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Study on martensite strengthening mechanism and phase transition

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ABSTRACT

Martensite is a type of ferrous. This paper was started with the martensite morphology and transformation process and mainly describes strengthening and toughening mechanisms of martensite with new progress of martensitic transformation, including martensitic transformation characteristics, martensitic transformation thermodynamics, martensitic crystal transformation, and so on.

KEYWORDS: martensite, strengthening mechanism, martensitic transformation, phase change thermodynamics, phase change crystallography

1. Overview of martensite

Martensite is a kind of organization of ferrous metal material. The steel is heated to a certain temperature (after the formation of austenite) after the rapid cooling (quenching), can make steel hardened, enhanced a quenched tissue.

Martensite was first discovered by a German metallurgist Adolf Martens (1850-1914) in a hard mineral in the 1890s. The three-dimensional morphology of martensite usually has a plate or lath, but in gold phase observation (two-dimensional) usually appears as needle-shaped, which is why in some places usually described as needle-like reasons. The crystal structure of martensite is body-centered quadrilateral structure (BCT). Accelerated cooling in medium and high carbon steels is usually possible to obtain such tissue. High strength and hardness are one of the main characteristics of martensite in steel. Since the 20th century, the martensitic transformation of steel in the characteristics of the accumulation of more knowledge, and have been found in some pure metals and alloys also have martensitic transformation, such as: Ce, Co, Hf, Hg, Ag-Zn, Au-Cd, Au-Mn, Cu-Al, Cu-Sn, Cu-Zn, In-Tl, Ti-Ni, and so on. At present, the basic characteristics of the martensitic transformation of the phase change products are collectively referred to as martensite.

2. Martensite morphology

A great deal of research has been done on the morphology of martensite, and many different forms of martensite have been found, and the relationship between martensite and its fine structure and properties has been found resulting deeper understanding about crystal structure of martensite. Although the martensitic morphology is diverse, but its morphological characteristics can be summarized as the strip martensite and lamellar martensite two categories, the fine structure can be divided into dislocations and twins. At the same time, it was found that the martensite and the mother phase maintained a strict crystal degree relationship.

2.1. Striped martensite

Mainly formed in the lower carbon content of steel, also known as low-carbon martensite. Because of its formation in the high temperature above 200 °C, it is also known as high temperature martensite; because of its fine (sub) structure for high density (usually $0.3 \sim 0.9 \times 10^{12} \text{cm} / \text{cm}^2$) dislocation, it is also called dislocation horse body.

Under the optical microscope, the main morphological features of the strip martensite are: in the form of bundles. Close to the parallel length and almost equal to the composition of a piece of martensite, or martensite 'field' (for example, plate group). The size of the slabs is about 20 to 35 μm , and the composition of the slats is approximately parallel to each other in the space, and in the grains of the original austenite, several clusters of martensite (that is, a few

slats, often 3 to 5, each slat is a martensitic single crystal, its size is about $0.5\mu\text{m} \times 5.0\mu\text{m} \times 20\mu\text{m}$), martensite slab has a flat interface, the interface approximation parallel to the austenite $\{111\} \gamma$, that is, habitual surface, the same habit of martensite slats arranged in parallel to form a martensite plate group. It has been determined that these dense martensite slats are separated by successive highly deformed retained austenitic films (about $20 \mu\text{m}$), and the inter-slab residual austenite films have a higher carbon content at room temperature. Under the very stable, the mechanical properties of steel will have a significant impact. The martensite beam is separated from the beam by a large angle phase interface, typically 60° or 120° , and the martensite does not go beyond the original austenite grain boundary. The martensite strips in the same bundle are separated by a small angle crystal interface. Each bundle will be black and white tone contrast, the same tone area of the slats with the same bit direction, called the same slab area.

