J. Micromech. Microeng. 1 (1991) 34–41. Printed in the UK

Vacuum-deposited TiNi shape memory film: characterization and applications in microdevices

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Received 10 October 1990, accepted for publication 18 November 1990

Abstract. Thin-film nickel-titanium shape memory alloy has been vacuum sputter deposited, characterized by crystallographic, electrical, and mechanical tests, and incorporated as an actuator in miniature devices. The composition and heat treatment of the film are critical as contamination by oxygen and other species affects the transition temperature. A variety of substrates have been utilized, with good adhesion. Shape memory behavior comparable to that of bulk TiNi has been observed in free-standing film. The work output per unit volume of TiNi is much greater than can be achieved with electrostatic or piezoactuators. Actuators in the few-micrometer size domain are feasible and have desirable characteristics for electrical and optical activation. Anticipated applications include miniature valves, bistable optical memory elements, and microactuators for silicon microelectromechanical devices.

1. Introduction

In April 1988 this research was commenced with the aim of showing that titanium–nickel film can be made by vacuum sputter deposition and that this film can be used to actuate very minute mechanical devices. Shape memory alloy (SMA) film with a transition temperature somewhat below ambient temperature was successfully demonstrated in September–October of the same year. Successively improved transition temperature, mechanical properties, and adhesion to substrates have been accomplished in the interim, and research is now focussed on application to millimeter and smaller actuation devices. This paper is a progress report on our research.

2. Vacuum deposition of shape memory film

Films of titanium–nickel were deposited in an NRC 3110 vacuum system equipped with a single four-inch sputtering cathode. A six-inch diffusion pump, backed by a conventional roughing mechanical pump, with ion gage and thermocouple gage instrumentation, evacuated an aluminum chamber of about 160 liters capacity. A liquid nitrogen trap is used to remove water vapor, yielding system pressures below 10^{-6} Torr. A range of argon pressures, substrate temperatures, and substrate distances have been explored.

Among the early difficulties to overcome was oxygen contamination. One per cent of oxygen contamination in TiNi is known to lower the transition temperature by 100 °C [1]. Analytical methods for measuring composition of thin film are barely able to detect one-tenth of one per cent oxygen, nickel, or titanium, so at times it was necessary to improvise appropriate solutions.

First success was with a mildly contaminated sample which showed a strong shape recovery below 0 °C. This sample displayed very good mechanical properties despite its low transition temperature, and convinced us of the potential utility of shape memory film. Films have now been deposited up to 20 μm in thickness, with the phase transition to and from martensite entirely above ambient temperature. These films show good shape memory qualities, and are usable in devices.

Film has been deposited onto Si, GaAs, CdS, CdSe and other substrates. A substrate heater capable of achieving temperatures up to 500 °C has been used to deposit films with crystal structure and to study deposition of films in tension and compression. The films, a few micrometer thick, are characterized by crystallography, resistivity, stress–strain analysis, and differential scanning calorimetry. The objective is to learn methods of achieving adhesion to substrates, tensile strength and toughness, appropriate transition temperatures, patterning by selective etching, and other techniques of importance in using these films to create devices.

3. Characterization of shape memory film

When deposited at ambient temperature, TiNi films are amorphous. Having no crystal structure, these films have no phase change and hence no shape memory. Heating to

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(a)

(b)

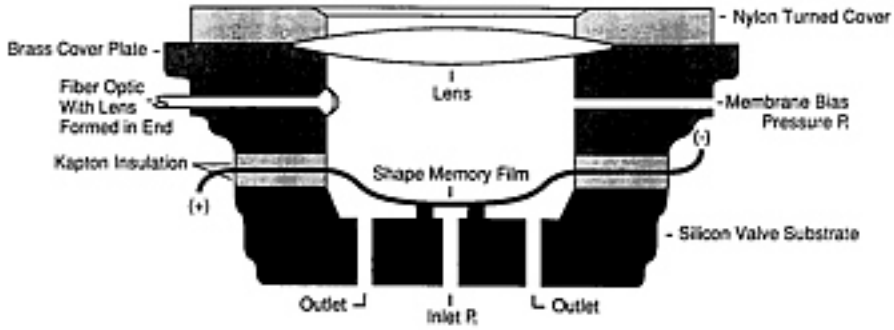

Figure 5. The valve design. The operating prototype has been cycled more than two million times.

