

THE RULE OF MARTENSITIC TRANSFORMATION IN THE PHENOMENA OF SHAPE MEMORY

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Abstract

The authors are analysing the connection between the deformation and martensitic transformation. The essence and character of this connection is, that the mechanism of the plastic deformation agrees with that of the martensitic transformation, as both are going on with twinning and slipping. This fact gives the opportunity to connect plastic deformation and martensitic transformation in such a way, which makes the alloy forced to transformation having a shape memory.

Keywords: shape memory, martensitic transformation.

1. Introduction

The behaviour of the unalloyed steels but in many cases even of the low alloyed steels as a function of the temperature is to be determined based on the Fe-C equilibrium diagram. From the point of view of the workability or heat treatment of the steel, the interesting part of the diagram is the part of the eutectoid transformation, as seen on *Fig. 1*.

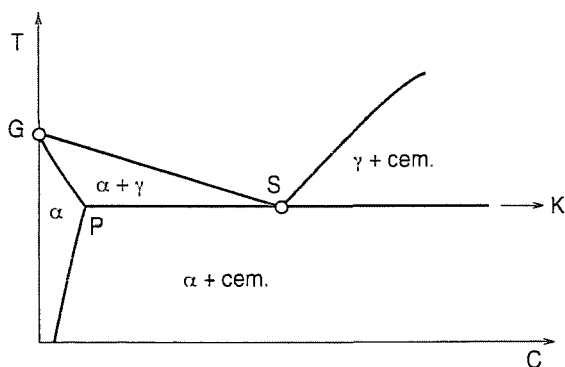


Fig. 1.

In equilibrium state the alloy is consisting of ferrite and cementite. In case of hypoeutectoid alloys these two phases are forming two different structures, the proeutectoid ferrite precipitated from the austenite, and the perlite, originated from the austenite with 0.8% C concentration – in an isothermic way at 723 °C – consisting of ferrite and cementite. For this transformation a rather long time is necessary because the carbon content of the ferrite at 723 °C is 0.02%, while that of the cementite is 6.687 weight %. Theoretically, the distribution of carbon in austenite is uniform, so the carbon contents of the developing two new phases are deviating from each other with more than 334 times.

In case of quenching, there is no time for these atomic movements, the austenite transforms without diffusion, the structure is martensitic, it is a composition of martensitic crystals – which are needle or plate shaped – and rest austenite.

If the cooling is not quick enough, there is a possibility for developing different structures with diffusion, like bainite, and the already mentioned ferrite and perlite.

2. Survey of Formulations

2.1. About the Martensitic Transformation

During the martensitic transformation the locations of the atoms are understandable on the basis of the Bain model, shown in *Fig. 2*.

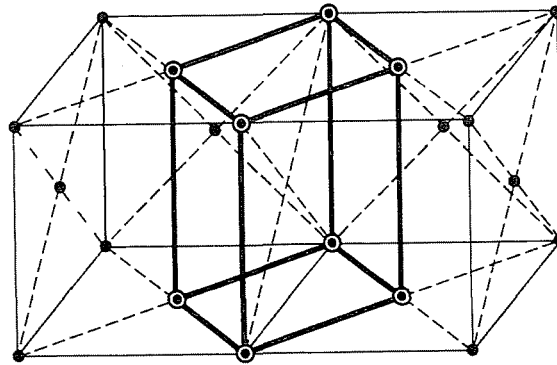


Fig. 2.

According to this in two neighbouring austenite cells, the bcc type structure of the ferrite is already included. This unit is of course tetragonal, with a height similar to that of the austenite, the bottom edge half of the face diagonal of it. For the location of the carbon atoms there are possibilities in the centre of the austenite unit cells, and in the middle of the cell edges. In

the reality the nature is not in the need of this. For instance a carbon content of 0.3% is equal with 1 atomic percentage, two iron atoms are belonging to one ferrite unit cell, that is with some approximation there will only be one C atom in each 50's ferrite unit cell. In accordance with this the tetragonality is dependent of the carbon content, and has not the same character like tin, in which all the unit cells are tetragonal regularly.

In case of the martensite, which is a ferrite structure oversaturated with carbon, the unit cell, which contains a carbon atom is highly deformed, while the neighbouring cells are deformed less and less, in a decreasing degree. In this structure the tetragonality of the crystal structure can be interpreted only on a statistical average.

2.2. Volume Changes

The transformations are accompanied with the changes of the properties, among which the most characteristic are the mechanical- the magnetic properties and the change of the specific volume. Even the process itself is usually followed by the measurement of the expansion - contraction.

