Characteristics and applications of Fe-Mn-Si-based shape memory alloys

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(1) Introduction

Fe-Mn-Si based shape memory alloy (Fe-Mn-Si SMA) is known as the only material in practical use among iron-based shape memory alloys. The basic components are Fe, 32% Mn, and 6% Si, which are the base components, but alloys with added Cr and Ni have also been developed in terms of corrosion resistance (Table1). Most of the studies on practical application are being carried out using Fe-28Mn-6Si-5Cr alloy(mass%) and only this alloy is currently manufactured.

Table 1. Main compositions of Fe-Mn-Si SMAs (mass%)

Fe-32Mn-6Si
Fe-28Mn-6Si-5Cr*
Fe-20Mn-5Si-8Cr-5Ni
Fe-16Mn-5Si-12Cr-5Ni

*Currently only Fe-28Mn-6Si-5Cr is manufactured

It is noteworthy that this alloy has been mainly carried out in Japan from the discovery[1] and development of materials to its application. Since it does not contain elements that are expensive in composition and can be produced using mass production equipment for steel and stainless steel, it can be said that it is an inexpensive material for mass production as an SMA. However, it does not mean that the limited usage and material costs in the early stages of small-scale production are comparable to ordinary steel and stainless steel. This is because these mass production facilities cannot be used unless the production scale commensurate with them is secured.

Although the shape recovery strain of the Fe-Mn-Si SMA is not as high as that of the Ti-Ni alloy, a maximum of about 4% can be obtained (when the training treatment described later is applied). Moreover, since there is little difference in the strength of the material before and after phase transformation, bidirectional operation using the bias spring cannot be expected. Furthermore, the temperature for shape recovery requires a higher temperature than the Ti-Ni alloy, and the shape recovery gradually progresses over a wide temperature range from about 90 ° C to 350 ° C. As a field in which the above characteristics of Fe-Mn-Si SMA can be utilized, application to relatively large connecting members is being focused on. Applications, therefore, are mainly considered as relatively-large components to take advantage of such characteristics.

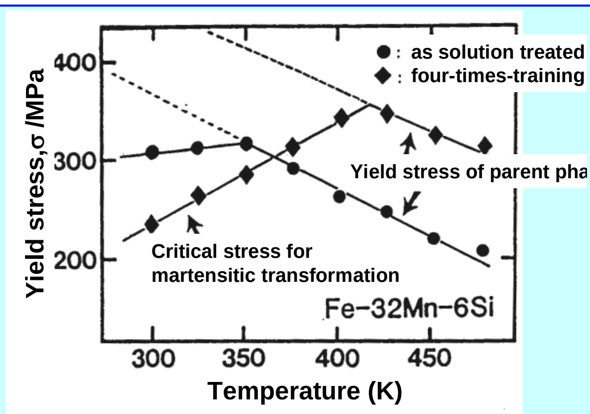
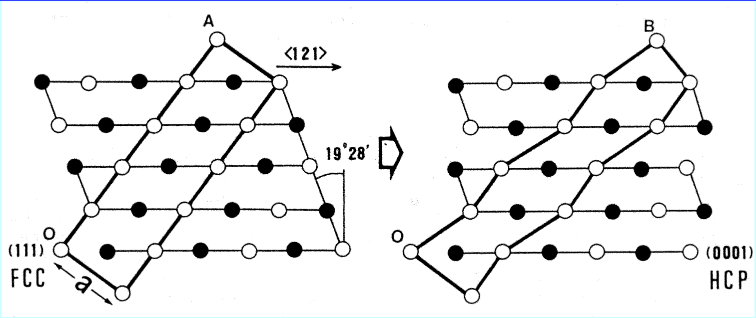


Fig. 1 The dependence of yield stress on temperature[2]

