Recent Progress in Shape Memory Alloys

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In this paper, the progress on shape memory alloys (SMAs) for the past 10 years was reviewed and research trends in the field were briefly introduced. Especially, basic properties in some novel alloys, such as the ductile Cu-Al-Mn SMA, ferrous superelastic alloys and Ni-Mn-based metamagnetic SMAs are focused on and the superelastic behavior at cryogenic temperatures in some SMAs, such as TiNi and Ni-Co-Mn-In alloys, was introduced. [doi:10.2320/matertrans.M2017340]

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1. Introduction

The shape memory effect (SME) in a TiNi (Nitinol) alloy was first reported in 19631), and almost half a century has passed since the practical shape memory alloy (SMA) was discovered. In the history of TiNi alloys, the basic properties, including superelasticity, have drastically been improved, mainly through the work of Miyazaki et al. from 1980s2) and have so far been widely used for industrial and medical applications. Although many SMAs in other systems have been reported, the only SMA that has practical applications is actually the TiNi alloy owing to its good shape memory properties, mechanical properties and corrosion resistance. For several decades, while their presence in medical devices has increased, TiNi alloys have exhibited some drawbacks that impede the rapid expansion of their practical use. The problems with TiNi alloys, which are sometimes pointed out, are poor ductility, high material cost, slow response to a thermal input signal rate-determined by temperature change, human allergy to Ni, small operation temperature window, and a poor cyclic property. For the past 10 years, some important progress, such as (1) improvement of superelastic (SE) properties in Cu-based SMAs3) and development of ferrous SE alloys4,5), (2) development of metamagnetic SMAs6), (3) improvement of SE properties in Ti-based SMAs7), (4) reports on SE behavior at cryogenic temperatures8) and (5) ultra-small transformation hysteresis9), (all of which aimed at compensating for the drawbacks of TiNi alloys) have been achieved. In this paper, the details of these recent achievements are reviewed in the same order as presented above.

2. Novel SMAs with High Ductility

2.1 The Cu-Al-Mn system

In the TiNi alloy, cold deformations apart from drawing are difficult in industrial settings owing to the low deformability and frequent intermediate annealing required even in the drawing process. This results in processing costs as high as the material cost. Therefore, to develop a low-cost SMA, high cold deformability is one of the most important objectives. The ductile Cu-Al-Mn (CAM) Heusler alloy with relatively high Mn composition (L21-ordered bcc structure) was first reported in 199610,11) and the SE properties continue to be improved through texture12) and grain-size13) control. So far, the SE properties have already reached the level of the TiNi alloy. The high ductility of the CAM alloy is due to the low degree of atomic order, which enables it to deform into complex shapes through rolling, cutting and punching. Furthermore, because the shape memory properties completely disappear by low temperature annealing, no die is required for shape setting, unlike with TiNi alloys. Recently, a medical device to relieve ingrown-toenails (shown in Fig. 1) was developed and started to be sold in Japan in 201113). The clip-type device is composed of a straight sheet body and four hooks, and is fabricated by cold-rolling, punching and bending deformation, whose processes are industrially impossible in TiNi alloy. It has been reported that the relief occurs immediately after setting the device, and a relatively flattened toenail shape is realized in about 3 weeks on average.

In 2013, a novel technique to obtain samples with extremely large grain sizes over several centimeters was reported for the CAM alloy14). In that method, the large grain structure was obtained by only cyclic heat treatment between a β (bcc) single-phase and a β + γ (fcc) two-phase re-
gion. Very recently, fabrication of single crystal rods with a length of 0.7 m was achieved\(^5\). The SE property in the CAM alloy is drastically improved by increasing the relative mean grain size to the cross section area of a sample\(^3\) and an excellent SE property has already been proved in large-scale samples\(^{[14,15]}\). The single crystal of CAM is expected to be used for producing large parts in the fields of architecture and civil engineering\(^{15}\).