The unalloyed, in principle carbon free austenite is the densest modification of the iron. The atoms considered rigid balls are filling in the space in 74%, while in case of the ferrite this factor is only 68%. The specific weight of the cementite and carbides are hardly different from each other.

The expansion curve of a non alloyed steel with very low carbon content is shown on *Fig. 3.a*. The section 1 ... 2 presents the austenization of the perlite, which in case of binary systems is an isothermal process. In case of steel this process, because of the presence of alloying elements and impurities, is a process with one degree of freedom, it is going on with increasing temperature. At the point 3, the curve becomes straight and follows a higher slope according to the higher heat expansion coefficient of the austenite ($\sim 10 \times 10^{-6} \text{K}^{-1}$), in comparison with the section concerning the perlite. In point 2 the sample contains ferrite and austenite, in the section between points 2 and 3 the ratio of ferrite is gradually decreasing, while the volume of austenite is increasing. Point 3 is the temperature marked by the GOS curve, or the A_{c3} temperature.

If the carbon content of the alloy is higher (but less than 0.8%), the ratio of ferrite austenite is higher already through the austenitizing of perlite, and the section of 1...2 gets longer, while the beginning of section 2...3 is lost. Such an expansion curve can be seen on *Fig. 3.b*.

The thermal expansion curve, as a result of the normal processing, a relatively quick heating up, followed by quenching is shown on *Fig. 4*.

During the heating by the contraction demonstrating the austenization, processes outlined above are merging. During quenching the sample is contracting with a higher steep according to the higher heat expansion co-

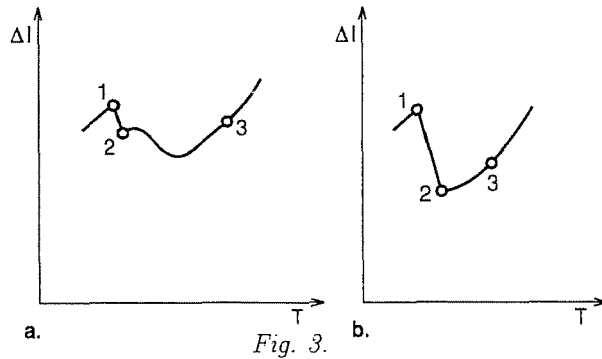


Fig. 3.

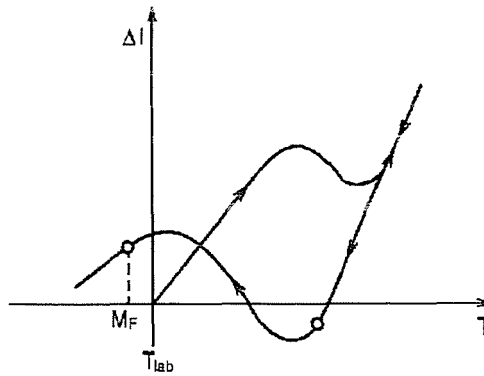


Fig. 4.

efficient of the austenite, and where the curve is deviating from the straight (M_s temperature), the martensitic transformation starts, which is accompanied with expansion. The formation of this section is dependent on the M_s temperature. The completion of the transformation, the M_F temperature, in case of alloys having higher carbon content falls below the normal room temperature. The M_s and M_F temperatures are practically dependent on the carbon content, and other alloying elements.

2.3. Thermal Characteristics of the Transformations

Fig. 5 is the free enthalpy of phases α and γ of the alloy with the given carbon concentration. T_o is the temperature where the free enthalpy of the two phases is equal, at the temperatures above the free enthalpy of the austenite, at temperatures below that of the α is lower. (The marking of α' is frequently used indicating that this is a ferrite oversaturated in carbon).

After a given overcooling ΔT the free enthalpy of γ at this temperature is so much higher than that of the α , that this surplus energy (ΔG) forces

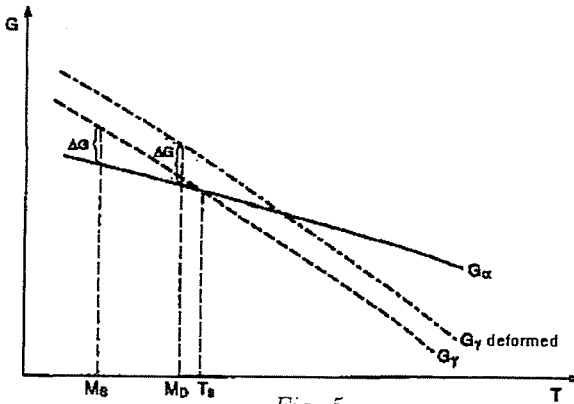


Fig. 5.

the crystal structure transformation. The M_s is the temperature of the overcooling measured to T_o , at which the metastability of the austenite becomes so high, that the energy difference available is able to produce the transformation without diffusion.

