THE MARTENSITIC TRANSFORMATION: SOME CURRENT TOPICS OF INVESTIGATION

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Se discuten algunos aspectos en la investigación y en el desarrollo de materiales que presentan una transformación martensítica. Se subdivide la discusión en base a cinco preguntas:

1. cómo puede nuclearse y crecer la martensita dentro de una matriz, siendo que los átomos no pueden reacomodarse por difusión, y a pesar de que, al ser la transformación de primer orden, hay coexistencia de fases con grandes cambios de estructura cristalina?
2. por qué ocurre la transformación a las temperaturas y composiciones observadas? Cuáles factores controlan la energía libre de Gibbs de las estructuras involucradas?
3. qué pasa cuando se permite difusión en la martensita? Cómo se relaciona la martensita con las fases de equilibrio?
4. cómo se modifican las propiedades por tratamientos termomecánicos?
5. para qué aplicaciones serán útiles las transformaciones martensíticas?

Se dan algunos ejemplos de actualidad con referencia a estas preguntas, comprendiendo aleaciones con memoria de forma, como las aleaciones de metales nobles, aleaciones de Ni-Ti, aleaciones de Heusler ferromagnéticas y aceros. Se muestra que todavía quedan muchas preguntas por contestar.

Palabras claves: Martensitic transformation, shape memory alloys.

1. INTRODUCTION

The martensitic transformation is a first order phase transition which is diffusionless and is associated with a large shape change. The study of the martensitic transformation in metals and alloys is a very active field of research. This is due, on the one hand, because it presents very interesting aspects in the understanding of the properties of the solid state. On the other hand these alloys have found wide applications in technology and medicine. In this short review some current problems of general interest are briefly discussed. The paper is subdivided into chapters, each of which is introduced by a question.

2. How is it possible that the martensitic structure can nucleate and grow within a solid matrix phase without the possibility for the atoms to readjust themselves by diffusion, in spite of being a first order transformation with large changes in the crystal structure?

It seems surprising that this question has not been resolved long time ago. The first attempts were made by Burgers in 1934 [1], but since he was not able to rationalize the observed transformation crystallography, his approach was not further developed. A great progress meant the publication of the phenomenological theory by Wechsler, Lieberman and Read, and equivalently by Bowles and Mackenzie [2]. They could account for the crystallography of the martensitic transformation by describing it as a homogeneous distortion called the Bain distortion and a lattice invariant shear. In this way it became possible to account for the crystallography of most of the martensitic transformations. But how the atoms move at the tip of the growing martensite plates remained unanswered.

There is however a simple martensitic transformation whose mechanism is quite well understood. This is the change from the face centered cubic (fcc) to the hexagonal (hex) structure by the movement of partial dislocations on the close packed lattice planes that occurs for example in the Co alloys. Shape changes by the movement of dislocations can occur down to the lowest temperatures in the absence of diffusion, as is well known from the plastic behavior of metals. Therefore these types of martensitic transformations are nothing special, they can nucleate by the dissociation of parallel dislocations on each second close packed plane when the stacking fault energy becomes negative. They then move as a group through the lattice with a certain friction. They create a distortion around them, which can be taken up by the surrounding matrix. Thus the question asked above can be answered very simply.

The answer is not so simple when other types of martensitic transformations are considered, for example the transformation from the bcc to the close packed fcc or hex martensite, or vice versa from fcc to bcc in the steels. As shown by Rapacioli [3] for the transformation in Cu-Zn from long-range ordered B2 to close packed martensite, the propagation looks very similar to that for fcc to hex in many Co alloys: Thin plates grow into the matrix. Behind the growing tip the structure is that of the final martensite. An additional feature that is absent in the Co-alloys is that the thin plates can grow by the thickening of the plates. The important fact is that the transformation is completed at the tip, as in the Co-alloys. However it is
not possible to describe the transformation by dislocations with partial Burgers vectors moving on low indexed glide planes, although formally a Burgers circuit around a tip can be made.

How to treat this type of transformation has already been shown by Burgers [1]: A combination of two shears is necessary simultaneously at the tip. The only additional question that has to be asked is what are the most favorable shear systems. This aspect has been discussed [4] for a large group of transformations, permitting not only to rationalize the crystallography consistent with the phenomenological theory, but in addition to understand why a certain crystallography is favored. To clarify this a little bit better, in the following some examples shall be presented.