2.2. Chip martensite

Flaky martensite is mainly formed in high carbon content of steel, also known as high-carbon martensite; because it is formed in the low temperature below 200°C , it is also known as low temperature martensite; because of its fine (sub) structure for a large number of twin, it is also known as twin martensite. This twins disappear at the boundary near the martensite slice and do not pass through the martensite boundary, while the sub-structure on the boundary is a complex dislocation network, which has been identified: the mid-ridge of the martensite is still the density of the ultra-fine twin.

The form of the lamellar martensite is lenticular. Under the optical microscope is the observation of the cross-sectional shape, because the sample grinding surface of each martensite cutting angle is different, it is needle-like, bamboo-like, so called needle (bamboo) -like martensite, the martensite pieces are not parallel and intersect at an angle (such as 60° , 120°). In the original austenite grains, the first formed martensite film is through the entire grain, but generally do not pass through the grain boundary, only the austenite grain division, after the subsequent formation of martensite due to be limited getting smaller and smaller. Therefore, the maximum size of the sheet martensite depends on the original Austenite grain size, the original austenite grain thicker, and the larger the martensite, and vice versa is finer. When the largest size of the martensite film to the optical microscope cannot be resolved, it is called latitude (or known as hidden needle) martensite.

The basic feature of the flaky martensite is that the first martensite needle formed in an austenite grain is thicker and tends to traverse the whole austenite grains, and the austenite grains are divided so as to form later of the size of the martensite needle is limited, so the needle-like martensite of different sizes, but its distribution has a certain law, basically martensite by approximately 60° angle distribution. And in the martensite needles in a ridge surface, the higher the carbon content, the more obvious, and around the travertine in the retained austenite. As the needle-like martensite formed at a lower temperature, so the self-tempering phenomenon is very weak, in the same reagent etching, the lath martensite is always bright.

The hardness of martensite depends mainly on its carbon content. With the increase of carbon content, the hardness of martensite increased, when the carbon content of the mass fraction of 0.6%, the hardness of hardened steel close to the peak value. When the carbon content is further increased, although the martensite hardness has increased, but the amount of retained austenite also increased, will make the hardness of steel decreased. The alloying element has little effect on the hardness of martensite, but it can improve its strength.

2.3. Other forms of martensite

(1) Latitude (or hidden needle) martensite

In the actual production, high-carbon steel or high-carbon high-alloy steel normal heating and quenching, the original austenite grain is very small, the formation of the martensite crystal is very fine, in optical microscope cannot see the martensite form, known as the latitude (or hidden needle) martensite. In general, when the carbon steel is heated rapidly, fine austenite grains are obtained. After quenching, the mixed structure of fine strip and lamellar martensite is obtained, and the martensite morphological characteristics are not observed under the optical microscope, is also a kind of aphanitic martensite.

(2) Butterfly martensite

In the Fe-Ni alloy and the Fe-Ni (-Cr) -C alloy, when the martensite is formed in the temperature region between the tandem martensite formation temperature range, martensite having a specific morphology, the martensitic three-dimensional form of 'V' -shaped column, the section was butterfly-shaped, it is called butterfly martensite or polygonal martensite. The habitual surface of the butterfly martensite is $\{225\} \gamma$, and the joint surface of the two wings intersects $\{100\} \gamma$. Electron microscopy showed that the internal substructures of the butterfly martensite were high density dislocations and no twins existed, and the relationship with the crystallographic orientation of the parental phase was in good agreement with the K-S relationship.

(3) Flaky martensite

In the very low Fe-Ni-C alloy at the Ms point, a sheet-like martensite having a thickness of about 3 to 10 nm was observed, and its shape was flaky, and the surface of the Fe-Ni-C alloy was flat the latitudinal band, the belt can intersect with each other, showing the shape of twist, branch and so on. The habitual surface of the flaky martensite is $\{259\} \gamma$, the relationship between the belt direction and the austenite is KS, and the internal substructure is $\{112\} \alpha / \text{twin}$, the width of the twins decreases with increasing carbon content. The straight belt is in the middle of the ridge, which is the difference between it and the chip martensite.