(2) Mechanisms of shape memory

The temperature dependence of 0.2% proof stress of the Fe-Mn-Si SMA shows a characteristic shape as shown in Fig.1[2] Looking from room temperature to higher temperature, there is a region where the 0.2% proof stress increases as the temperature rises in the range up to a certain temperature, and beyond that, 0.2% proof stress will be reduced as ordinary steels. Two different slopes in each curve are caused by two kinds of deformation modes in the Fe-Mn-Si SMA: one shows the critical stress of slip deformation, and the other shows the critical stress of ε-martensite transformation (FCC→HCP transformation). The critical stress for slip deformation decreases with the increase of temperature as shown by the broken line in Fig. 1. On the other hand, the critical stress for ε-martensitic transformation increases with the increase of temperature. That is to say, the two slopes in Fig. 1 indicate that ε-martensitic transformation preferentially occurs at low temperatures (including the room temperature) and slip deformation occurs at high temperatures.

Fig.2 shows the change in atomic arrangement during stress-induced martensitic transformation from γ-austenite(FCC) to ε-martensite(HCP). Up to about 20% strain can be introduced in a specific direction with little volume change by this transformation. As shown in Fig. 2, the length of OB after stress-induced transformation is about 23% longer than that of OA before transformation[3]. Namely, the stress induced ε-martensitic transformation yields the shape change without slip deformation. The SME is obtained through reversible transformation from HCP martensite to FCC parent phase.



○:Atoms on the bottom plane ●:Atoms on the one level higher plane from the bottom

Fig.2 Schematic illustration of the ε-martensitic transformation

In the region of large strain, not only martensitic transformation but also slip deformation inevitably occurs. Therefore, if the amount of deformation is kept within an appropriate range, the shape of the material can be changed only by stress-induced martensitic transformation without causing slip deformation. When the deformation is kept within such a range and then heated to a temperature at which the γ phase becomes stable, the reverse transformation to γ proceeds while recovering the strain introduced at the time of ε formation. The shape memory effect of Fe-Mn-Si SMA recovers the shape before deformation by this reverse transformation.

Generally, it is used in a form in which a strain of about 4 to 8% within a range in which some slip deformation occurs is applied, and about half to one-third of the applied strain is recovered as a shape recovery strain.

(3) Shape memory properties

① Shape recovery strain

There are two most important parameters for utilizing SMA. One is the shape recovery strain, which depends on the initial strain and the number of training cycles, and the other is the recovery stress. Therefore, the shape memory effect of Fe-Mn-Si SMA will be described separately for strain and stress.

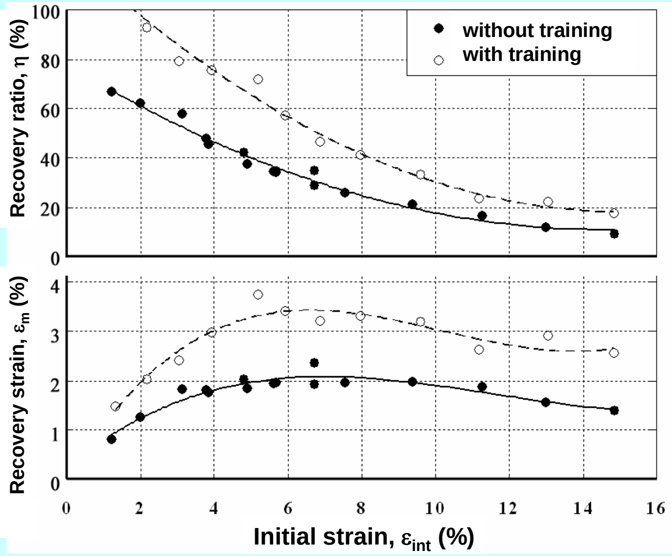


Fig.3 The relation between initial strain and recovery strain[4)]

First, the shape recovery strain changes depending on the amount of strain applied and the presence or absence of training treatment. Fig. 3 shows the relation between initial strain and recovery strain[4)]. Training treatment consists of repetitive processing of proper deformation and heating[2)]. The results in Fig. 3 are obtained after one cycle of training. Although multicycle training treatment increases the recovery strain, its effect is saturated gradually.