2.2 Ferrous systems

Two kinds of ferrous SE alloys, Fe-Ni-Co-Al-Ta-B (FNCATB)\(^4\) and Fe-Mn-Al-Ni (FMAN)\(^5\), were reported in 2010 and 2011, respectively, where the SE property was yielded by \(\alpha\) (bcc) to \(\gamma\) (fcc) martensitic transformation in the FMAN and by \(\gamma\) to \(\alpha^\prime\) (bct) in the FNCATB. Thus, the parent and martensite phases in the FMAN are basically opposite from those in the FNCATB, being abnormal in ferrous systems. In both alloys, however, coherent precipitates of ordered phase, i.e., \(\text{Ni}_2\text{Al}\) (L\(_{12}\)) in the FNCATB and NiAl (B2) in the FMAN, in the parent phase play a key role of changing the transformation behavior from non-thermoelastic to thermoelastic\(^{16,17}\).

In a Fe-Ni-Co-Al-Ta alloy without boron, the grain boundaries (GBs) are extremely brittle owing to the GB precipitation of the B2 phase during the aging treatment to obtain the coherent L\(_{12}\) nano-precipitates\(^4\). Because making the GB energy decrease, the addition of boron is very effective at suppressing the GB precipitation. To obtain sufficient ductility, however, reduce of fraction of the random GB with high energy is also necessary, which is achieved by forming strong recrystallization texture, \([035]<100>\), from annealing after cold-rolling. The FNCATB alloy with the texture exhibits a very large SE recoverable strain of about 13% and a huge stress hysteresis, expected as seismic parts of architecture. The shape of samples showing ductility and excellent SE is currently limited to a thin sheet because severe cold-rolling over 95% reduction is indispensable in the fabrication process. It is also difficult to fabricate wire by drawing, which restricts the practical application of the FNCATB alloy.

On the contrary, one of the most important features in the FMAN SE alloy is the extremely low temperature dependence of the critical stress in the stress-induced transformation. This is due to the transformation entropy change being about 10 times smaller than that in TiNi as shown in Fig. 2\(^5\). This means that the temperature window for SE operation in the FMAN is 10 times larger than that in TiNi, which makes it remarkably useful in automobiles and space out of the earth with large temperature change. The SE property of the FMAN is extremely affected by stress constraint from surrounding grains, and the relative mean grain size has to be large and have a bamboo-like structure\(^{18}\). Details of the recent progress in the FMAN alloy have very recently been reviewed in another paper\(^{17}\).

3. Metamagnetic SMAs

In conventional SMAs, including TiNi, while both the work output strain and stress by the shape memory effect are very large, the responsiveness to an input signal is very low, less than 10 Hz, because the strain is controlled by changing the temperature\(^{19}\). This problem is intrinsic for all conventional SMAs. Thus, a new novel SMA group, where other external fields apart from temperature, such as magnetic fields, are available, is required. In 1996, some strain induced by a magnetic field was first reported by Ullakko et al\(^{20}\) in the Ni\(_3\)MnGa (NMG) Heusler-type magnetic SMA\(^{21}\), where the strain was brought about by rearranging M variants owing to the large magnetic anisotropic energy in the M phase\(^22\). Although showing a very large strain of over 10% induced by the magnetic field, the NMG has not yet been practically used because of brittleness, the high cost and a low work output stress of less than about 5 MPa.

In 2006, a new type of magnetic SMA, NiCoMnIn (NCMI), which can solve the problems of brittleness and the low output stress, was reported\(^{20}\). NCMI shows a MT from a ferromagnetic parent to a paramagnetic martensite phase, and thermodynamic stability of the parent phase increases through Zeeman energy by a magnetic field, which induces reverse transformation (i.e., a metamagnetic transition) in a certain temperature region. Even at a fixed temperature, SME can be obtained using the metamagnetic transition by applying a magnetic field, as schematically shown in Fig. 3. In NCMI, an almost perfect shape recovery strain of about 3% can be realized by applying both steady and single-pulsed (several milliseconds wide) magnetic fields of 7 T\(^{23}\). This kind of SMA is called a metamagnetic shape memory alloy (MMSMA) because it is caused by a metamagnetic transition. It has been reported in other NiMn-based Heusler
alloys, such as NiCoMnSn\(^{24}\). The work output stress in the MMSMAs is roughly proportional to the magnetic field input and a large output stress of over 100 MPa has been realized\(^{25}\). Furthermore, an inverse magnetocaloric effect, i.e., endothermic change induced by applying a magnetic field, is detected in the MMSMAs and many investigations on this issue have been reported\(^{26,27}\).

