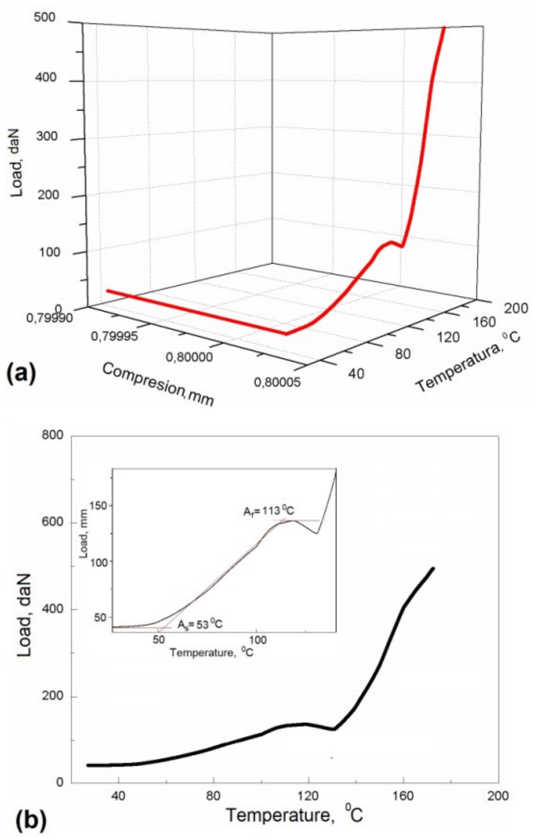

Fig. 10. Force (load) variation during constrained recovery tests: (a) global force variation in the deformation-temperature space; (b) variation of recovery force with temperature and detail of the determination of critical temperatures of reverse martensitic transformation

Fig.10(a) renders the global force evolution during constrained recovery tests. The module was first compressed, with approx. 0.8 mm, at room temperature and then heated in deformed (compressed) state, in order to develop constrained-recovery SME [36]. It is noticeable, form Fig.10(b), that the force levels developed by constrained-recovery SME, during constrained recovery tests were never reached during compression loading-unloading cycles.

By means of the "tangent method" [37] the critical temperatures of martensite reversion to austenite, during heating was determined as $A_s = 53^0$C and $A_f = 113^0$C.

4. Summary and conclusions

- An experimental CuZnAl SMA was developed to manufacture thermal and electrical actuators, able to produce repetitive reversible strokes.
- FeMnSiCrNi PM SMAs were produced with 50 MA'd powders, and pipe couplings were manufactured, which developed free-recovery SME.
- By HS-HPT, multifunctional modules were manufactured, from FeMnSiCr SMAs, being able to develop both superelastic-like and constrained-recovery responses.

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