The martensitic transformation has been interpreted for a long time, like an irreversible one, because the process was connected strongly to the Fe-C system, and got its name also from here. In reality the PSK horizontal line of the diagram (A1 isotherm), refers during the heating to the first transformation process. The alloy in quenched state cannot be heated to this temperature as rapidly as to prevent the formation of ferrite-cementite mixture. This is the reason why in case of steels the process is really irreversible, or at least behaves like this.

At other alloys the martensitic transformation appears to be reversible, so there is a possibility and it is necessary to interpret the A_s and A_f temperatures, that is the characteristics of the starting and finishing temperatures of austenization.

Because of T_o A_s is not determinable, its value can be given according to the formula:

$T_o = (M_s + A_s)/2$, supposing the temperatures M_s and A_s are known. (Although $A_s - T_o$ is certainly less than $M_s - T_o$, but in this case this is not important).

The mechanical stresses increase the energy content of the alloy, so the free enthalpy of the deformed austenite is higher than that of the non-deformed. The excess energy which is needed ΔG is reached earlier (compared to α). That is the reason that the starting temperature (M_p) of the martensitic transformation is higher for the deformed austenite, than the nondeformed (M_s). The characteristic of the martensitic transformation is that it is possible to stop within a given temperature range $M_s < M_p < T_o$ with an external stress. M_p is dependent also on the degree of deformation.

The deformation with increasing of the starting temperature of the transformation ($M_s < M_p$), helps the martensitic transformation, decreases the volume of the always present second phase, so in case of steels helps the quenching process.

2.4. The Mechanism of the Transformation

The martensitic or diffusionless transformation is going on in each of crystals in a polycrystalline material independently and as we have seen the transformation itself is accompanied with shape and volume changes. Let us consider a transformation where the two phases in the transformation are α and γ . (Both can be equilibrium but metastable phase as well).

If the α phase is a single crystal the transformation takes place freely, but if in the neighbourhood of the α there are more crystals, neither shape nor volume change can happen without restraint. The originating γ crystal – as it can be seen on *Fig. 6* – can transform in the place available, if the structural change is going on together with twinning or slipping. Slipping and twinning are at the same time the basic mechanisms of plastic deformation.

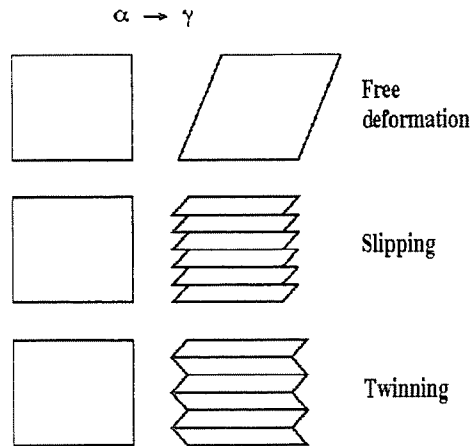


Fig. 6.

There is not even any other mechanism known for the formation of twinning. Based on this it is fully definite that the mechanism of the martensitic transformation is plastic deformation.

In such a way the martensitic transformation is connected to the orientation of the crystals, in each crystal independently of the neighbours. The product is the martensite, which is the result of the transformation of the austenite, a part of the matrix, with slipping. The conclusion is that the matrix and the product are in a crystallographic connection with each

other. The shape of the martensite is either needle- or disc-like. So among the three dimensions of it, the size of only one or two is important. The slipping itself has the consequence that there is an atomic line which does not move during the transformation, which is a part of the so called habit plane. Because there is a crystallographic connection between the product and the matrix, the border between of them is in principle coherent, or at least semicoherent, as a consequence of the presence of lattice faults. The border prevents the smaller and smaller matrix parts in the transformation, that is the M_F and A_F temperatures at which the transformation is finished, the matrix transformation has not finished in full size. This means that there is always some rest austenite, or rest martensite. These are operating like 'nuclei' during the retransformations, practically they remember the previous structure. (The word 'nucleus' here is not used of its thermodynamical interpretation). The retransformation is reversible not only in thermodynamical sense, but also – more or less – in crystallographical sense, too.

Diffusionless transformation is mentioned by non-metallic material, for instance by ceramics as well. In such cases, because the lattice is non-metallic, the mechanism must be different.

