Good Memory?

Iron-based Shape Memory Alloys

By Kate Ireland

Professor Druce Dunne

Professor Druce Dunne is a materials engineer at the University of Wollongong and works as part of the Research Centre for Advanced Materials Processing. His training and interest have always been in the area of steel metallurgy. Dunne completed his PhD on the crystallography of martensitic transformations. Since then he has extended his research into the area of shape memory alloys.

There are two major classifications of shape memory alloys. They are biological and non-biological [Dunne 2000:95]. The focus of this article is on non-biological iron-based shape memory alloys. The shape memory effect occurs in alloys that exhibit a martensitic phase. It is enacted by the transformation from an austenite phase to a martensitic phase. The transformation must be reversible for the shape memory effect to be exhibited [Dunne 2000:96].

If deformation occurs at temperatures below the martensitic start temperature (M_s), then upon heating the alloys return to the pre-deformed state [Polmear:1995, 297].

At the austenitic start temperature (A_s), austenite starts to form on heating [Calka 2001]. At the austenitic finish temperature (A_f) the martensite to austenite transformation is complete [Calka 2001]. The martensite start temperature (M_s) signifies the formation of martensite on cooling and M_f shows the martensite finish temperature where martensite has completely formed on cooling [Calka 2001]. Shape memory alloys exhibit vastly different stress-strain behaviour in comparison to ordinary metals (Figures 1 and 2)

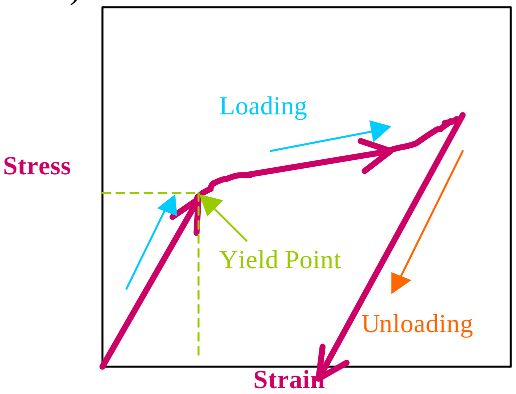

Figure 1. Stress-Strain behaviour of ordinary metal with permanent plastic deformation remaining after unloading (Adapted from A. Calka's MATE 203 Lecture Notes, 2001)

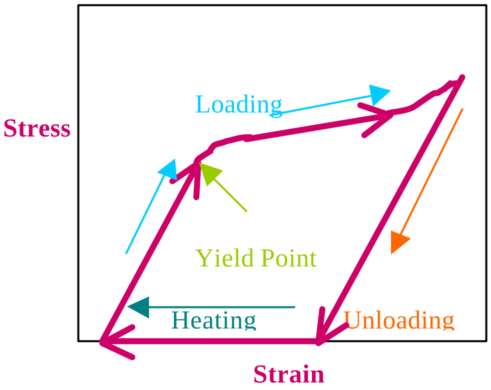

Figure 2. Stress-strain behaviour of shape memory alloy with original shape recoverable on heating (Adapted from A. Calka's MATE 203 Lecture Notes, 2001)

A thermal hysteresis is established during the transformation and is generally less than 50K in magnitude [Dunne 2000:96]. The thermal hysteresis is given by $\Delta T(A_f - M_s)$

[Li, et al 1999:518]. Dunne identifies four types of transformation (Table 1).

Table 1. Properties and applications of shape memory alloys. Also, behavioural mechanisms of transformation from initial shape (S1) to derived shape (S2). (Adapted from D.P. Dunne, "Functional Memory Metals", *Materials Forum*, Vol.24, pp.96-97, 2000, Institute of Materials Engineering Australasia Ltd, Melbourne)

Property	Stimulus	Function	Applications	Behaviour
1. Pseudo-elastic • Rubber-like effect • Super-elastic effect	Force	Energy storage <6.5J/g Elastic recovery <8%	Super springs	S1—[+force]→S2—[-force]→S1 ↑ ↑ stimulus remove stimulus
2. One-way SM	Temperature	Free shape recovery <8% Recovery force <800MPa	Deployable shapes + structures Connectors + couplings	S1—[force]→S2—[heat]→S1 ↑ set
3. Two-way SM	Temperature	Work output <5J/g	Thermal actuators Energy conversion	S1—[force]→S2—[heat]→S1—[cool]→S2 ↑ ↑ ↑ Set memory of initial shape memory of set shape
4. Internal Friction	Vibration	Energy dissipation (SDC*<15%)	Damping	

*SDC – specific damping capacity

The iron-based shape memory alloy applications researched by Druce primarily involve coupling systems for pipes. Currently nitinol couplings are used in some applications to join pipes together. This shape memory alloy is composed of nickel and titanium. The maximum recoverable strain in nitinol is approximately 8% [Brady, et al 1997:37]. Thus, for an iron-based shape memory alloy to effectively replace nitinol, it must consistently exhibit a similar strain recovery.