The recovery strain shows a maximum value with 5~8% initial strain and higher strain deteriorates its value. On the other hand, the training process is indispensable to restore the shape as close as possible to the state before deformation, and it is limited to the region where the processing strain is extremely small (2% or less).

② Shape recovery stress

Fe-Mn-Si SMA is generally used as a connecting member. Such applications using Fe-Mn-Si SMA require recovery stress rather than recovery strain. For example, Fe-Mn-Si SMA first undergoes tensile deformation and then memorizes its shape (described later). This shortens the length when heat is applied. Next, if you constrain both ends and apply heat to prevent the material from shrinking, stress will be generated in the fixed parts at both ends. Fig.4 shows the results of measuring this stress generated during the shape recovery process. The solid and dashed lines show the behavior of recovery stress with and without training, respectively[5)]. Since both show similar behavior, the trained material will be described here as an example.

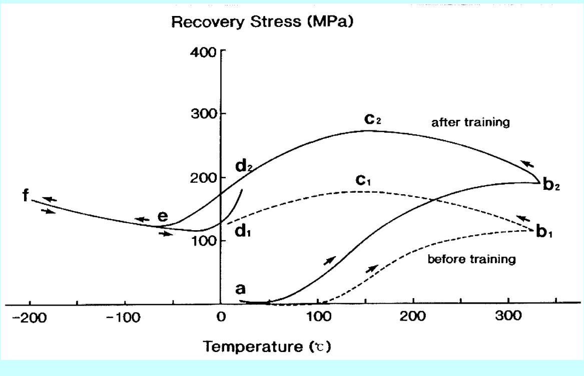


Fig. 4 Recovery stress vs temperature curve in the Fe-Mn-Si SMA[5)]

Recovering stress begins to generate at about 50 ℃ (about 100 ° C without training) and gradually increases until above 300℃. After heating until about 330℃ (b_2) at which the increase of the stress is saturated, the stress further increases by cooling. From this measurement, it can be seen that the generated stress includes two stresses, contraction due to shape recovery and contraction due to cooling after thermal expansion. Since the thermal expansion component acts in the direction of expanding the fixed parts at both ends in the heating process, the tensile stress shown in Fig. 4 is not a pure shape recovery stress, but a stress in which the contraction force due to shape recovery overcomes the thermal expansion. The stress increases further when heated to approximately 330 ° C (point b2) and cooled after the stress has saturated. This increase in stress is caused by the forces that pull the fixed ends together, turning thermal expansion into contraction during the cooling process. However, the stress decreases after reaching the maximum value at point C2, and the stress at point d2 remains when cooled to room temperature. This stress corresponds to the shape recovery stress that can be used as a connecting member at room temperature.

In spite of the continuous shrinkage during the cooling process, the stress decreases below the point c_2. This comes from the fact that the temperature at c_2 corresponds to the upper limit of the temperature range for ε-martensitic transformation shown in Fig. 1. Therefore, below this temperature, stress-induced martensitic transformation can occur again if a certain amount of stress is applied. That is, when the cooling progresses and the temperature reaches the c2 point or less, the stress accumulated in the material promotes the stress-induced martensitic transformation, and it can be considered that this transformation relaxes the internal stress. As a result, Fig.4 shows that the available recovery stress is about 200 MPa with training and about 130 MPa without training. However, these values are ideal ones that do not allow any existence of recovery strain in the process.

In fact, it is difficult to prevent the occurrence of recovery strain completely. The actual stress is less than the ideal value because of the occurrence of recovery strain in general process of joining.

Fig. 5[6] shows an overview of the pipe connection method using the SMA joint. The SMA pipe joint is machined into a ring shape with an inner diameter that is slightly smaller than the outer diameter of the connecting pipe (Fig. 5A). It is made by expanding the inner diameter of this joint to a size that allows the pipe to be inserted at room temperature (Fig. 5B). When pipes are inserted at both ends of the SMA pipe joint and then the joint part is heated, the inner diameter shrinks due to shape recovery, and the inserted pipes are connected (Fig. 5C and D).