(4) ϵ martensite

Each of the above martensite is a martensite (α / γ) with a body-centered cubic (square) lattice structure. In the Fe-Mn-C (or Fe-Cr-Ni) alloy with low austenite layer, it is possible to form ϵ -martensite with dense hexagonal lattice structure. ϵ martensite is very thin sheet, the thickness of only 100 ~ 300nm, the internal sub-structure of high-density layer fault. ϵ -martensite has a habit of $\{111\} \gamma$, and the relationship between the austenite is $\{111\} \gamma // \{0001\} \epsilon, \langle 110 \rangle \gamma // \langle 1120 \rangle \epsilon$.

2.4. Factors that affect martensite morphology

Experiments show that the martensite morphology of steel mainly depends on the martensite formation temperature and the content of carbon and alloying elements in supercooled austenite. For carbon steel, with the increase in the amount of carbon in the steel, the relative amount of striped martensite decreases, the number of plate-like horse body is relatively increased. In general, when the austenite carbon content greater than 1%, after quenching almost completely flaky martensite; when the austenite carbon content of less than 0.2%, after quenching almost completely strip martensite. When the carbon content is between 0.20 and 0.40%, the mixed martensite is the main structure. When the carbon content is between 0.40 and 0.80%, it is mixed structure of strip and lamellar martensite. In addition to cobalt, aluminum, the majority of alloying elements are so Ms points decline, it is increased martensite twin tendency. Although cobalt increased Ms points, but cannot reduce the martensite internal twins.

In addition, stress and deformation can also change the martensite morphology, in the high static pressure, can significantly reduce the Ms, in the low carbon steel to obtain large martensite. If the Ms point is not too high temperature plastic deformation, will significantly increase the content of strip martensite.

3. Martensite strengthening mechanism

The strengthening mechanism of the metal can be divided into solid solution strengthening mechanism, second phase strengthening, deformation strengthening and fine grain strengthening. In recent years, the nature of martensite high strength and high hardness has been studied extensively. It is concluded that the high strength and high hardness of martensite are the result of comprehensive effect of various strengthening mechanisms. The main strengthening mechanisms include: phase change strengthening, solid solution strengthening, aging strengthening, deformation strengthening and fine grain strengthening.

3.1. Phase change enhancement

(6Cr-1C) (640-700 [HV]) with the highest hardness in stainless steel belongs to the martensitic stainless steel, the structure of the martensite structure is very high. Fine, but also in its internal high-density dislocation, if the carbon super-saturation solution can also improve the strength. On the other hand, after the final tempering treatment can be carbide and other precipitates dispersed finely distributed organization. For example, SUS 420J2 (13Cr-0.3C) from the 1000 ~ C high temperature austenite quenching, the occurrence of solid solution 0.3% C of the Martensitic body phase change, and then by the tempering heat treatment will make carbide and other precipitates were fine dispersion distribution of its strength can reach about 550HV.

3.2. Fine grain strengthening

People already know that grain size affects metal strength. The effect of ferrite grain size on the yield strength of annealed soft steel shows that there is a linear relationship between grain diameter d and yield strength, and the grain yield is higher. The relationship between the yield strength and the grain size is called Hall-Petch's law. Because of the dislocation of the motion in the grain, the motion is blocked at the grain boundary. Therefore, grain size of the fine grain material high. If the solid solution strengthening, precipitation strengthening, and work hardening are excessively increased, toughness is impaired. Therefore, sometimes depending on the processing, the use of conditions to a certain degree of strength restrictions. On the other hand, when grain refinement not only does not damage the toughness, but also can improve the strength. Now, study of the grain refinement of steel materials is very popular, and the development of super metal technology development. The development of stainless steel grain diameter is usually tens of microns,

but in these subjects is studying, for example, an austenitic stainless steel having a grain diameter of 300 nm having a tensile strength of 1100 N/mm², which is about the average particle size of the material. 2 times in order to be able to damage without damage to the premise of high strength, this method has a great hope in the JIS stainless steel with the existence of microstructure of stainless steel, which is the composite of different organizations biphasic stainless steel, SUS329J4L (25Cr-6Ni-3Mo-N) has a structure in which the island-like austenite phase is distributed in the ferrite matrix, and the microstructure is fine because of the composite structure. The strength of the biphasic steel is better than that of the austenite and the iron system due to the combined effect of grain refinement and solid solution strengthening.