The nitinol industry is well established. However, use of this alloy is restrictive due to its high cost and is not appropriate for general applications. Thus, the development of an iron-based replacement has the potential to be extremely cost effective. Druce states that "the steel processing industry is well established and very cost effective so if you could make an iron-based shape memory alloy with the same properties as nitinol then you would make a fortune".

Druce claims that the major obstacle for development of an iron-based shape memory alloy is the limited strain recovery and force. He states that "the martensitic transformation occurs with a large temperature hysteresis and so the fundamental focus is on improving reversibility of the transformation. Hence a high recovery strain and force are needed". A limiting factor is that the recovery strain of these alloys is less than 4%, much less than that of nitinol.

Dunne recognises the current need for "costly training schedules to increase the recovery stress and strain". He describes the training process as involving "several cycles of deformation to generate stress-induced martensite at room temperature. The material is heated to revert back to the austenite structure".

Previous applications of iron-based shape memory alloys have been restricted to large diameter pipes that have greater dimensional tolerances to accommodate the small recovery strain. This includes uses in the relatively low pressure oil and gas pipelines [Dunne 2000:98].

Druce cites that "they also need to have high enough strength to have enough force to create a pressure seal". Dunne's research involves trying to strengthen the austenitic parent phase. He recognises that increasing austenitic strength inhibits the formation of irreversible plastic deformation and improves the sealing capacity.

An advantage can be achieved by optimising the effect between the two competing phases: stress-induced martensite and plastic deformation. His research focuses on increasing the stress for dislocation movement as the formation of dislocations is irreversible. Also the stress required for the martensite transformation to occur should be minimised, according to Dunne. This process is reversible and gives the shape memory effect.

Druce cites that by decreasing the stacking fault energy of the austenite, martensite can form more readily. So the shape memory effect is maximised if the strength of austenite is increased and by manipulating the stacking fault energy.

Factors influencing the shape memory effect:

Dunne has worked in conjunction with Huijun Li and Noel Kennon in order to identify "factors that influence the shape memory effect and phase transformation behaviour of Fe-Mn-Si based shape memory alloys" [Li, et al, 1999:517]. They investigated three major alloy types [Table 2].

Table 2. Compositions of alloys investigated [Li, et al, 1999:518].

Alloy	Fe	Mn	Si	Cr	Ni	Cu
#1	Bal	28	6	-	-	-
#2	Bal	13	5	10	6	-
#3	Bal	20	6	7	-	1

The shape memory effect in iron-based shape memory alloys is governed by the transformation from austenite (γ) to martensite (ε) [Li, et al 1999:517]. They determined the factors influencing the transformation to be the extent of pre-strain, the deformation temperature, the degree of thermo-mechanical training and the annealing temperature.

Li, Dunne and Kennon [1999:518] determined that the increase in pre-strain adversely affected the reverse transformation by increasing the driving force required for it to occur. They also found that the optimal annealing temperature was 873K with superior shape memory effect exhibited by alloy compositions #2 and #3 [Li, et al 1999:523]. They attributed this to the growth of pre-existing ε martensite plates, not the nucleation of new plates [Li, et al 1999:517].

Annealing affects the defect concentration in the austenite phase and stacking faults in the martensite assist the transformation [Li, et al 1999:517]. They discovered that dislocation barriers for the austenite to martensite transformation were unrecoverable at low annealing temperatures. However, at higher temperatures the transformation was enhanced by a decrease in dislocation density [Li, et al 1999:523].

High pre-strains were found to increase the austenite finish temperature (A_f) and permanent plastic strain acted as a barrier to transformation [Li, et al 1999:523]. Cold and hot working strains adversely affected the shape memory effect [Li, et al 1999:517]. These strains prevented the rearrangement of Shockley partial dislocations, inhibiting the transformation.