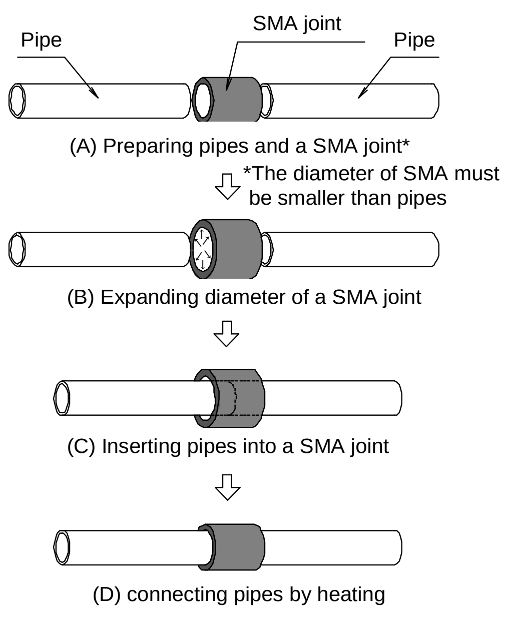


Fig.5 Connecting pipes with Fe-Mn-Si SMA joint[6]

At this time, if a certain gap is not secured between the outer diameter of the pipe and the inner diameter of the SMA joint at the stage of Fig.5B, the pipe cannot be inserted into the joint. On the contrary, if the gap is made too wide, even if the joint contracts due to heating, a sufficient tightening force cannot be exhibited. Therefore, it is extremely important to set the size of the gap appropriately.

This gap corresponds to the distance that the SMA joint contracts freely due to shape recovery and before it comes into contact with the outer surface of the pipe. It is preferable to make the gap as narrow as possible in order to give the connecting portion a sufficient tightening force.

Figure 6 shows the shape memory effect described above on the stress-strain diagram. First, in order to use SMA as a joint, deform it in the path of [O → a → b] shown in the figure. After unloading, 2.5~4% recovery strain corresponding to [b → e] is obtained by subsequent heating. If there is an obstacle in the direction of the shape recovery at b, recovery stress corresponding to [b→b'] can be attained by heating (130～200 MPa). If some interval is present between an obstacle and a SMA, the available recovery stress decreases with the increase of the interval. This is because if the obstacle is at c or d, the shape recovery occurs along [b→c→c'] or [b→d→d']. The more recovery strain is consumed, the smaller the recovery stress that can be extracted.

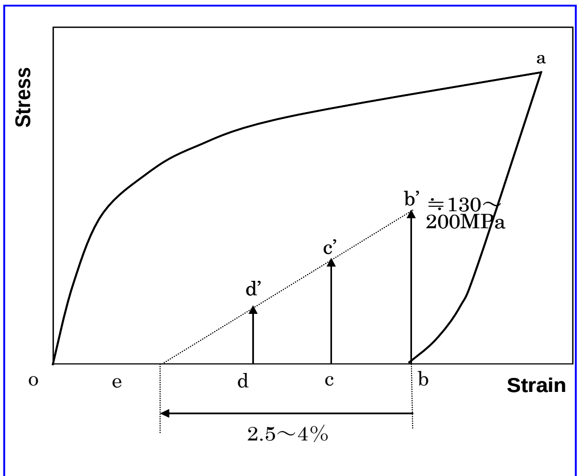


Fig. 6 Schematic diagram of the SME

(4) Other fundamental properties

Since Fe-Mn-Si SMA is often used as a part of large structural members, basic properties required for general steel materials are also important in addition to shape memory properties. Table 2[7] shows the basic properties of the materials after hot working and solution heat treatment. Many properties, such as proof stress and tensile strength values, as well as the shape of the stress-strain curve, are similar to SUS304 stainless steel.