In the noble metal alloys based on Cu, Ag or Au it has been observed that the elastic constant C' = (C_{11} − C_{12})/2 in the B2 β phase decreases with decreasing temperature and becomes very low near the martensitic transformation, much lower than any other elastic constant. Therefore a shear on a (110)<110> system would be very easy. Indeed the bcc structure would be quite unstable were it not for the high vibrational entropy. At lower temperatures when the entropy plays a lesser role a transformation by a shear on a (110) plane with Burgers vector

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becomes favorable energetically. This shear alone does not produce the martensite lattice, at variance with the analogous case for the fcc to hex transformation. That a structure with only this type of shear can be stable though has been observed in the form of small precipitates during the dezincification of Cu-Zn at elevated temperatures [5]. But it is very easy to get to the observed martensite structure by adding small displacements on an inclined plane. During this first shear which will be called the “primary shear” an inclined (011) plane is transformed into a close packed plane that has already the structure of the martensite phase. However the stacking is not correct, but this can easily be remedied by a small displacement, called a “shuffle” of one plane with respect to the neighboring one. The shuffles can occur in two different directions, and their combination permits to adjust to the requirement that a low energy undistorted interface between the martensite plate and the matrix is created, called the “habit plane”.

The present description of the martensitic transformation leads to the same crystallography as the phenomenological theory. The Bain distortion is now decomposed into the long-wave primary shear and a shear component on the secondary shuffle plane, to which is added the large secondary shear of the phenomenological theory combining into the small shuffles of the present description. This is a very satisfactory result since the stress to activate a lattice invariant shear in the martensite by dislocation movement is much higher. It also permits to understand why the hysteresis between the transformation and retransformation is small in this shape memory alloy. The reason is simply that the atoms have no other choice than to move back on the same path they had taken during the transformation, thus restoring the original configuration. This is due to the inherited long-range order.

The primary and shuffle systems in the noble metal alloys are favored because C' is low and the ratio of the elastic constants C'/C_{14} is of the order of 10. In the Ni-Ti alloys the martensitic transformation proceeds also from the ordered bcc to a close packed structure. But in these alloys the ratio C'/C_{14} is only of a factor two and other shear systems can become favorable. For example a primary shear on a (112) plane with a (110) shuffle plane as proposed by Burgers [1] can be an alternative, and has been suggested to be active for the Ti- and Zr alloys, in addition to Ni-Ti [4]. A more quantitative evaluation is clearly needed to put this possibility on firmer ground. The ordered Ni-Ti alloys have a small hysteresis, whereas the disordered Ti and Zr alloys have a wide one related to the multiplicity of the transformation-retransformation paths of the atoms.

In the steels sometimes a martensite with a (225) habit and for other alloys a (259) habit is observed. The reason has been unknown till now but is easy to rationalize when the transformation from fcc to bcc is described by the combination of a long wave shear on the commonly observed close packed (111) plane with a shuffle shear on the secondary plane with the lowest elastic constant. It has been observed that in ferromagnetic Fe-alloys the C' is very low, a shuffle on a (110) plane therefore is expected and indeed leads to the observed martensite crystallography with a (259) habit. In the absence of ferromagnetism C' is high and an inclined (111) plane becomes more favorable, leading to a habit near (225). There is a discrepancy, however, between the predictions and the observations and in many publications it has been attempted to solve this puzzle.

The (225) martensite brings to the attention another problem: Since the elastic constants are high, the elastic distortion energy at the tip of the growing martensite plate is high. Furthermore the calculated transformation strain is too high to be absorbed elastically by the matrix. There are several ways out. One possibility to reduce the transformation stresses is by a plastic deformation of the martensite plate, if the critical stress is sufficiently low. This occurs probably for Fe-C alloys with small amounts of C and leads to lath martensite. Another possibility is to reduce the transformation shear by an additional twin shear within the plate. This indeed is observed during the growth of the thin (225) plates, but is no longer needed once the plate has formed and only starts to thicken, because then the stress fields are no longer present.

The iron alloys are generally disordered with a hysteresis of several hundred degrees. In the Fe-Pt alloys it is possible to introduce long-range order by the adequate heat treatment, leading to a small hysteresis and a single transformation-retransformation path [4]. If other Fe-alloys with long-range order that are cheaper than the Fe-Pt alloys can be found that

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transform martensitically, it can be expected that they have shape-memory properties.