3.3. Solid solution strengthening

Pure metals, due to their low strength, are rarely used as structural materials, and are widely used in industrial alloys than pure metals. The uniformity of the lattice formation of the alloying element into the matrix metal is called a solid solution. Pure metal once the alloy composition into a solid solution, its strength, hardness will increase and plasticity will be reduced, this phenomenon is called solid solution strengthening. The mechanism of solid solution strengthening is: the deformation of the metal material is mainly to rely on dislocation slip to complete, so those who can increase the dislocation slip resistance factors will increase the deformation resistance, so that the material to strengthen. Alloy composition into the matrix metal lattice to form a solid solution, not only the lattice distortion, while the dislocation density increased.

The results show that the yield strength of martensite increases with the increase of carbon content when the carbon content is less than 0.4%. When the carbon content is more than 0.4%, the yield strength of martensite is not increased. This phenomenon is generally explained that the solid solution of the gap C atoms in the Fe atom composition of the octahedral center of the position, the octahedron in the martensite octahedron (austenite in the austenite), after C atoms are dissolves, then formation of C atoms as the center of the distortion of the dipole stress field, the stress field and dislocation have a strong interaction, so that dislocation movement to martensite strength. When the carbon content is higher than 0.4%, the C atom spacing is too close, the resulting distortion dipole stress field cancel each other, reducing the strengthening effect.

3.4. Deformation strengthening

The main method of producing metal materials is plastic processing, that is, under the action of external forces in the metal material plastic deformation, so that it has the expected performance, shape and size. The plastic deformation below the recrystallization temperature is called cold deformation. Metal materials in the cold deformation process strength will gradually increase, this phenomenon is called deformation strengthening.

When the steel is deformed, the shear stress is added to the crystal, and a large amount of dislocations are introduced into the crystal at the same time as the dislocation movement. Machining hardening, machining rolling and roasting, this plastic deformation increases the dislocation density within the crystal and is a method of strengthening the steel. According to Chongqing 304 stainless steel coil research shows that this work hardening effect Austenite system is much larger than the ferrite system. In the 18Cr-8Ni composition of the metastable austenite system, due to the dislocation density increased hardening and martensite formation (processing caused by phase change) easy to get high strength. The strength of the hardened material can be divided according to the H (hard), 3 / 4H and 1 / 2H strength levels according to the change of the rolling rate. The SUS 301 (17Cr-TNi) hardening material is used in the household electrical machinery of the spring and the engine of the engine washers, communications machinery, connecting equipment, such as board spring products is very popular. The martensite caused by work hardening has magnetic properties, so that the hardened materials of SUS 301 and SUS 304 are also magnetic. Non-magnetic spring material contains high manganese stainless steel AISI205 (17Cr-15Mn-1.5Ni-O.35N), the steel is replaced by manganese in the SUS 301 nickel, because of its different nature, more nitrogen. That is, the effect of the solid solution strengthening can be obtained. The hardness of the SUS 304 is about 1801 tV in the solution treatment state, and the hardness of the AISI 205 is about 2701] V, and a significant work hardening characteristic can be found in the processing. All steel grades increase as the reduction rate increases.

3.5. Aging enhancement

Temporal strengthening is also an important factor in martensite strengthening, martensitic transformation is no diffusion phase transition, but after the formation of martensite, martensite in the carbon atoms of the poly (martensitic self-tempering) can occur, carbon atoms segregation (aging) results, the higher the carbon content, the more significant the aging effect.