Table 2. Fundamental properties of Fe-Mn-Si SMA[7]

Term	Unit	Values
Proof stress	MPa	200～300
UTS	MPa	680～1,000
Ductility	%	16～30
Hardness (Hv)		190～220
Density (25℃)	g/cm^3	7.2～7.5(7.454)
Melting point	℃	1,320～1,350
Thermal expansion (0～500℃)	℃$^{-1}$	16.5×10^{-6}
Thermal conductivity	cal/cm･deg･sec	0.02
Specific heat	cal/g･deg	0.13
Specific resistance	Ω･cm	100～130×10^{-6}
Young's modulus	GPa	170.0
Shear modulus	GPa	65.0
Poisson ratio		0.359
M_s	℃	-20～25
A_f	℃	130～185
Recovery strain	%	2.5～4.5
Recovery stress	MPa	150～200
Magnetic property		Paramagnetism

In case of using SMA, it is

indispensable to apply strain in advance. Especially when performing training processing, the deformation of strain application must be repeated at least twice.

Tungsten inert gas (TIG) or plasma welding are applicable to the Fe-Mn-Si SMA. Further heat treatment after the welding gives shape memory properties comparable to the parent materials. It is also possible to bend and form a plate and weld it to make a pipe[8]. (Currently no product is manufactured this way) In addition, there was a study that tried to improve the shape memory characteristics by adding a small amount of Nb and V, but currently only Fe-28Mn-6Si -5Cr with the original composition is manufactured[9,10].

(5) How to use Fe-Mn-Si SMA

Fe-Mn-Si SMA material is produced by combinations of hot rolling, cold rolling, forging, drawing, etc. Table 3 shows the basic steps required to use this material.

Table 3. Basic steps for using Fe-Mn-Si SMA

process	abstract	detail
Shape memory treatment	Memorize the shape you want to achieve when you finally apply heat.	Heating at 950℃ or higher under constraint after working at room temperature (working at 950℃ or higher is also effective)
Training treatment	Training enhances recovery strain and recovery stress.	Repeating 4～8% strain and heating at 600℃. You can repeat it more than once, but the effect will gradually saturate, so you can repeat it once or twice.
Deformation for initial strain	Deforms the shape after shape memory processing	Deforms near room temperature. Perform processing methods such as tension, compression, twisting, bending, etc. alone or in combination
Shape recovery treatment	Recovery to the memorized form or obtain recovery stress	Preferably heated to 350℃ or higher. Heat the material uniformly so that the temperature difference is as small as possible.

The above is the standard process for using Fe-Mn-Si SMA. Of these, the heat treatment performed in the shape memory processing is basically performed by constraining the shape to be stored. However, when manufacturing a steel pipe joint by cutting from a round bar, it may be possible to just heat it without restraint.

(6) Applications of Fe-Mn-Si SMA

① *Pipe joint for steel pipes*

Pipe joint has been considered as the most important application of the Fe-Mn-Si SMA. While the Ni-Ti SMA had already had good records of application in military-related fields, it has been considered promising if the inexpensive Fe-Mn-Si SMA can substitute the Ni-Ti SMA as consumer pipe joints.

However, steel pipes have variations in outside diameter which is allowed in official standard. This variation is not negligible compared with the magnitude of the shape recovery strain in Fe-SMAs. Moreover, tensile strength and sealing properties are also required. Even if the constituent elements have a high cost performance, it is still necessary to spend some money to meet these requirements. As a result, the total cost performance was not a sufficient advantage to substitute the Fe-Mn-Si SMA for conventional pipe joints.

The solution to this problem was suggested as follow. For instance, proper resin coating on the inner surface of a joint is efficient to improve the sealing property and the strength of the joint[11]. Inserting C-rings[12] or using screws[5] at the interface of pipe and joint was developed as a method of enhancing the joint strength. Through these processes, the Fe-SMAs were put into practical use. Some other examples are introduced as below.