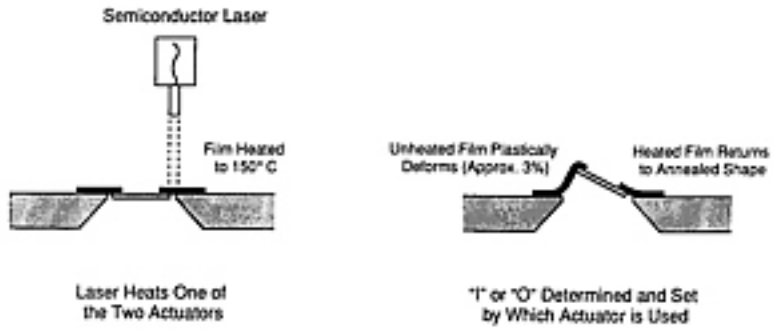

Figure 6. The mirror actuator concept

metal–semiconductor junction. In collaboration with Professor Arthur Ellis and Kathleen Collen at the University of Wisconsin–Madison, we are studying whether the phase change in a film may be detected as a shift in the Fermi energy of the electrons in the semiconductor surface. By proper derivitization it should be possible to attach ion-selective coatings to the TiNi thin film. Under certain conditions, it is expected that an adsorbed layer will invoke the phase change in TiNi via chemical potentials, and that these will be referred to the Fermi levels in the semiconductor, thereby creating a new type of electronic chemical sensor.

These examples illustrate what we believe are interesting future uses of SMA in thin-film form, and the type of devices that have become the focus of our small group of researchers.

5. Anticipated applications: the future of microactuators

The advent of micromachines will undoubtedly have a social and economic impact on society, because they will alter the way people work. From a historical perspective, one now can see that such devices as wrist watches, telephones, electric motors, and personal computers have this in common: they became available before they were perceived as needed. Within relatively short periods of time, each moved from being a novelty to being a necessity because they altered the way people worked and lived. As people continue to explore space, oceans, the work place, and potentially hazardous environments, the need for devices that monitor and/or affect their environment will increase. Portable gas chromatographs will revolutionize the way industrial chemistry is done. Miniature medical appliances to determine blood type quickly or control the effects of heart disease and diabetes will become commonplace. All of these devices will require microactuators.

Acknowledgments

This work has been supported largely through Small Business Innovation Research grants and contracts with the National Aeronautics and Space Administration, the National Institutes of Health, and the National Science Foundation.

This research was done in collaboration with the University of California–Berkeley Materials Science Department, Lawrence Berkeley Laboratory, the Chemistry Department of the University of Wisconsin–Madison, Stevens Institute of Technology, and Stanford University.

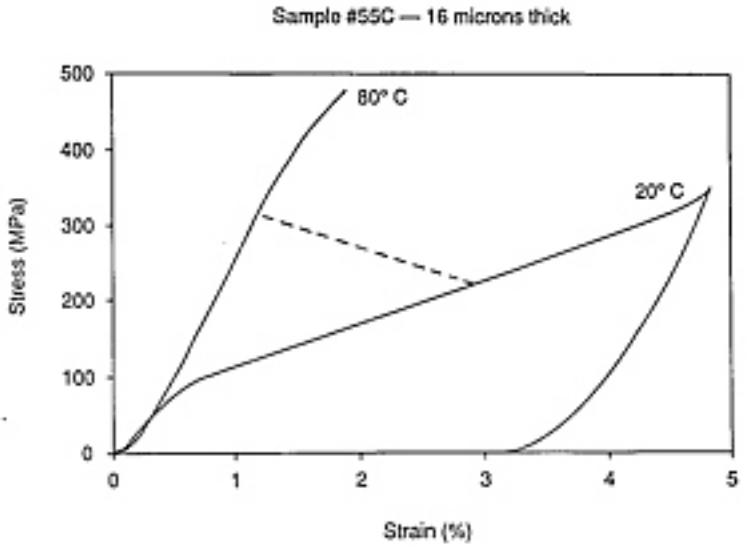

Figure 4. Stress–strain curves for TiNi film. The sloping broken line indicates a load line for a spring force resisting the actuator, showing 2% repeatable strain recovery.

Table 1. A comparison of SMA with piezoelectric, electrostatic, and bimetal actuators. (Source: Sean Cahill, Technekron Sensor Development Corporation.)