To conclude, the question listed at the beginning of the chapter can be answered in a little bit more complicated but similar terms as for the fcc to hex transformation by the activation of the most favorable transformation shear systems.

3. The martensitic transformation temperature depends strongly on composition. What are the factors that control the difference in the Gibbs free energy between the structures involved?

The martensitic transformation is a first order transition in the solid state, and involves a change in enthalpy and entropy. A main problem is that the differences are much smaller than the enthalpies and entropies of formation of each phase separately. This makes a quantitative evaluation in general very complex. But fortunately the differences can be determined experimentally with high degree of precision, at least in the shape memory alloys with the small hysteresis between the transformation and retransformation. Results for the Cu-Zn-Al alloys have permitted to determine the enthalpy and entropy differences between the β phase and the martensite. Different martensite structures are observed, depending on composition and applied stress, namely the face centered 3R with stacking sequence ABCABC, the orthorhombic 9R with ABCBCACAB stacking and the hexagonal 2H with ABAB stacking [6]. (When the β phase has L2₁ long-range order they are denoted by 6R, 18R and 2H, respectively).

In the following some results are analyzed for the transformation from β to the 3R or 6R martensite in Cu-Zn-Al alloys as a prototype. It seems to be the only system for which a quantitative evaluation is available till now on which a discussion can be based. The transformation occurs between a long-range ordered bcc to a fcc based structure with the inherited long-range order. This is different from the transformation between the disordered phases by the contribution of the long-range order. The disordered phases are the equilibrium fcc α and bcc β phases that are present at elevated temperatures. Thus by simply adding the long-range order contribution it should be possible to describe the martensitic transformation.

Long-range order generally is described in terms of pair interchange energies \( w_{AB} \), which are a measure of the difference in electronegativity between the atoms. They are defined for an A-B alloy as the energy difference between two A-B pairs in i-th neighbor composition compared to an A-A + B-B pair in the same i-th atom distance, \( w_{AB} = -2V_{AB} + V_{AA} + V_{BB} \). When A-B pairs are favorable \( w_{AB} \) is defined to be positive. To carry out this program it is first necessary to derive the difference in Gibbs free energy between the α and β equilibrium phases. However, the enthalpy and entropy differences are so small that they cannot be measured experimentally with the required precision. The only well determined quantity is the temperature at which the difference in Gibbs free energy is zero. It lies within the α+β two-phase region, more precisely in the middle of it, as can be justified. The composition dependence of this equilibrium temperature \( T_{αβ} \) is thus known. It is the ratio of the enthalpy change \( ΔH_{αβ} \) and of the entropy difference \( ΔS_{αβ} \). In the Hume-Rothery noble metal alloys \( ΔH_{αβ} \) is due solely to an electronic contribution from the interaction of the Fermi surface with the Brillouin zone boundaries. The configurational contribution due to the pair interchange energies determines largely the enthalpy of mixing of each phase but does not contribute to the entropy difference. \( ΔS_{αβ} \) results mainly from the higher vibrational entropy of the more open bcc structure.

To describe the martensitic transformation, only an order term has to be added to \( ΔH_{αβ} \), whereas \( ΔS_{αβ} \) can remain unchanged. This has been justified elsewhere [7]. \( ΔS_{αβ} \) can be obtained from the martensitic transformation. The long-range order contribution is obtained by summing over all pair interchange energies in the disordered and the ordered state and taking the difference. It generally has been assumed that only the first and second neighbor pair energies are different from zero and that it is sufficient to sum only over them. This concept is not correct, however. It has been shown experimentally [8] that up to 20-th neighbor pairs contribute, consistent with the well established Friedel oscillations. Although the pair interchange energies have been found to decrease with increasing pair distance, the number of pairs increases, such that the product of both cannot be neglected when the total contribution to the configurational enthalpy of mixing is calculated.

Fortunately, the evaluation of the order contribution in the β phase and in the martensite, which is of interest here, is easy based on the following approximation, well known from many fields of physics. In it the discontinuous distribution of atoms is replaced by a continuum above a minimum distance from the reference atom. Ordering involves only atom redistributions of about an atomic distance, which in a continuum averages out to zero since the composition remains constant. Below this distance the real atom distribution has to be taken into consideration. A good approximation is obtained already by including only first and second neighbor pairs. Their pair interchange energies are quite large [8] and can also be evaluated reliably from ab initio calculations [9]. Thus if the first and second neighbor pair interchange energies are known for the β phase and the martensite the order contribution to \( ΔH_{αβ} \) can be calculated.