A construction method for tunneling work co-called the "curved boring method[12]" has been developed. This method is noted as an important technology in tunnel construction in deep underground areas with unstable ground. Curved steel pipes are laid in the wellbore after boring outward from the ground, which constitutes a curved pipe roof. Digging of the main tunnel is conducted under this curved pipe roof. However, the curved steel pipes are too long for such a narrow work space. The curved pipes, therefore, must be cut into proper length and inserted into wellbore at one time. Each pipe is jointed with the preceding pipe. In this process, safety and efficiency are required. That is why the Fe-Mn-Si SMA is selected to ensure the bending and drawing strength of the joint. As schematically shown in Fig. 7, the C-ring is inserted into a ditch formed on the SMA joint and curved pipe[13]. In this method, the strength at the joint part strongly depends on the number of C-rings. Table 4 shows the result of tensile tests for 100A SMA pipes. The strength with three C-rings on both sides is comparable to the case of welding[14].

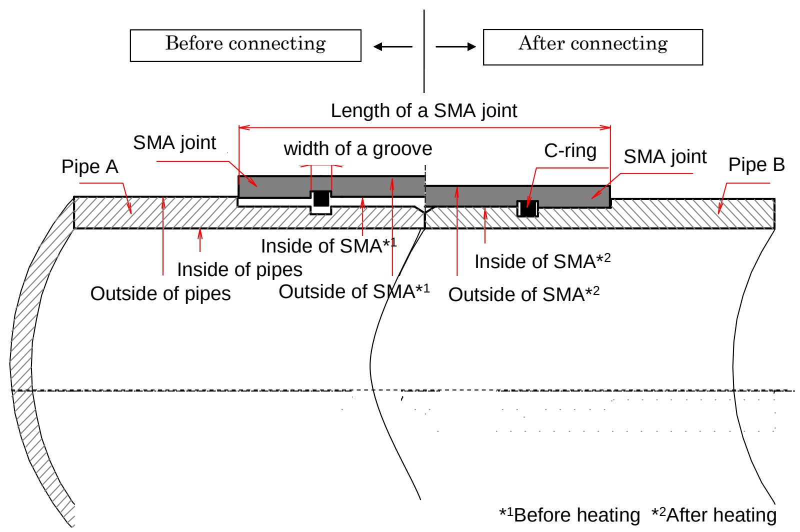


Fig.7 Schematic illustration of Fe-Mn-Si SMA joint with C-ring

Table 4. Relationship between the number of C-rings and the UTS (in 100A steel pipes) [14]

	[Force (kN)]		[Ratio respective to the steel pipe (%)]	
	2%strain	Max	2%strain	Max
STPG370 pipe (114.3φ×6.0t)	580(439)	789(755)	100(100)	100(100)
without C-ring	110	110	19(25)	14(15)
With a C-ring for each side	430	500	74(98)	63(66)
With two C-ring for each side	520	580	90(118)	74(77)
With three C-ring for each side	550	610	95(125)	77(81)

( ) :Force corresponding to UTS and yield stress as standard lower limit

Bending strength is also required to endure soil pressure. The results of 4-point bending test (with C-ring attached on both sides) shown in Fig. 8 are almost the same as the pipe without joint[14].

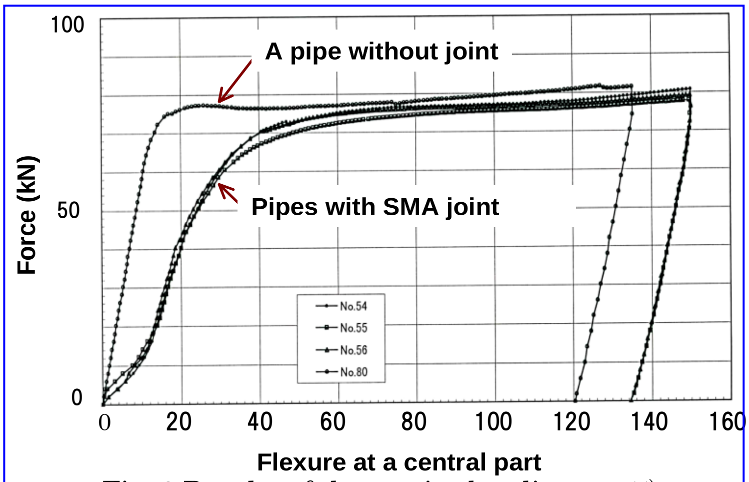


Fig. 8 Results of the 4-point bending test[14]

Through the above experiments, the method was actually adopted on a trial basis in 2003[5]. In this work, the SMA joint was used for 250A curved pipes (outside diameter 267.3 ㎜ϕ, bend radius 6000mm in Photo 1). The SMA joints are produced by centrifugal casting[15] with a composition of Fe-28%Mn-6Si-5Cr. The joint is heated by high-frequency induction heating. This method can be performed by fewer workers in less working hours compared with welding.

