

## WHERE ARE WE AT WITH SHAPE-MEMORY ALLOYS IN THIS ‘HIGH-TECH’ WORLD?

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**ABSTRACT:** Some of the basic physics of shape-memory materials is outlined. Shape memory relies on a change in the crystallography of the material via a martensitic transformation. While many alloys show shape-memory properties, only certain materials have ‘made it’ to technological applications. The most notable of these is *Nitinol*, the commercial name for a nickel–titanium alloy which was discovered in the US Navy Laboratories almost by accident. The most important current and future applications for *Nitinol* are, and will continue to be, as various medical devices. The material is most favourable for medical applications, firstly, because it exhibits shape-memory behaviour at very close to body temperature (37°C) and, perhaps equally importantly, only an extremely small percentage of human beings have any allergic reaction to either nickel or titanium. Not so important are magnetic shape-memory materials for which, particularly the material  $\text{Ni}_2\text{MnGa}$ , there are increasing numbers of applications requiring the shape-memory behaviour to be controlled by an applied magnetic field. The properties of some shape-memory materials relevant to current applications are summarised and, consistent with the theme of sustainability, some comment is made on the likely future of shape-memory materials in the market place.

**Keywords:** shape-memory, martensitic transformation, twinning, Nitinol, magnetic shape-memory,  $\text{Ni}_2\text{MnGa}$

When lecturing throughout my academic career, I always found that a demonstration was of great assistance in maintaining the students’ attention. So I thought for this Humboldt presentation, I should continue this tradition. Using two pieces of metal, each about 120 mm long, 10 mm wide and 2 mm thick — with the first being a single crystal of a copper–aluminium–nickel (Cu–Al–Ni) alloy discovered by my PhD supervisor, Professor Bill Rachinger, and the second being a piece of pure copper — the property of shape memory can be clearly demonstrated. When both pieces of metal are bent to an approximate U-shape and then submerged in warm water, the Cu–Al–Ni piece returns to its original straight shape while the pure copper remains bent. At the time of Rachinger’s discovery of this property of Cu–Al–Ni, he was a research scientist with the Department of Defence at the then Aeronautical Research Laboratories in Melbourne and he had been given the task to produce a material which could be used as an accurate and reliable measure of strain. The discovery was reported in a paper entitled ‘A “super-elastic” single crystal calibration bar’, in the *British Journal of Applied Physics* (Rachinger 1958). But what was more important, irrespective of how many times Rachinger stressed and heated his single crystal sample of Cu–Al–Ni, he produced exactly the same strain result, totally different of course, from the piece of pure copper. He had inadvertently discovered that his single crystal underwent a martensitic transformation on application of the applied stress.

### MARTENSITIC TRANSFORMATION

A martensitic transformation is a change in crystal structure for a material, that proceeds without any diffusion of atoms in the structure. The name ‘martensite’ is attributed to the German metallurgist, Adolf Martens, who, in 1878, used the term *Spiegeleisen* (or ‘fried eggs’) to describe what he observed in an optical microscope for a polished sample of a low-carbon steel which had been quenched, as illustrated in Figure 1<sup>1</sup>. But in a paper published in France, in 1898, Floris Osmond used the term ‘martensite’ to describe the same microstructural features in a polished steel sample<sup>1</sup> and this term has remained (Portella 2006).

Martensite is formed when a sample of iron–carbon is quenched from high temperature where the material is in its state called ‘austenite’ and it is the extent of this phase change from austenite to martensite, which determines the strength of steel. In the case of steel, the change of crystal structure in going from austenite to martensite is from cubic to tetragonal. There are now many materials which exhibit a similar ‘martensitic transformation’ and Bill Rachinger’s single crystal of Cu–Al–Ni is one such material.