Principle	Maximum work energy density ($J\,cm^{-3}$)	Drive conditions/ biocompatibility	Scalability (shrinkability)	Power/weight
DC magnet motor	0.9	$B = 1.5\,T$ Yes	Poor	Low
Micro-electrostatic	0.4	$E = 300\,V\,\mu m^{-1}$ No	Good	High
Piezoelectric (PVDF)	4.8×10^{-4}	$E = 30\,V\,\mu m^{-1}$ No	Good	High
Shape-memory alloy (TiNi)	10.4	$P = 1.4\,W\,mm^{-3}$ Yes	Good	High

machines the size of microelectronic circuits to do chemical sampling and analysis, to sort biological samples, and for a host of tasks that we imagine others will invent as soon as the means exist. There are not many solutions available: electric motors, solenoids, electrostatics, piezoelectric stacks, solid–liquid phase changes, and bimetallic strips. In design of devices below a millimeter in size it becomes difficult to contain strong magnetic fields in devices such as solenoids. Electrostatic actuators require high fields which are incompatible with electronic microcircuits which we envision being built on the same chip with micromechanical machines.

As things become smaller, some variables scale linearly and others obey a power law. Heat transfer is one that is very non-linear [4]. A wire half a millimeter in diameter cools so slowly in still air that it is not practical to cycle it more than once every few seconds. But a membrane of TiNi stretched over an orifice to form a valve can be cycled at a rate of twenty Hertz. Figure 5 illustrates a prototype valve that was constructed in our laboratory and was cycled more than two million times. The size of this valve is appropriate for a miniaturized gas chromatograph [5].

A second device under study is a microactuator for a mirror to be used as a refreshable optical storage device, shown conceptually in figure 6. This is intended to be a two-state device: a microscopic mirror that tilts right or left depending upon which actuator has been heated by a laser pulse. The state of tilt is discerned with a laser beam of less intensity which reflects from the mirror. The advantages foreseen stem from the fact that such a system is completely optical, so it may be integrated with optical computers.

Other microactuators are being considered for prototyping. Because of the high force attainable, microswitches and circuit breakers are feasible. These will be software resettable components that have low insertion losses and fit on standard integrated circuit frames.

A completely different property of SMA is being investigated in what we call a variable Schottky barrier

line four-point contact arrangement was mounted on an aluminum block which was enclosed in a dewar. A resistance heater was used to raise the temperature, and chilling was accomplished by circulating cold air through the aluminum block. A constant-current circuit maintained a fixed current through the outer contacts to the sample while the temperature was varied. Voltage across the inner pair of contacts was recorded using an Analog Devices digital-to-analog circuit in an IBM PCXT computer.

Resistivity is used as a means of calibrating compositional changes in samples from one run to the next. See figure 3 which presents resistivity and DSC data for a typical sample. As the temperature decreases through the B2-to-martensite phase transition, a 20 to 30% increase in resistance is observed, which disappears below the martensite finish temperature. This peak is attributed to formation of a rhombohedral or R-phase intermediate between the B2 and martensite states. This hysteresis is not repeated during the martensite-to-B2 (heating) transition.

The cross-section of the film used was not measured accurately, and hence the resistivity was not precisely determined. Calculations based on resistances from the four-point measurement range from 60 to 100 $\mu\Omega$ cm, which is compatible with known properties of bulk TiNi [2]. Measurements on amorphous film yield resistivity values about twice as great as in the crystalline form.

To determine the work output that may be obtained with TiNi film we have measured the stress–strain characteristics of free-standing film. The film is first deposited on a glass or silicon substrate to a thickness of 5 to 15 μm, released from the substrate, and annealed in a sealed vacuum ampoule at an oven temperature above 500 °C for times varying from five minutes to several hours. Strips of film are cut from these samples and mounted on a stress–strain apparatus—see figure 4. Stress–strain isotherms have been measured with residual strains of up to 4%. These isotherms may be compared with published isotherms for bulk wire samples [3]. From these measurements the work output is calculated at about one joule per gram.

4. Devices made with TiNi film

Table 1 compares TiNi film with electrostatic, piezoelectric, and bimetallic actuators. Two distinct advantages emerge from this comparison: the energy output per unit volume is high compared with that for other means of actuation, and the voltage requirements are compatible with TTL. As our goal is to create hybrid microelectromechanical systems, it is important to use actuators that do not require high voltages.

As can be seen, there are orders of magnitude of work output to be gained, but the trade-offs make shape memory alloy actuators impractical for some uses. The phase change is temperature driven, meaning that the efficiency of energy conversion is subject to the second law of thermodynamics. In a nutshell this means that fifty joules of heat energy input are required to obtain a joule of mechanical energy output. This heat must be removed before the next cycle can start, which means that the system is inefficient and the cycle rate may be slowed down by the achievable rate of heat transfer. However, in very small devices, heat transfer is very rapid, and, for low-duty-cycle machines, compactness may be more relevant than thermodynamic efficiency.