Druce states that the "thermal hysteresis of iron-based shape memory alloys is approximately 200°C which is high in comparison to thermo-elastic martensites that have a hysteresis of less than 50°C". The martensitic start temperature of the alloys was approximately room temperature.

The microstructure was an influencing factor on the transformation temperature. Increasing the annealing temperature resulted in a small increase in the martensitic start temperature. However the austenitic start and finish temperatures were found to decrease by 10-30°C [Li, et al 1999:518]. Thus increasing the annealing temperature decreased the thermal hysteresis, which is desirable.

Fe-Mn-Si couplings for high pressure applications:

Dunne also worked with Li on a project with manufacturing company HI Fraser to develop an iron-based shape memory alloy coupling that could be used for in pressure systems in the military.

The aim of the project was to design a stainless steel shape memory alloy that could be used in a coupling system with brass tubes [Li and Dunne 2000:1]. It was to replace the traditional joining methods of welding and brazing which require the use of a skilled technician. The fitting also had to be able to withstand very high pressures and resist corrosion [Li and Dunne 2000:1].

Druce acknowledges that "a problem with the alloys researched previously was that they required heating to very high temperatures to enable the transformation to take place. This was impractical for commercial uses". A low transformation temperature iron-based shape memory alloy was explored however that alloying elements added reduced the extent of the shape memory alloy effect.

A good shape memory alloy was produced using pure elements and produced the best recovery strain of 5.4% after training [Li & Dunne 2000:4]. Druce state that "this was a very high recovery strain". It was composed of Fe-20Mn-6Si-7Cr-1Cu [Li & Dunne 2000:3].

The material was cast in a cylindrical shape and forged at a maximum temperature of 1323K. The coupling was then machined and expanded using a die. This resulted in the formation of stress induced martensite. The expanded coupling was then placed over the pipe joint [Figure 3]. The original austenitic shape is recovered on heating [Li & Dunne 2000: 2].

Dunne and Li also explored the use of RTV silicon adhesive sealant (a high temperature polymer adhesive) mixed with pure alumina powder (75-105µm) to enhance the adhesion between the pipe and coupling [Li & Dunne 2000: 13]. It created in interlocking mechanism [Figure 4]. Testing determined a maximum pressure of 63MPa, results that are "currently better than reported joint strengths [Li & Dunne 2000: 13].

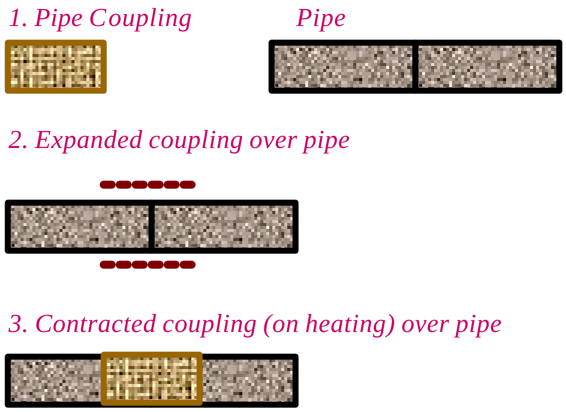

Figure 3. A schematic drawing of a coupling system between a pipe and a shape memory alloy (Adapted from Li & Dunne, Final Report on Shape Memory Alloy Couplings for Joining Pipe and Tubing, p.3, June 2000, CRC Australia)

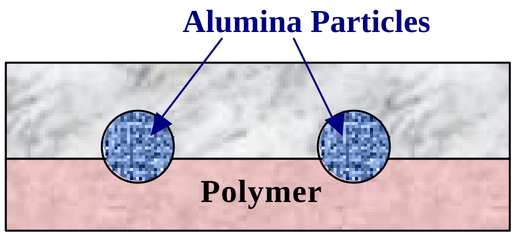

Figure 4. A schematic drawing of an alumina particle reinforced joint (Adapted from Li & Dunne, Final Report on Shape Memory Alloy Couplings for Joining Pipe and Tubing, p.13, June 2000, CRC Australia)

Unfortunately, the HI Fraser hydraulic tester failed at 40MPa [Li & Dunne 2000: 1]. The coupling was still intact and further testing of this alloy was not conducted.

Current research is continuing on the strengthening of the parent phase by precipitation methods. Dunne states that they have discovered an increased strain recovery as a result of precipitation strengthening. Various alloying elements have been tested by Dunne.