It is important to observe that for any martensitic transformation which is induced in a particular alloy by

<sup>1</sup> Historical facts and Figure 1, concerning martensite, are taken from a presentation file delivered at ESOMAT, 2006 by P.D. Portella entitled ‘Adolf Martens and his contributions to materials engineering’ accessed on [phase-trans.msm.cam.ac.uk/2002/Martens.pdf](http://phase-trans.msm.cam.ac.uk/2002/Martens.pdf) on 6th January, 2023



Figure 1: Optical micrograph of a section of a mould made of gray iron (Martens 1878) copied from Portella (2006).

lowering the temperature, the transformation does not occur instantaneously, but rather we would observe a ‘martensite start temperature’,  $M_s$ , and then a ‘martensite finish temperature’,  $M_f$ . Upon increasing the temperature, the austenite phase will be recovered and we can observe an ‘austenite start temperature’,  $A_s$ , followed by an ‘austenite finish temperature’,  $A_f$ . As illustrated schematically in Figure 2 there will normally be some overlap between these two temperature ranges. There is one other temperature to be appreciated for any martensitic transformation and particularly in relation to the demonstration described above, where the martensitic transformation was induced in the single crystal sample by the application of a stress. For all materials exhibiting this behaviour, there is one other temperature,  $M_d$ , above which it is impossible to induce the martensitic transformation by applying a stress.

**Martensitic Transformation**

“martensite”  $M_f \leftarrow M_s \Leftarrow$  (Cooling)  
 (Heating)  $\Rightarrow A_s \rightarrow A_f$  “austenite”  
 Highest temperature for transformation by stress:  $M_d$

Figure 2: Schematic representation of the relevant critical temperatures for any martensitic transformation. Temperature is increasing from left to right.

Because a martensitic transformation involves a change in crystal structure, there are many ways to observe the transformation. The oldest was via optical microscopy of a polished surface, as is illustrated schematically in Figure 3 (upper image) and for an actual martensitic transformation in Figure 3 (lower image). But one fairly simple way is to measure the electrical resistivity for a sample of the material. Figure 4 shows a couple of typical results for two

alloys which exhibit a martensitic transformation — gold-cadmium and iron-nickel — from which we can observe the first four of these temperatures. But the other point to note is the significant difference in the extent of reversibility for these two materials. Indeed, it is this degree of reversibility which is a requirement for the property of shape memory, as a consequence of a martensitic transformation.

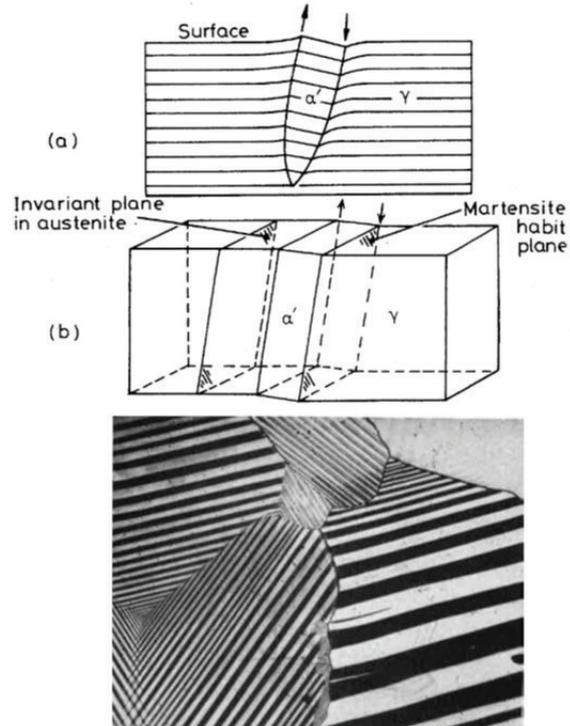


Figure 3: (Upper) — Schematic representation of the tilting observed in optical microscopy on a polished surface for a sample undergoing a martensitic transformation. (Lower) — Optical micrograph of an In-20at%Ti alloy showing the tilt bands across adjacent grains in a polished surface as a result of a martensitic transformation as the sample would have been cooled through the  $M_s$  to  $M_f$  temperature range, (x50). (after Bowles et al. 1950)