Photo 1. Pipe coupling with Fe-Mn-Si SMA joint

② *Fish plate for crane rails*

In large factory cranes, gaps in the rail seams can cause local wear on the rail ends, causing dents and chips. Once a dent or chip occurs, the gap gradually expands, eventually impeding the running of the crane. The Fe-Mn-Si SMA fishplates were developed to solve this problem.

Generally, rails are connected by applying fish plates on both sides and bolting them together. Since there is a certain amount of clearance between the bolt hole and the bolt diameter, even if you try to pull the rails on both sides to fix it, it is inevitable that a gap will be created due to vibration caused by the movement of the crane. A tight connection of the rails can be realized by connecting the tension-deformed Fe-Mn-Si SMA fish plates to the rails with bolts and then shrinking it by heating.[16] (Fig. 9).

This fish plate has been used for actual crane rail connection of major steel manufacturers since the fall of 2004, and SMA fish plates as shown in Photo 2 are used in a total of about 2200 locations (As of August 2020). In the case of the fish plate shown in Photo 2, the product weight is about 10 kg (currently about 7 kg), and the on-site heating to restore the shape of this fish plate uses the flame of the gas burner. The connection time at one location is about 10 minutes. The gap between the rail joints is almost completely eliminated, and the state is maintained for a long period of time, so that the traveling of the crane becomes extremely smooth. Therefore, it is said that the rail connection by this method also contributes to extending the life of crane rails, runway garters, and overhead cranes[17]. It is still in regular use, and no particular problems have occurred until now, about 16 years after its practical use.

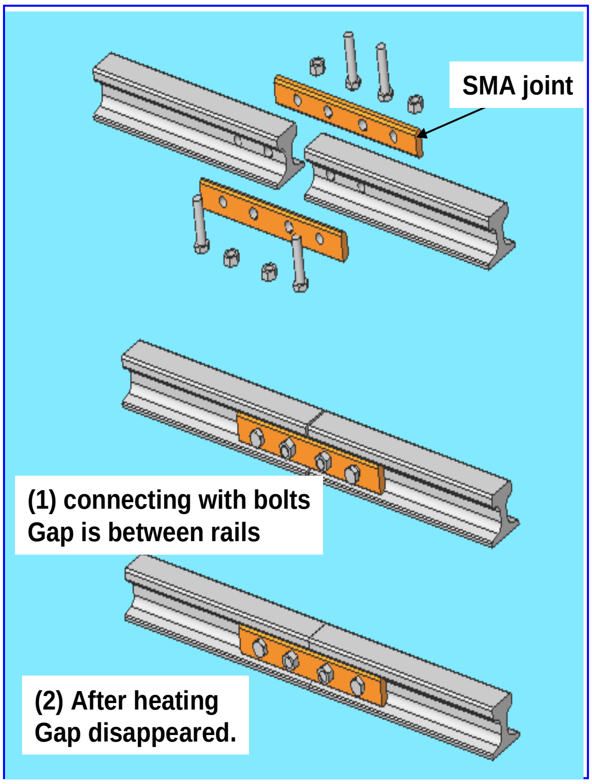


Fig 9. Rail connection with Fe-Mn-Si SMA fish plates

Photo 2. Fe-Mn-Si SMA fish plates for crane rails

③ *Other applications*

Employing the Fe-Mn-Si SMA as joints for frame pipes of bicycle was actually the first practical application of this material[17]. Grooves were formed inside of a receiving pipe and outside of an inserting pipe. Contracted SMA C-rings are set in the grooves of the inserted pipe. After inserting, the SMA C-ring expands toward the groove of the receiving pipe by heating, which connects the pipes. Since the movement of the C-shaped ring is fixed by injecting adhesive into the gap between the recesses, it was possible to realize a connection that can withstand vibration sufficiently. This method was used on high-end sports bicycles for about two years, but has since been changed to eliminate the need for SMA rings.