There is a very simple relationship between the pair interchange energies of the different structures, namely that they depend solely on the pair distance, but are independent of the crystal structure. This is not surprising for alloys whose core diameters are much smaller than the distances between the atoms, and in which the nearly free electrons provide the bonding. This behavior has been justified by the simple pseudopotential theory. This relationship is also
The shape memory alloys that have found a widespread application are those based on Ni-Ti. Nevertheless no quantitative evaluations seem to exist, although they would be of considerable interest. There are essentially two complications compared to the Cu-Zn based alloys. First there is a high entropy difference associated with the martensitic transformation, which furthermore seems to be strongly temperature dependent. It cannot be due to the soft long-wave \( \{110\}<1\bar{1}0> \) modes, because they are much stiffer as evidenced from the elastic constant \( C' \). Also in these transition metal alloys the density of states at the Fermi surface is very high, and it cannot be excluded that they also contribute to the enthalpy and entropy changes. A more quantitative evaluation would also be of advantage for the search of alloying elements that can increase the transformation temperatures and extend the use of the Ni-Ti based alloys at higher temperatures.

Thus the question proposed in the beginning can be answered at least for the Cu-Zn type alloys, and most likely also for other noble metal alloys. Contributions to the enthalpy difference arise from an electronic and a configurational part, and the entropy difference is due to a vibrational contribution. In the transition metal alloys the quantiative evaluation can be complex due to the contribution of the directional d-electrons, but the example of the Cu-Zn based alloys could be of some help.

4. What happens if after the martensitic transformation diffusion processes are permitted to occur?

This question is of considerable interest for the use in technological applications. Martensitic alloys that change their properties with time are not useful. This is one of the reasons why the Cu-Zn-Al alloys are not used extensively, in spite of being very cheap. If however the Zn is replaced by a few percent of Be or Ni in the Cu-Al based alloys a very different behavior is observed. The question in which way aging changes the properties and how it depends on composition and alloy system remains still open. This problem is being studied in the Centro Atómico Bariloche, and a few results shall be briefly mentioned.

During the martensitic transformation atom redistributions cannot occur. After the transformation changes can take place if in this way the Gibbs free energy can be reduced and if sufficient mobile vacancies are available for diffusion. The diffusion has been observed to lead to an increase in the retransformation temperature to the \( \beta \) phase and therefore is called stabilization. It also causes the martensite crystal to become more stable with respect to other variants of the same structure when it is attempted to stress induce them. Since on releasing the stress the original variant is restored, this is known as ferroelasticity, and more popularly as rubber-like behavior.

A great deal of experimental information on the stabilization and on the ferroelasticity is available for 18R [10-12] and for 2H [13, 14] Cu-Zn-Al alloys. Calculations have been performed for Cu-Zn-Al alloys to determine the atom distribution with the lowest Gibbs free energy in the martensite, using only the energy contributions from the first and second neighbor pairs [10]. Since the transformation entropy remains constant, it is only the enthalpy that is changed by the redistribution of the atoms. The calculations permit to identify the diffusion processes that are responsible for stabilization and ferroelasticity [10]. They indicate, however, that the stabilization should proceed to a larger extent than actually observed. This points to the other factor, the presence of mobile vacancies.

Very high excess vacancy concentrations can be made available. Since the vacancy formation energy is low in the \( \beta \) phase, a large number of excess vacancies can be retained after quenching from high temperatures. They are inherited after the martensitic transformation and accelerate diffusional processes, which are normally very slow in the close packed structures in which the vacancy formation energy is high. It seems to be reasonable to expect that the lowest energy configuration can be obtained if the vacancies remain available, but that it will not be reached if the excess vacancies anneal out earlier. A comparison with the experimental results [11, 12] shows that the maximum degree of stabilization depends on the quenching temperature. This seems to imply that the vacancies anneal out before the most favorable energy configuration is reached because otherwise the amount of excess vacancies should have no influence on the saturation stabilization once they are present in a sufficiently high concentration.