The aging enhancement is caused by the C atom diffusion segregation pinning dislocation. Therefore, if the martensite is formed at room temperature and the diffusion of the C atoms is not suppressed during the quenching and cooling, the C atom diffusion segregation is naturally formed during quenching to room temperature, and the aging

is exhibited. Therefore, for MS above the room temperature of the steel, in the usual quenching cooling conditions, quenching process that is accompanied by self-tempering.

3.6. Sub-structural strengthening

Sub-structural strengthening mainly refers to the strengthening of twin or stacking, which is manifested in the following aspects:

- (1) The elastic interaction of dislocations and twins;
- (2) Dislocations through twins to form a slip track;
- (3) Twins block dislocation movement.

It should be noted that the strengthening of twinning is believed to be due to the segregation of carbon atoms at the twin interface, and its contribution to the strengthening effect is closely related to the carbon content of the steel: when the carbon content is less than 0.3% the strengthening of the body mainly lies in the solid solution strengthening of the interstitial atoms. When the carbon content is 0.3% -0.6%, the increase of the martensite strength is in addition to the solid solution strengthening, but also the twin and dislocation substructures strengthen the contribution; when the carbon content is greater than 0.6%, the twin effect of strengthening is very weak.

4. Martensitic transformation

4.1. Martensitic transformation concept

The martensite (M) is a supersaturated solid solution of carbon dissolved in α -Fe and is a metastable phase of austenite transformed by a non-diffusion phase transition. Its specific volume is greater than the austenite, pearlite and other organizations, which is produced quenching stress, leading to deformation and cracking of the main reasons. Martensite was originally found in steel (medium and high carbon steels): the steel was heated to a certain temperature (after the formation of austenite) after the rapid cooling (quenching), can make steel hardened, enhanced one quenched tissue.

4.2. Martensite concept proposed

The concept of martensite was first discovered by a German metallurgist Adolf Martens (1850-1914) in a hard mineral in the 1890s. Austenite carbon content $\geq 1\%$ of the steel quenching, the martensite sheet formed, when the austenite carbon content $\leq 0.2\%$ of the steel quenching, the martensitic shape of the basic slats martensite. The crystal structure of martensite is body-centered quadrilateral structure (BCT). Accelerated cooling in medium and high carbon steels is usually possible to obtain such tissue. At present, the basic characteristics of the martensitic transformation of the phase change products are collectively referred to as martensite.

4.3. Martensitic transformation characteristics

The general definition of martensitic transformation is that the undercooled austenite is cooled at a faster rate to suppress its diffusivity decomposition, and the non-diffusion phase transition occurring at a lower temperature is called martensitic transformation. Its main features are the following:

1) Martensitic transformation is a non-diffusion phase transition. Martensitic transformation does not cross through the interface of the atomic random walk or jump in sequence, so the new phase (martensite) inherited the parent of the chemical composition, atomic sequence and crystal defects. When the martensitic transformation, the atoms regularly maintain the relative relationship between adjacent atoms to displace, this displacement is shear type. The result of atomic displacement produces lattice strain (or deformation). This shear displacement not only changes the matrix lattice structure, but also produces a macroscopic shape change.

2) To produce surface phase transition when the float. The shape of the martensite changes so that the surface of the polished sample is floated. When martensite is formed, it is tilted on the surface intersecting with martensite, and the height of the float and the sharp edges are seen under the interference microscope.

3) The new phase (martensite) and the mother phase always maintain a certain bitwise relationship. Martensite transformation in a certain phase on the mother phase to form a new phase martensite, the surface known as the habit (analysis) surface, it is often not a simple exponential surface, such as nickel steel martensite in austenite (γ) $\{135\}$. There is a large strain on the interface between the martensite and the parent phase. In order to partially reduce this strain energy, auxiliary deformation occurs and the interface is changed. As the martensitic transformation of the atoms

when the regular displacement, so that the new phase (martensite) and the mother phase always maintain a certain bitwise relationship.