Despite many basic investigations, neither the MMSMAs nor the NMGs have yet been implemented. One of the major reasons in the MMSMAs may be that a large magnetic field of over 3 T is required for operation. When applying either magnetic actuators or magnetocaloric devices, the magnetic field for operation should be less than 2 T, which can be easily fabricated, and the magnetic field hysteresis in the transformation should be less than 1 T.

4. Biomedical SMAs (TiNi and Ti-Based Alloys)

TiNi alloys possess not only good SM properties, but also excellent corrosion resistance. Thus, they have been used widely in the biomedical field. According to Jani et al.\(^{19}\), in the duration from 1990 to 2013, although the percentage of papers in the biomedical field in all the papers published on SMAs is only about 13%, the percentage in all the patents on SMAs is around 60%, which is extremely higher than that (of about 4%) on the aircraft at the second position. Furthermore, papers and patents for SMAs have exponentially increased in the last several decades\(^{19}\). This tendency seems to result from the drastic increase of interest in applying TiNi SMAs to medical fields, such as being used as guide wires and stents in catheter operations. Ni is known as an element that causes allergic reactions in the human body. However, because Ti oxide layer is easily formed on the surface and prevents elution of Ni atoms, TiNi SMAs continue to be used for many medical applications.

Currently, novel detox-element-free SMAs for medical use are being developed\(^{28}\). Typical examples are Ti-based SMAs such as Ti-Nb-based and Ti-Ta-based alloys\(^{7}\). Ti has \(\beta\) (bcc) to \(\alpha\) (hcp) transformation at 882°C. Adding Nb and Ta, which are \(\beta\) stabilizers, makes the transformation temperature decrease and a martensitic transformation from \(\beta\) to \(\alpha\)\(^{\prime}\) (orthorhombic structure), which yields SME, appears. The SME is improved by the appearance of the \(\omega\) phase obtained by low temperature aging\(^{7}\). So far, many kinds of SMAs, mainly in the Ti-(Ta,Nb)-(Zr,Hf) combination\(^{28}\), which were alloy-designed with biocompatibility and elastic constant in mind, have been reported.

5. SMAs for High or Low Temperature Operation

The operation temperature window of TiNi alloys is limited to -50 to 100°C owing to the limitation in the transformation temperature. Because there are many candidates for applications, high temperature SMAs (HTSMAs), which can be operated at temperatures over 100°C, are required and many investigations have been performed. Recently, new groups of HTSMAs, such as Ni-Mn-Ga\(^{29}\) and Co-Ni-Ga\(^{30}\), have been reported in addition to conventional HTSMAs, such as Ti(Ni,Pd,Pt) and (Ti,Nb,Zr)Ni. However, it is difficult to satisfy all the important issues of practical application, such as shape memory property, formability, cost, and thermal stability. Furthermore, the SE properties at cryogenic temperatures in SMAs have not been reported even in TiNi alloys, just starting to be researched. In 2013, Niitsu et al. studied the SE properties for Ni-rich TiNi alloys and reported that the stress hysteresis drastically increased with decreasing temperature in the region below 150 K, as shown in Fig. 4. A similar behavior has also been found in the single crystals of the NCMI MMSMA\(^{31}\). In this system, the increase of hysteresis was also reported in the magnetic field-induced transformation\(^{2}\) and it was proved that the dissipation energy, which corresponds to the area of the hysteresis loop, in the stress field was almost coincident with

![Fig. 3 Origin of the metamagnetic shape memory effect.](image-url)
that in the magnetic field\textsuperscript{31}. This behavior is similar to temperature dependence in the critical resolved shear stress (CRSS) and the phenomenological theory for the CRSS can be diverted for analysis of the hysteresis. In this theory, the stress hysteresis is divided into thermal activated (TA) and non-thermal activated (NTA) terms. The TA term is strongly affected by the testing temperature and stress rate\textsuperscript{3,31}. Because the origin of hysteresis in MT is basically friction energy against the migration of the phase interface, the presence of the TA term means that the lattice vibration contributes to the primitive process of the interface motion. To date, details on the primitive process remain unknown.

6. Transformation Hysteresis and Cycle Property

The MT is basically classified into 1\textsuperscript{st} order transformation, which passes through two phase conditions, and the appearance of hysteresis is unavoidable. In the martensitic transformation of SMAs showing a relatively large transformation strain, the thermal hysteresis is usually around several decades K and directly connects to the error of the working temperature in a smart actuator system, in which the SMA itself feels temperature and generates stress. Furthermore, the dissipation energy yielded by hysteresis corresponds to energy loss in the system. Thus, reducing hysteresis without losing large transformation strain is one of the most important problems that needs to be solved.