The transformation is always more different inside the material than on the surface. The clear evidence of it is the hardness difference measured on the surface of a Jominy test sample – near to the quenched end – and in the centre of the same diameter cylindrical sample. The transformation on the surface takes place much easier compared to that in the centre of the sample, because the neighbourhood inside the material prevents the volume increase. This results a delay in the transformation, which happens than only in a lower temperature, where the formation of nucleus and growing with the help of diffusion is not possible any longer.

2.5. Shape Memory

The martensitic transformation accompanied with shape and volume changes modifies the attitude to treat the change of sizes as caused by heat expansion or mechanical stresses, and gives opportunities for the observation and use of new phenomena.

If there has been no martensitic transformation inside the metal or alloy, the size of the sample (in theoretical tests the length) is really determined by the temperature and the mechanical stresses as shown in *Fig. 7*.

If there were no external forces in operation, or the value of them can be considered as constant, the material changes its sizes because of the temperature changes. If at the same time there is also a martensitic transformation, the accompanied volume and length changes are taking place freely, as can be followed on *Fig. 8*.

transformation becomes oriented. That is the reason why the 'training' is unavoidable by the application of the phenomena. Many transformations in the proper behaviour of the alloy can be trusted only after producing.

A new phenomenon is met with, if the alloy – participating in the transformation – is loaded by external mechanical stresses. The alloy (in stable α state at lower temperature), following the Hooke law is elongated, while inside, as an effect of a stress less than the yield stress, martensitic transformation takes place. In some certain crystals, oriented favourable for the σ stress, as a result of slipping or twinning γ phase is formed. In case of further loading new and new slip systems are activated, and as a consequence of their interaction a so called elastic hardening can be experienced, after which the curve is increasing considerably.

During downloading, the as long piled up transformation stresses in the matrix (in the γ phase) make possible the martensitic transformation – with some hysteresis – to take place into the opposite direction. *Fig. 9* helps to understand the process.

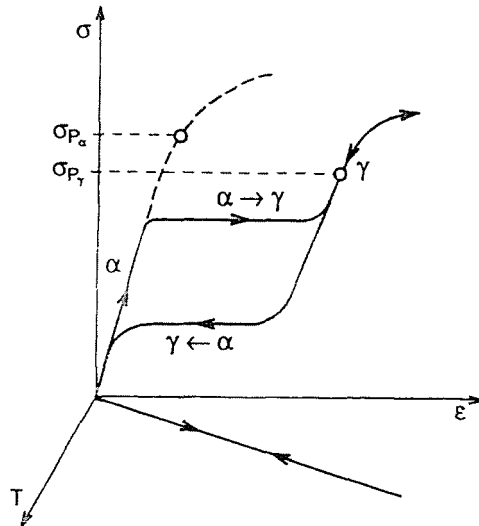


Fig. 9.

In the literature these phenomena are mentioned as pseudo-elasticity, because the volume changes with the transformation are increasing the elastic deformation. This deformation is relatively high, based on the references in the literature can reach even 22%. The phenomenon is called pseudo-elasticity if in the – at given temperature (i.e. room temperature) stable – α phase some mechanical stresses create the γ phase with martensitic transformation, which stays at this temperature stable also after downloading.

For retransformation as it can be seen in *Fig. 10* heating is necessary.

This version in the literature is called 'single way', because at constant temperature as we have seen, there is a relatively important length change.

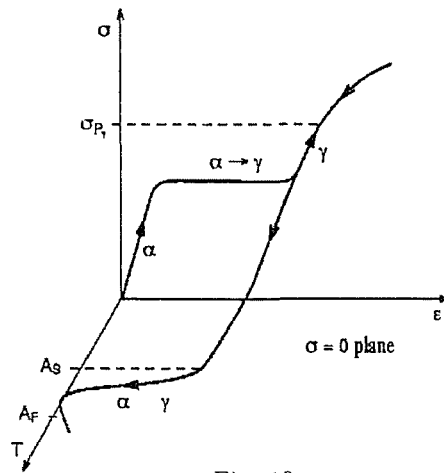


Fig. 10.

This characteristic behaviour of the so called 'shape memory' alloys is based on the martensitic transformation, the γ phase (austenite) stable at higher temperature during cooling at lower temperature transforms to stable α (martensite) phase, without diffusion. The temperatures of transformation are determined not only by the chemical composition, that is the thermodynamic equilibrium, but is effected by the mechanical properties of the given phase as well. Among the lot of crystallographic slip systems some, the orientation of which to the external stresses are favourable, are activated, the transformation takes place, which is accompanied by deformation. The process taking place together with the changes of the temperature and mechanical stresses, is practically reversible.

3. Conclusion

This type of interpretation of the connection of plastic deformation and martensitic transformation that such a fundamental structural condition is required for the shape memory are new results.

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