Surprisingly, this supposition does not agree with the observations. They show that the excess vacancy concentration remains high even after the saturation stabilization has been reached: When the stabilization effects are annealed out after retransformation and aging in the \( \beta \) phase, a second transformation and aging of the martensite leads to the same saturation stabilization as during the first time. This would not be expected if the excess vacancies had annealed out. A further support for the long lifetime of the vacancies in the martensite comes from the positron annihilation measurements [15]. The conclusion that has to be drawn from these results is that the excess vacancies decay very slowly, that they remain mobile in the Cu-Zn-Al alloys, but cannot redistribute the atoms that are responsible for stabilization. The reason for this unexpected behavior remains a puzzle.

To this puzzle has to be added the observation that the addition of a few percent of Be accelerates the decay or increases the inefficiency of the vacancies [17], whereas Ni seems to immobilize the excess vacancies from the start [18]. Furthermore, the 2H martensite at higher electron concentrations can be stabilized to a much higher degree than in the 18R martensite. It has been speculated [13] that the...
conduction electrons play an important role, since in many noble metal alloys hexagonal phases appear as equilibrium phases at similar electron concentrations, due to the interaction of the Fermi surface with the Brillouin zone boundaries [16].

It always has to be kept in mind that in the long-range ordered structures not all sites are equally favored by the vacancies. Instead a good rule of thumb indicates that a vacancy prefers to be located at a site in which it is surrounded by atoms with local configurations that correspond to an alloy with the lowest possible melting point. It therefore should not be surprising that the vacancies diffuse along easy paths that do not involve a redistribution of atoms responsible for the stabilization, once these configurations have been created during stabilization.

It has been argued [11] that in the β phase some vacancy ordering takes place, similar to that in the equilibrium γ phase at the same electron concentrations. Right after the transformation from the β phase some of the vacancies find themselves in less favorable positions. While they diffuse to the more favorable configurations in the martensite they can contribute to the stabilization.

It should also not be forgotten that the excess vacancy concentrations are at most of the order of 10^{-4}, and that therefore additions of several percent or less of alloying elements can produce an interaction which sensitively leads to a change in vacancy mobility. In which way the Be or Ni atoms are affecting the vacancy mobility remains an open question.

Concerning the question proposed above, it can be stated that on the basis of experimental results some suggestions can be made, but that the definite answer requires some more research. It is hoped that in the future the reasons for these peculiar behaviors can be better understood, helping also to develop cheap shape memory alloys with improved time stability for technological applications.

5. How can the properties of shape memory alloys be improved by thermomechanical treatments?

There is an ample spectrum of possibilities to modify the martensitic transformation in shape memory alloys by thermomechanical treatments. These modifications are often essential to obtain materials with the required properties for technological applications. In the following only a few examples will be given for the Cu-Zn-Al alloys and for the widely used Ni-Ti polycrystals. These examples are selected because they are considered to be useful to improve the required technological applications in many different alloys.

First example: The influence of grain size on the two-way shape memory effect (TWME) in Cu-Zn-Al alloys. As in many fields of materials science the grain size has an important influence on the properties of materials. It can be selected by an adequate thermomechanical treatment. This also occurs for the TWME. After cooling to the martensite below the Mₜ transformation temperature the shape of the sample can be changed by an applied stress, due to the increase of the favorable martensite variants. On reheating into the β phase matrix the original sample shape is restored. This shape does not change on a subsequent cooling below Mₜ without applied stress, and is called the one-way shape memory effect. By a special training the sample shape can be changed repeatedly during heating and cooling through the transformation temperature without an applied stress. This is the TWME. The quantities that are most important in the evaluation are the total strain obtained during the temperature change, and the work the sample can do against an opposing force.

Two types of training have been used, a cycling through the transformation or an aging of the martensite. The aim is in both cases to retain after retransformation a sufficiently high density of small martensite nuclei whose growth on cooling leads to the preferred martensite variants. The cycling can be done by repeatedly stress inducing the martensite above the Mₜ temperature, or by the temperature cycling around Mₜ at a given deformation. It leads to the formation of dislocation tangles. They favor on cooling the nucleation and growth of the variant that most effectively reduces the dislocation energy [19].

A disadvantage is the need to apply many cycles before a good TWME is obtained. The aging of the martensite is an alternative method that does not need the cycling, but that has been little applied till now.