Despite these limitations, in micromachines thin-film SMA has great potential advantages over alternative methods of actuation. Consider the problem of generating motion on a very small scale. We want to make

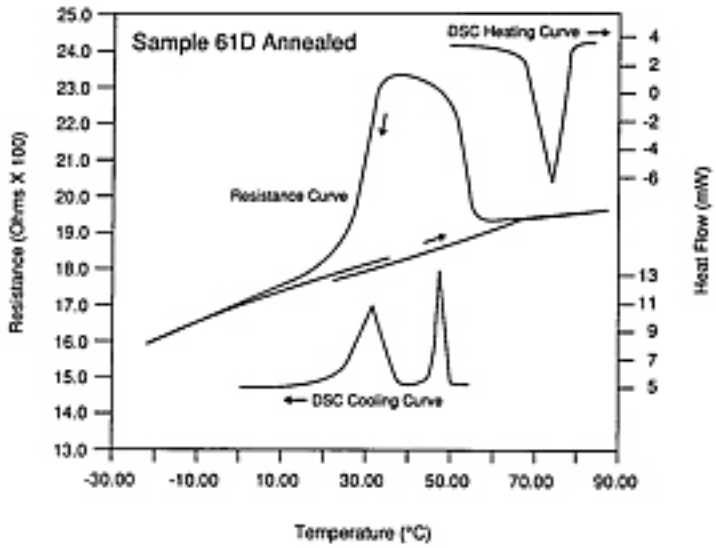

Figure 3. The resistivity curve for TiNi film showing the dependence on temperature. R-phase transformation is believed to account for the hysteresis. For comparison, DSC curves are laid alongside the resistivity curves.