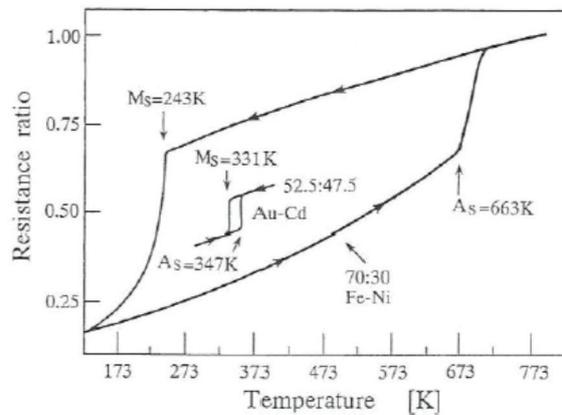


Figure 4: Electrical resistance changes during cooling and heating gold-cadmium and iron-nickel alloys, illustrating the signatures for the  $M_s$  and  $A_s$  temperatures and the temperature hysteresis accompanying the martensitic transformation on cooling and the reverse transformation on heating. (after Kaufman & Cohen 1958)

## THE PHENOMOLOGICAL THEORY OF MARTENSITIC TRANSFORMATIONS

Quite independently, two Australian scientists, Professor John Bowles and Dr Jock Mackenzie, and three American scientists, Monroe Wechsler, David Lieberman and Thomas Read, produced what we now call the phenomenological theory for the martensitic transformation, which is based on the observed crystal lattice correspondence between the parent phase (or austenite) and the martensite phase, including the habit plane, the orientation relationship between the austenite (or parent) phase and the martensite as well as the shape strain, and the crystal lattice vector to transform from the one to the other (Bowles & McKenzie 1954; McKenzie & Bowles 1954; Wechsler et al. 1953). The theory can be advanced for any material from a knowledge of: (i) the lattice parameters of the martensite and parent phases; (ii) the lattice correspondence; and (iii) the lattice invariant shear.

It is interesting to observe this crystallographic relationship for the Cu–Al–Ni crystal mentioned in the introduction, which I have reproduced from a publication by Professor Kazuhiro Otsuka and his long-term colleague, Professor Kenichi Shimizu (Figure 5) (Otsuka & Shimizu 1974).

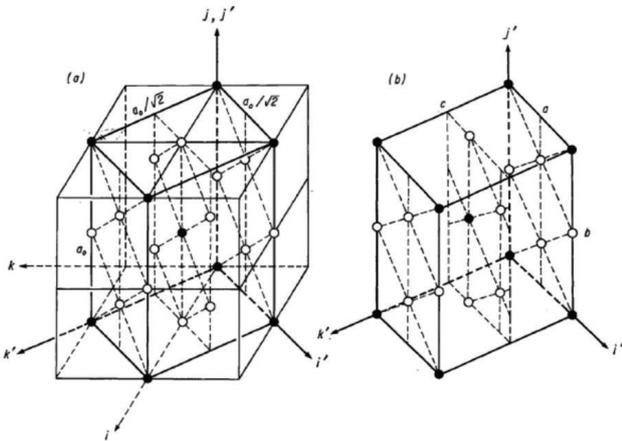


Figure 5: Lattice correspondence in the  $\beta_1$  parent phase matrix (a) to the  $\gamma'$  martensite (b) for Cu-14.2wt% Al-4.3wt% Ni alloy. Closed circles: Al atoms, open circles: Cu or Ni atoms. (after Otsuka & Shimizu 1974)

### Shape memory

If we now consider the details of the demonstration which I have mentioned, and look at the stress vs strain result followed by the heating of the sample, we would reproduce the result shown schematically in Figure 6. When the Cu–Al–Ni sample was unloaded, there was some relaxation of the strain but once the sample was plunged into warm water, such that the initial shape of the sample was recovered, we can see from this figure that when the  $A_s$  temperature was reached, the reverse transformation commenced and