The TWME obtained by aging has been studied for Cu-Zn-Al single and polycrystals of different grain sizes [20]. The single crystals were grown in the usual way by the Bridgman method. The polycrystals were obtained by quenching from the liquid. The addition of grain refiners permitted to reduce the grain size. When the single crystal is stressed in tension or in compression until the most favored single martensite variant has formed and subsequently is aged, stabilization occurs with an increase in retransformation temperature. After heating without applied stress to temperatures not far above the retransformation temperature of the stabilized variant, the sample shows a perfect TWME. It is due to the retention of a high density of thin retained martensite plates, called nuclei [21]. The reason why a high density can be obtained is the following. Initially the martensite plates have formed by the thickening of a small number of thin plates that have formed first on cooling. Due to the applied stress only one variant is induced in the whole sample. However, on reheating in the absence of stress they do not shrink in the opposite way. Instead, it is observed that the thick martensite is broken into thinner fragments by the growth of β phase plates that enter from the sides. In this way a large number of smaller martensite plates are retained. This fragmentation can be further increased by the repeated temperature cycling without an applied stress. If it is taken care that the sample is not heated to such a high temperature that even the small martensite plates disappear, a single crystal with a high density of
nuclei of a small volume fraction can be obtained. The advantage of the stabilization is that the nuclei remain stable up to elevated temperatures, about 100°C, whereas after the retransformation of the bulk the stabilization effects anneal out fast and the TWME can be obtained around room temperature. A high density of nuclei makes it difficult to create martensite variants of other orientations. Thus, even when an opposing stress is applied, the corresponding variants form with great difficulty or do not form at all. The aim of all aging treatments (and also the training by cycling) is to obtain a high density of favorable stable martensite nuclei, which permit that work against an opposing force can be done.

The TWME in single crystals has two disadvantages and one advantage, compared to the polycrystals. The production of the single crystals is costly, and the temperature to which the stabilized martensite can be heated without loosing the nuclei is very critical. But on the other hand the total TWME strain is higher in the single crystal. For these reasons polycrystals can often be more convenient. Whereas in the single crystal a martensite plate can cross the whole sample, in the polycrystals the grain boundaries constitute obstacles for the plate propagation. The stresses can be relaxed by the formation of compensating variants near the boundary. By aging, rather complex and stable configurations can be produced. Their stability can be expected to be a function of local and average grain size, and not all nuclei configurations have to disappear at the same retransformation temperature, as in the single crystals. Instead their density decreases gradually with increasing temperature, becoming also more stable with decreasing grain size. This is shown by the experiments [19]. Whereas for the single crystals a temperature is well defined above which the efficiency of the TWME decreases rapidly, in the polycrystals this decrease is slower at the smaller grain size. Therefore the temperature to which the stabilized martensite can be heated without loosing the TWME is not so critical as for the single crystal. Simultaneously, a sufficient density of stronger obstacles makes the formation of other variants more difficult and permits to do work against a higher opposing stress.

**Second example:** The influence of precipitates. The alloys that transform martensitically are generally only metastable and decompose on slow cooling by the formation of precipitates. The precipitates that most easily and rapidly grow are coherent and produce coherency stresses around them which influence the formation of the martensite variants. In the Cu-Zn-Al alloys the cubic γ phase precipitates are most easily formed. Their presence modifies the martensitic transformation, as has been amply analyzed [19].

The influence of coherent precipitates manifests itself spectacularly in the Ni-Ti alloys [22]. In alloys with more than 50.5 at% Ni coherent plates of $\gamma$Ni$_4$Ti$_3$ form easily on aging between 300 and 500°C. They produce an anisotropic stress field. If during the precipitation an external stress is applied, only the most favorable orientations grow. Their presence leads to the formation of selected martensite variants on cooling and is associated with a shape change. This TWME has been called the all-round shape memory effect.