Recently, Song \textit{et al.} reported that the thermal hysteresis of bcc/monoclinic (6M) martensite in a Cu-Au-Zn SMA possessing a transformation strain of about 8\% was lowered to only 2 K in a specific composition, and the transformation temperature hardly changed after thermal cycles of $1.6 \times 10^5$ times\textsuperscript{9}. Such low hysteresis was explained by an excellent matching in the crystal structure and lattice parameters between parent and martensite phases. Furthermore, Chluba \textit{et al.} reported that a Ti-rich TiNiCu thin film obtained by sputtering, where fine nanoscale precipitates were introduced, showed very stable cyclic SE properties up to $10^7$ times\textsuperscript{31}. These results suggest that even in bulk SMAs with a large transformation strain, hysteresis can drastically be reduced by introducing suitable precipitates and/or appropriate matching in lattice parameters between the parent and martensite phases. This encourages us to solve the historically most difficult problem, which continues to impede expanding the fields in which SMAs can be applied.

7. Other Research Progress

In all the papers with keyword “shape memory alloy” published from 2005 to 2015, the papers on magnetocaloric and mechanocaloric (i.e., elastocaloric and barocaloric) effects, which are related to energy conversion\textsuperscript{34}, occupy a noticeable percentage. This tendency may result from some demand on the recent energy problems. In the field, extremely large cycle properties of transformation are required, but conventional SMAs are inadequate (especially regarding the elastocaloric effect) for practical application. We, however, can expect to develop novel SMAs that meet the difficult field applications by alloy-design, in line with the recent finding on the TiNiCu thin film mentioned above.

SMAs have received much attention as a component in micro electro mechanical systems (MEMS), and the size effect on SM properties has been reported by many investigators\textsuperscript{35,36}. According to Gómez-Cortés \textit{et al.}\textsuperscript{36}, the SE property of a micro pillar starts to drastically change at a diameter smaller than about 1.0 \(\mu\)m, and the critical stress obeys a power law of diameter. It is also interesting to note that a single-crystalline micro pillar in ZrO\textsubscript{2}-based ceramic shows a perfect SE property\textsuperscript{37}.

In other issues, some progress, such as strain glass\textsuperscript{38}, precise self-accommodation theory\textsuperscript{39}, and an abnormally low Yang modulus in Fe-(Noble metal) systems\textsuperscript{40} should be pointed out. Moreover, it is worth noting here that an Fe-Mn-Si-based ferrous SMA by \(\gamma \rightarrow \varepsilon\) transformation has been used practically as a damper material for an anti-seismic system in buildings\textsuperscript{41}, while neither SME nor SE itself is used in the application.

8. Conclusions

In this paper, the progress on shape memory alloys over the past 10 years was reviewed. The essentials of the main issues are summarized as follows:

(1) The SE properties in the ductile Cu-Al-Mn (CAM) SMA were drastically improved by microstructure control, including single-crystallization using abnormal grain growth. In 2011, a medical device with the CAM alloy was developed and is now in practical use.

(2) Two types of ferrous SE alloys in Fe-Ni-Co-Al-Ta-B (FNCATB) and Fe-Mn-Al-Ni (FMAN) systems were reported. The FNCATB and FMAN show a huge recoverable strain and a very low composition dependence of SE stress, respectively.

(3) A new type of magnetic SMA, known as a metamagnetic SMA, in the NiCoMnIn (NCMI) system was introduced. NCMI shows magnetic field-induced reverse transformation, which yields many useful functions, such as a magnetic field-induced SM effect and a magnetocaloric effect.

(4) In medical fields, the use of TiNi continues to expand despite the existence of Ni, which is an element that causes allergic reactions. However, many Ni-free Ti-based SMAs, such as TiNbZr, have been developed and the properties were improved.

(5) The SE behaviors at cryogenic temperatures in TiNi and NCMI were reported. It was clarified that their stress hysteresis drastically increased, which means that the thermally activated process may be included in the elementary process of transformation.

(6) Ultra-small temperature hysteresis was found in some alloy systems, such as CuAuZn, which have extremely high lattice compatibility between the parent and martensite phases.

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