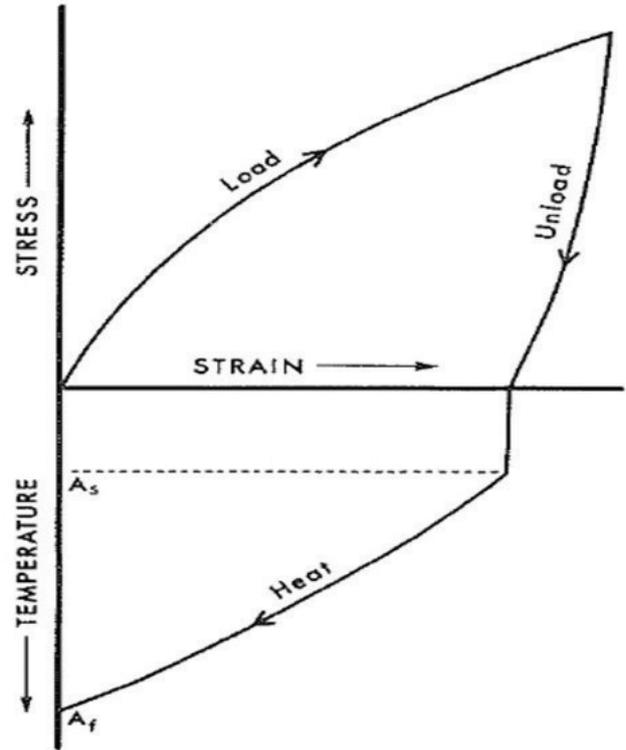


Figure 6: Representation of the result of the demonstration described in the introduction showing the initial stress vs strain curves for the Cu–Al–Ni single crystal sample upon loading and unloading and then submerged into warm water. When the sample reached the  $A_s$  temperature, the reverse transformation commenced and was complete at  $A_f$ , at which point the sample had regained its initial shape. (after Kennon & Dunne 1981)

was complete at  $A_f$ , when the strain was reduced to zero, or in other words, the original sample shape had been remembered.

The question is, what is the difference between our copper–aluminium–nickel single crystal and the copper sample of similar size and shape? What has occurred microstructurally in the single crystal, as has been beautifully demonstrated by the work of Professor Hiro Otsuka (Otsuka 1971), is that when the sample is bent, twins are formed and subsequently, it is the behaviour of these twins, as Otsuka showed through electron microscopy, that explains the property of shape memory (Figure 7). The fact that the original shape can be recovered is one property which results in certain applications of shape-memory materials, which I shall discuss later.

## NITINOL

There are now many materials that exhibit a martensitic transformation and shape memory. But one which has led to the most applications is an alloy of nickel and titanium at about 50/50 concentration. Back in the early 1960s, Ni–Ti was thought to be a useful material on account of its strength and corrosion resistance. The story goes that

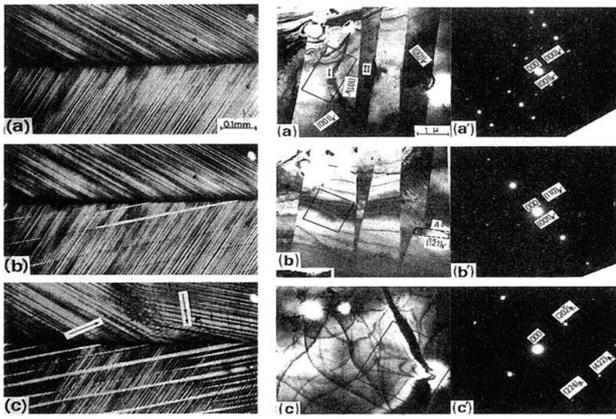


Figure 7: (Left) — Optical micrographs showing structural changes in a Cu–Al–Ni alloy caused by a bending stress: (a) is the undeformed sample; (b) after slight bending showing new twins forming in the lower variant; (c) upon further bending, the same twins increase in width and the number increases while new twins form in the upper variant.

(Right) — Electron microscopy showing the structural change in  $\gamma'$  martensite following deformation and subsequent heating: (a) undeformed microstructure; (b) twin I in (a) has grown at the expense of twin II and a new twin appears in A; (c) after heating to 130°C, the reverse transformation is complete. (after Otsuka 1971).

a young metallurgist, William Buehler, who was working at the US Naval Laboratories, was assigned the task to investigate the fatigue properties of this alloy. He would have done this on a mechanical testing machine where the sample was put into cyclic loading. To Buehler's initial disappointment, after thousands of loading cycles there was no evidence for the fatigue of his sample. Indeed, Buehler had inadvertently discovered the most important shape-memory material that we have today, which has the commercial name, Nitinol (or **Nickel Titanium Naval Ordinance Laboratory**) (Buehler et al. 1963).