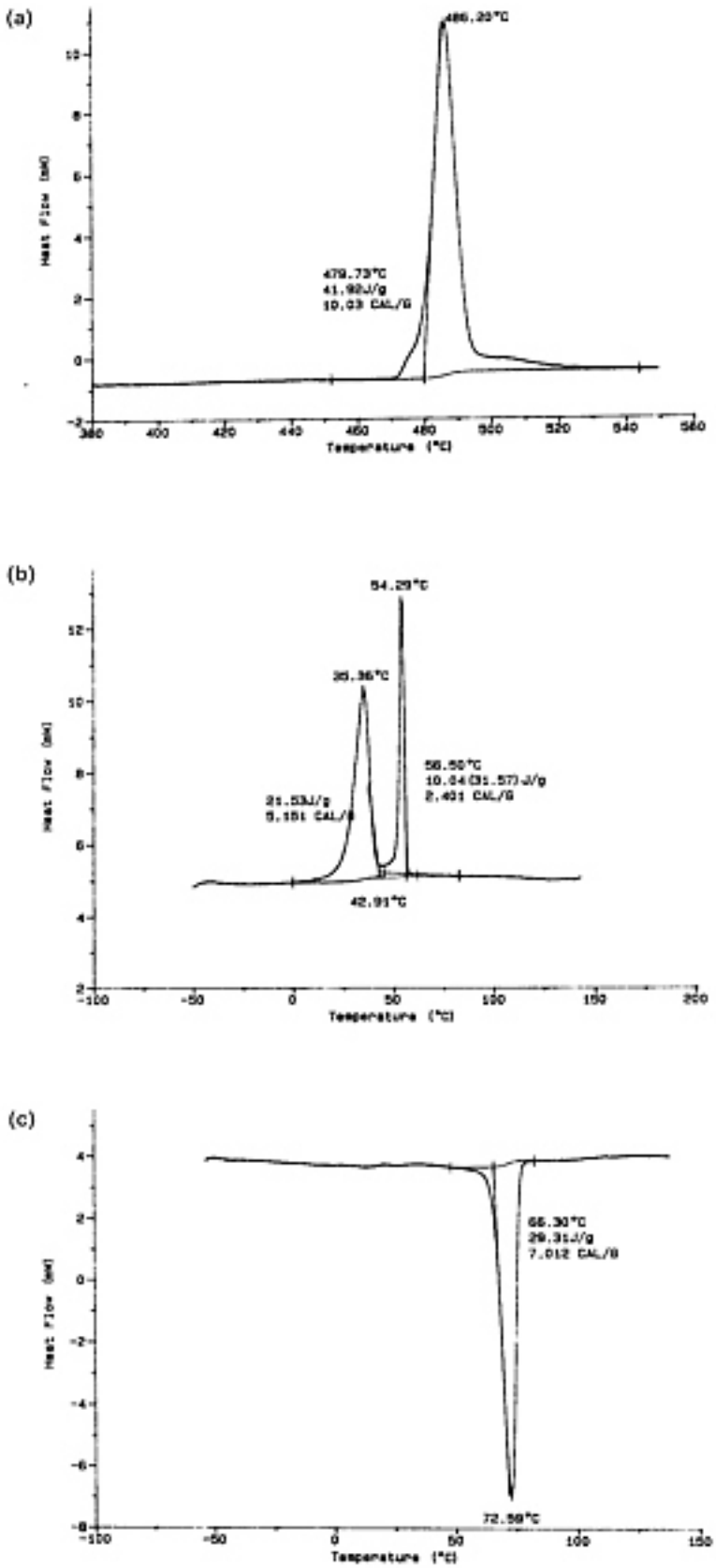

Figure 2. Differential scanning calorimeter measurements: (*a*) temperature of crystallization (500 °C) and (*b*) B2–martensite transformation between 0 and 60 °C, and (*c*) martensite–B2 transformation between 65 and 75 °C.

(c)

Figure 1. (*a*) A transmission electron microscope photograph of B2 crystals forming in amorphous TiNi film. The thickness varies from zero at the edge of the etched hole to a few thousand ångströms. The rate of crystallization depends upon the thickness, i.e. upon the number of nucleation sites rather than upon surface energies. (*b*) Fully crystallized B2 grains in TiNi film annealed at 500 °C for about 30 min in vacuum. Grains are 1 to 3 μm in diameter. Precipitates can form at grain boundaries and within the volume of each grain, an indication of instabilities in the phase diagram of TiNi near 50–50 at.% as well as the possible influence of oxygen contamination. These precipitates have been identified as Ti_2Ni_4 and other metastable phases such as $Ti_{11}Ni_{14}$. (*c*) Martensite crystals, the low-temperature phase of TiNi. Striations indicate the twinning structure which accounts for the large plastic deformations tolerated by this phase. In thin films the number of variants that can grow is expected to be limited. Some grains in this photograph seem to have only two pairs of twinned variants.

500 °C causes the film to crystallize. This manner of forming shape memory crystalline material is new: bulk material exists only in the crystalline (martensite–austenite) forms. Amorphous TiNi gives materials scientists a new perspective from which to study shape memory phenomena. Figure 1 shows transmission electron microscope photographs made by Warren J Moberly of the Stevens Institute of Technology using equipment at the Lawrence Berkeley Laboratory, and by Mitchell Berkson at the University of California–Berkeley Materials Sciences Department.

When these TEM micrographs were taken, images were also recorded on video tape. The video shows how the crystals originate, grow, and interact with each other, in real time. In the micrograph figure 1(*a*), one can see the edge of the film which was prepared by chemical jet polishing. It is apparent that crystallization progresses more rapidly in the thicker part of the film, indicating that the rate is governed by the density of nucleation sites rather than by surface energy phenomena. Crystals seem to grow from nuclei throughout the volume, from which we can anticipate that the B2 structure and therefore the shape memory effect exists for all film thicknesses, even down to sub-micrometer dimensions. Grains in these photographs are about a micrometer in size, which is much smaller than the grain size known to exist in bulk material solidified from melt.

Differential scanning calorimetry was used to determine crystallization and transformation conditions. Figure 2(*a*) shows that crystallization takes place at near 500 °C. Figure 2(*b*) shows that the B2-to-martensite transformation occurs during cooling at slightly above room temperature, and figure 2(*c*) shows the reverse transformation during heating.

An apparatus was constructed to measure the resistivity of the film as a function of temperature. An in-

References

[1] Funakubo H (ed) 1984 *Shape Memory Alloys, Precision Machinery and Robotics* vol 1 (translated from the Japanese by J B Kennedy) (New York: Gordon and Breach) p 99

[2] Jackson C M, Wagner H J and Wasilewski R J 1972 55-Nitinol-The Alloy With a Memory: its Physical Metallurgy, Properties, and Applications *NASA Technical Brief* NASA-SP5110 p 23

[3] Cory J S 1979 Thermomechanical behavior of NITINOL Johnson A D 1979 Training phenomena in NITINOL *Proc. NITINOL Heat Engine Conf. (Silver Spring, MD, 1978)* ed D M Goldstein and L J McNamara (Silver Spring, MD: Naval Surface Weapons Center) pp 7-1 and 10-1

[4] Manz A, Graber N and Widmer HM 1990 Miniaturized total chemical analysis systems: a novel concept for chemical sensing *Sensors Actuators* B 1 244

[5] Busch J D and Johnson A D 1990 Prototype micro-value actuator *Proc. IEEE Conf. on Micro Electro Mechanical Systems (Napa Valley, CA 1990)* (Piscataway, NJ: IEEE)