This material is also used for connecting small-diameter and short-diameter ceramic tubes, which are difficult to make long products[19]. The pipe (tens of centimeters in length) is made of Fe-28Mn-6Si-5Cr alloy, and short ceramic pipes are inserted side by side and heated to restore the shape. Since the ceramic tube is protected by the SMA tube and the entire inner surface is made of ceramics, a structure that is resistant to corrosion and wear from the inner surface and impact from the outside is realized. This application has been put into practical use since around 1994 and is still in regular use (as of 2021).

(7) Future prospects and summary

Fe-Mn-Si SMA, which appeared as one of the new materials, has been around 40 years since the discovery of the material, and more than 30 years have already passed since the start of development (as of 2021). However, the reality is that full-scale practical use has finally begun to progress after 2000. At the end of this article, I would like to consider the background that took such a long time to put into practical use.

The goal of this material at the beginning of its development was to position it as a low-cost type of Ti-Ni SMA, and to trace the successful application fields of Ti-Ni. From the recognition that SMA is the Ti-Ni type, it is natural that expectations from the surroundings for Fe-Mn-Si SMA is in that direction. However, the targets for which expensive Ti-Ni SMAs were put into practical use were mainly small parts. When trying to utilize Fe-Mn-Si SMA for small parts, it was a big constraint that the shape recovery strain was small and bidirectional operation was not possible. It soon became clear that it was impossible to aim for a target similar to the Ti-Ni SMA simply because of low cost. Against the enthusiastic background of new material development, several iron-based alloys have emerged, but none of them disappeared from the front stage when it became clear that they could not replace Ti-Ni SMA. Only Fe-Mn-Si SMA has continued to make efforts to find a way to develop unique new application fields suitable for this material. The aim was to put it into practical use as a "structural material with a function of shape memory effect" as a large structural member, which is difficult for Ti-Ni SMA. But, while small members can be easily prototyped from laboratory test melt materials, large members have a series of processes such as melting, forging, hot rolling, cold rolling, cutting, plastic deformation, and welding. It was required to reexamine the conditions suitable for this material for the entire manufacturing process. It took more time than expected in this process, which is one of the reasons why it took so long to put it into practical use. It can be said that the current situation is that they have finally begun to bear fruit.

In recent years, it has been discovered that stress-induced martensite in Fe-Mn-Si SMA returns to the original austenite phase if it is deformed in the opposite direction instead of heating, which causes superior fatigue durability against repetition of plastic deformation[20]. That is, the Fe-Mn-Si alloy has two functions of shape memory effect and fatigue durability. The representative of the former is the Fe-28Mn-6Si-5Cr alloy described in this paper. On the other hand, the latter is a Fe-15Mn-4Si-10Cr-8Ni alloy whose composition has been adjusted so that it is suitable for developing fatigue durability and can be mass-produced. The latter alloy can then be manufactured by the continuous casting method22), and has already been implemented in actual buildings as a maintenance-free steel-based vibration damping damper core material that can withstand continuous use for a long period of time. The paper [24] summarizing from the beginning of the development of Fe-Mn-Si SMA to new applications as a steel vibration damper is often cited, and due to its influence, the papers about Fe-Mn-Si SMA written 30 years ago [2] [3] are also often quoted. This indicates that research on stress-induced transformation of Fe-Mn-Si alloys, which began in the early 1980s, is once again receiving worldwide attention.

In the world of SMA, Fe-Mn-Si alloys have survived by finding unique applications such as crane rail joint plates for applications different from Ti-Ni alloys. Thanks to that, in recent years, we have come across new features with excellent fatigue resistance. In the future, although the fields and scales will be different, we would like to move forward strongly with two applications, shape memory applications and fatigue endurance applications.

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