#### Progress with Nitinol

Following William Buehler's accidental discovery, it was very soon realised that Nitinol was a most important alloy for the future applications of shape-memory materials. Firstly, its critical temperatures were quite close to human body temperature (37°C). But perhaps more importantly for the many current-day applications, the statistics for rejection of nickel and titanium by the human body is extremely low, so that many of the medical devices that are now made from this alloy, can be reliably used in human beings without biological rejection. Indeed, judging from the medical literature, one must be extremely unlucky to have a resistance to a medical device made from Nitinol.

There are now many biomedical devices made from Nitinol, such as neurological stents, spinal vertebrae spacers, orthodontic wires and bridges, etc. (Duerig et al. 1999). Applications can be classified into four categories, depending on the particular aspect of the behaviour of

the martensitic material on which the functioning of the device relies. **Free recovery** is a category for which the function of the memory material element is to cause motion or a strain. For **constrained recovery**, the memory element cannot change shape with the result that a stress is generated. **Actuator or work production** applications involve motion against a stress and hence work is done by the memory element, while **superelastic or pseudo elastic** applications are isothermal and involve the storage of potential energy.

#### Current excitement in Ni–Ti research

On account of the many applications for Nitinol, there continues to be research on alloys which vary slightly from the original 50/50 composition, either by variation of the alloy composition itself or by studying the properties of third element additions to Ni–Ti. One most interesting aspect of this research is the discovery of a 'strain glass' for alloys slightly richer than 50/50 in nickel content, for which one observes response to a cyclic stress, as shown in Figure 8, in which the frequency dependence of both the

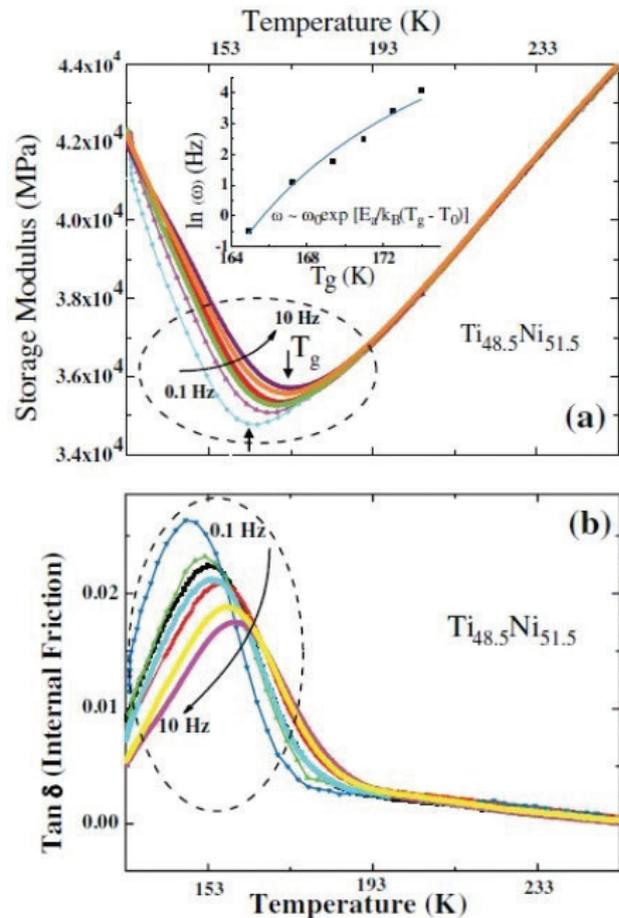


Figure 8: Temperature dependence of the ac storage modulus,  $S(\omega, T)$  (a) and internal friction,  $Q^{-1}(\omega, T)$  (b) for 'non-transforming'  $\text{Ti}_{48.5}\text{Ni}_{51.5}$  at various frequencies (0.1 – 10 Hz). The inset in (a) shows the fit for  $\ln(\omega(\text{Hz}))$  vs Temperature,  $T_g$ , corresponding to the minimum in the storage modulus. (after Sarkar et al. 2005).