**Third example:** The aging of the deformed matrix or martensite at more elevated temperatures, but below the temperatures at which recrystallization takes place. Many studies have been published with the main aim to produce shape memory materials with improved properties for applications [23]. One example in which deformation and annealing treatments in the martensite are essential for the production of alloys useful for application are the nearly equiatomic Ni-Ti alloys [22, 23] with an $M_s$ temperature between about +70 and −70°C. The problem with the Ni-Ti alloys is that they are only partially pseudoelastic in the fully annealed state. The martensite can be stress induced, but on unloading a large fraction of martensite is retained. The treatment that is applied to improve the degree of pseudoelasticity is to deform the material heavily, for example by cold rolling. By subsequently annealing at 400°C below the recrystallization temperature of about 600°C a very complex structure is created consisting of dislocations and small twinned martensite variants. In this way a full pseudoelastic martensitic transformation is obtained. Furthermore, the martensite grows in an applied stress by the propagation of Lüders bands at constant stress. This is an additional important feature, since generally in polycrystals the transformation stress increases with the degree of transformation.

6. **For what applications are shape memory alloys useful?**

The Ni-Ti based shape memory alloys have found widespread applications in medicine, due to their compatibility with the living organism. Different shape memory alloys are also being used for many technological applications, in some cases opening up new fields of application, in others improving the performance compared to the more traditional materials. In the following a few examples will be listed in order to show that the shape memory alloys are not only interesting from a scientific point of view, but are also new materials that have found already and continue to do so - uses in our modern material world.

**First example:** Medical applications. The Ni-Ti ‘nitinol’ materials are nowadays widely used to straighten out irregularly grown teeth, or a bent column by using the pseudoelastic behavior. As mentioned above, by the thermomechanical treatment the desired properties can be obtained, namely full pseudoelasticity and a constant transformation and retransformation stress, independent of the amount of transformation. Traditionally stainless steels had been used, but their disadvantage is that they behave elastically, with a strong decrease in stress with a
decrease in strain. Therefore they have to be adjusted frequently with the decrease in distortion.

Other important applications are the stents, devices that are used to expand diseased and constricted vessels and arteries [24]. They can be inserted in the pseudoelastic state, constrained by a surrounding flexible tube which is pulled off when the stent is located at the desired site and expands to the final diameter. An alternative is to introduce a stent in the compressed martensitic state at a lower temperature letting it expand when reaching the body temperature. One important problem is fatigue. The pressure at a stent installed in an artery varies periodically with the heartbeat of about one cycle per second producing internal friction. As an alternative stents of stainless steels are used. After insertion they have to be expanded by plastic deformation which is achieved by inflating a balloon from the inside.

**Second example: Nonmedical applications**

There are many nonmedical applications, and good summaries can be found in the literature [23, 25]. Some items are produced because they increase the comfort, as eye glass frames and the headband of headphones. Their pseudoelastic behavior guarantees that they exert a constant pleasant pressure at the head.

Couplings made of shape memory alloys have some definite advantages over the more traditional soldering. Rings of this material are cooled into the martensite phase, then are expanded. In this shape they are slipped over the tube ends which are to be connected. After warming up they retransform to the original smaller diameter. As an alternative alloys with a higher transformation-retransformation hysteresis have been developed that can be deformed in the martensitic state at room temperature. They retransform to the original shape only after heating and remain in this shape after cooling to room temperature due to the large hysteresis.

Microactuators have been developed in which a shape memory element changes its shape against an opposing force when the temperature is changed. The opposing force can be a spring that deforms the element at low temperatures in the martensitic state, but is too weak to prevent the original length from being restored on heating.

A great deal of activity is devoted to use the shape memory alloys as smart materials. When they sense an undesired change in temperature they change their shape on passing through the martensitic transformation temperature. This permits to activate a control system that cancels the temperature change, or takes other means to avoid damages. In this way the correct temperature for ‘mate tea’ can be guaranteed by cutting the electrical contact when the water gets too hot. Many other applications as smart devices that respond to a magnetic field by shape changes. The Heusler alloy Cu$_2$AlMn has the long-range ordered L2$_1$ structure, as Cu-Zn-Al and is ferromagnetic. Unfortunately it does not transform martensitically. Another alloy that is ferromagnetic and transforms martensitically is the Heusler Ni$_2$GaMn. Its study constitutes one of the most active fields of research [23,26], because it is expected that a shape change can be induced by magnetic fields that is much larger than the commonly used magnetostriction effect. Unfortunately the Curie temperature is the same in the β phase and in the martensite. However, by coupling the magnetization direction with the crystal orientation in the martensite crystal a change in magnetization direction and with it a shape change can be induced when the variant orientation is changed, and viceversa.

7. REFERENCES