Dunne states chromium has been found to increase corrosion resistance and enhance the shape memory effect. Copper additions have been found to increase the effectiveness of the shape memory phenomenon. The effect is also enhanced by the creation of an interstitial solution of carbon in austenite.

The direction of the research on these innovative materials has now moved back to the fundamental phase in order to improve that alloy. However, Dunne believes that HI Fraser would be a major client if an effective iron-based shape memory alloy was available.

Dunne is also pursuing low pressure applications of these alloys, such as household water pipes. Water pipes are traditionally joined by brass fittings that require a silver solder. Dunne recognises that the pipes operate at lower pressures and are a possible avenue for the use of iron-based shape memory alloys. Steel-based couplings with an adhesive layer to prevent corrosion are proposed. The potential market for this component is enormous and according to Dunne "research is currently being conducted by colleagues in China".

Other research methods:

Dunne collaborates with a number of other researchers within his field. He stated that "there are no formal collaboration agreements between us, instead our communication is based on old friendships". This network of colleagues has an international span primarily in the University of Wollongong, the Catholic University in Belgium, Nippon Steel and Tsukuba University in Japan and Shanghai in China. Dunne recognises that the popularity of shape memory alloy research has declined in recent years. He cites the reason for this as the shift from fundamental research to a greater focus on practical research applications.

There are a variety of other research areas being investigated. Dunne makes reference to the possible applications related to the damping capacity of Fe-Mn-Si shape memory alloys. This includes the absorption and dissipation of vibrational energy through internal friction and has potential applications in components of tools to reduce vibrational noise [Van Humbeeck & Liu 1999:331].

Dunne acknowledges the work of one of his colleagues, T. Maki, who has discovered that increasing the carbon content of the alloy increases the shape memory effect. Druce cites this as "significant" as traditionally iron-based shape memory alloys had low carbon content.

Sato, et al [1999:223] have explored the increase in yield stress caused by grain size refinement. Their results concluded that this approach doesn't adversely affect the shape memory effect. They also found that the shape memory effect is increased by using a high speed deformation process [Sato, et al, 1999: 223]. They claim that the fine structure not only increases strengthening but recovery strain is increased under an opposing stress [Sato, et al, 1999: 225]. Sato, et al [1999:225] cite that "such a property must be important in practical applications such as in increasing the strength of a pipe joint". Thus it may be relevant to the research conducted at the University of Wollongong. Dunne has recognised this as an emerging avenue of research. However the two research groups focus on entirely different methods, with Sato exploring grain size refinement and Dunne focusing on strengthening through precipitation. Both avenues have yielded promising progressive results and are both valid areas of research.

Lin, et al [2002:103] considered the influence of geometry. Increasing the thickness of the material decreased the recovery strain and increasing the length decreased the fastening stress. Lin, et al [2002:103] also determined that the fastening force and shape memory effect were increased by thermo-mechanical training. These conclusions were also reached by Dunne's research, with remarkable increases in recovery strain after training [Li & Dunne 2000:4].

Further investigation in this area has been conducted by Dong, et al [2002:407] using an alloy composition of Fe-14Mn-6Si-9Cr-5Ni. They discovered that 0.5%Nb precipitated in austenite by ageing at 800°C for 46hours negates the need for training of the shape memory alloy. This research is focused on precipitation hardening, which is also the focus of Dunne's research. Dunne has investigated the advantageous properties of chromium, niobium and nickel. However Dunne highlights that "there is little fundamental reason to suggest that NbC is the best strengthening precipitate" and refers to the need for more fundamental research. He indicates future research involving both NbC and Ni_3Al alloying additions to improve properties.

Sun, et al discovered the 9% chromium addition used in the above composition (Fe-14Mn-6Si-9Cr-5Ni) to be optimal [2002:443]. They found that it enhanced he shape memory effect and workability of the alloy. However, it had a lower corrosion resistance in comparison to 12% chromium [Sun, et al 2002:443]. This highlights the problem of property compromise involving alloys. Dunne's results also cite the usefulness of chromium additions as previously discussed.

The research currently conducted in this field largely involves trial of different alloying elements, thermo-mechanical processing methods and the effects of defects and grain size to define the limitations and potential for iron-based shape memory alloys. Communication of results with the field means that researchers are able to investigate many approaches to enhance the shape memory effect in iron-based shape memory alloys.

The future of shape memory alloys:

Dunne envisions valuable applied uses for shape memory alloys, especially those based on iron. He believes that "Within ten years iron-based shape memory alloys will be well established as a commercial product".

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