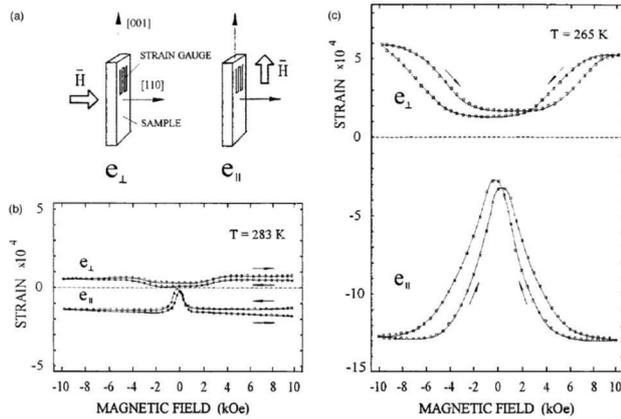


Figure 9: Magnetostriction data for  $\text{Ni}_2\text{MnGa}$  single crystals (after Ullakko et al. 1996). (a): Orientation of the sample, strain gauge and magnetic field for measurements shown in (b) and (c). (b): Strain vs applied field in the parent or austenite phase at 283K. (c): Strain vs applied field at 265K in the martensite phase.

storage modulus and the internal friction is plotted. This behaviour is very similar to what is now well known for ac susceptibility of a magnetic spin glass (Mydosh 1993), which was very popular research in the 1990s, and the ac electric susceptibility of a relaxor ferroelectric (Tan et al. 2000), common research in the early 2000s. It is even reminiscent of the mechanical behaviour of actual glass, as reported in the 1920s (Vogel 1921).

## FERROMAGNETISM AND MARTENSITIC TRANSFORMATIONS

Some shape-memory alloys are ferromagnetic and hence the force required to activate the shape-memory effect can be applied to the materials by a magnetic field. The mechanism here is based on the understanding that the twins which accompany the transformation and are fundamental to the effect will have a magnetic moment. Thus the change in the twin configuration which is fundamental to the shape-memory effect can be induced by the application of a magnetic field. When this field is cyclic, then the shape memory will also be cyclic, thus providing the basis for an actuator.

While in earlier times some iron-based shape-memory alloys such as iron–palladium and iron–platinum were known to exhibit magnetic shape-memory behaviour, the discovery of the alloy nickel–manganese–gallium ( $\text{Ni}_2\text{MnGa}$ ) as reported by Webster et al. (1984), led to a most important industry which utilises this material in many magnetic actuator applications.

### Magnetostriction

The operation of any magnetic actuator relies on the magnitude of the magnetostriction exhibited by the material, or the strain in response to an applied magnetic

field. The magnetostriction data for single crystal,  $\text{Ni}_2\text{MnGa}$  are illustrated in Figure 9, where we see that the strain response at 265K, at which the crystal is in its martensitic condition, is significantly greater than that at 283K.

### Magnetic shape-memory effect

There are two points to appreciate concerning the magnetic shape-memory effect, bearing in mind that both the austenite and martensite phases are ferromagnetic and most likely will exhibit different Curie temperatures. Firstly, the magnetic force, as a consequence of the applied magnetic field, could induce the austenite to martensite transformation. But in the martensitic condition where the crystal is twinned, the magnetic moment for each twin is dependent on its orientation so that the magnetic field will change the two configurations, giving rise to the strain. So for the magnetic field applied cyclically, the strain will be cyclic, which is the basis for an actuator.

### Applications

$\text{Ni}_2\text{MnGa}$  is an example of a material that has evolved from a material of research curiosity, as with its discovery by Webster et al. (1984), to its production as large single crystals for industrial applications, particularly as actuators in the aerospace, automotive and robotics industries.

## CONCLUSION

While there have been many materials discovered which exhibit the property of shape memory as a consequence of a martensitic transformation, only relatively few, for example, Nitinol and  $\text{Ni}_2\text{MnGa}$ , have evolved to the extent that they have a sustainable and viable future in terms of industrial applications. According to a recent review of this field, as was reported in a 2022 publication in the journal *Shape Memory and Superelasticity* (Pelton et al. 2022), the global Nitinol medical devices market was estimated to be of order US\$15 billion in 2018.

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### Conflict of interest

The author declares no conflict of interest.

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