4) Martensitic transformation is reversible. When the mother phase cooling at a certain temperature began to change into martensite, the temperature marked M_s , martensite transformation into the mother when heated, began to change the temperature marked as ' A_s '.

5) Martensite transformation is done in a temperature range. When the austenite reaches the martensitic transition temperature (M_s), the martensitic transformation begins to occur, and the austenite structure begins to be unstable. A small part of the austenite structure changes rapidly after a certain temperature below M_s , but does not continue. Only when the temperature is further reduced, more austenite is converted to martensite. Finally, the temperature reaches the martensitic transition end temperature M_f , and the martensitic transformation ends.

4.4. Martensitic transformation thermodynamics

The main task of the study of martensitic transformation thermodynamics is to theoretically determine the temperature at which the material begins to undergo martensitic transformation. This temperature is not only a major parameter in the material heat treatment process, but also often characterizes the properties of the material after quenching such as brittleness. The study of martensitic transformation thermodynamics not only reveals some natural laws of material phase change (and consequent changes in internal organization and performance changes), explains some experimental phenomena, and more importantly, the design and processing of new materials design basis. The thermodynamics of the martensitic transformation of the Fe-based alloy has been embryonic in the 1940s, but it cannot be directly calculated by thermodynamics. The thermodynamic problem of the martensitic transformation of the copper-based alloy is only slightly involved in 1979 and is very immature. In the past 10 years, we have made important research on the thermodynamics of martensitic transformation of Fe-based alloy and copper-based alloy. Thermodynamics can be used to calculate iron-carbon alloy, iron alloy (such as Fe-Ni), ternary alloy steel (such as Fe-Ni-C), multicomponent alloy steel, and copper-based alloys (such as Cu-Zn), and are in good agreement with the experimental values. (And the amount of retained austenite) In different parts of the infiltration layer after carburization, and the copper alloy in the thermoelastic martensitic transformation, the parent phase influence of ordered states of atoms on M_s . For the iron-based alloy, the face-centered cubic austenite into the body-centered cubic (or tetragonal) martensitic thermodynamic study, in the past because of the non-chemical free energy terms difficult to estimate, so that cannot be successfully obtained by thermodynamics M_s , a few study has been stagnant over the past decade. According to recent research results, the non-chemical free energy is proposed as parameter. The thermodynamic model (including the Fisher model, the KRC model and the central atom model) is improved and developed by the yield and the martensite storage energy (the result is almost constant), got a satisfactory result. The study of B-Cu based alloys solves the orderly thermodynamics, the use of phase diagrams or interatomic exchange to establish a regular solution model, and establishes the basis for thermodynamics of thermo-elastic martensitic transformation. The experimental method for the determination of non-chemical free energy in the martensitic transformation of Cu-based alloys has been developed, which enriches the contents of phase change and is also beneficial to the development and application of shape memory materials. At home and abroad research work that Cu-Zn-Al slightly lower than the M_s isothermal, will form the so-called 'isothermal martensite.' It is proved that this is not isothermal martensite, but in the isothermal state of the orderly change, M_s is rising, continue to form the temperature martensite. The thermodynamics can be used to determine the M_s required by the engineering industry, to identify and explain the existing experimental phenomena and data, and to quantitatively predict the change of M_s in different quenching states. These copper-based shape memory alloy composition design, heat treatment process development is essential.

4.5. Martensitic transformation crystallography

In the past 40 years, the theory of martensitic transformation has been widely used. The prediction of martensitic transformation of Au-Cd alloy and iron (3, 10, and 15) martensite is in agreement with the experimental data, which proves the correctness of the theory; but the Cu-Zn and Cu-Al-Ni alloy will need to be developed. We use the WLR theory to study the Cu-Zn-Al alloy, and obtain the thermo-elastic martensite habit of (1, 7.71, and 9.32) and the experimental value (1, 6.88, and 7.90) difference of only 1.6°. So that the original representation theory has its vitality. Martensitic transformation process, the new and old phase between the symmetrical connections. In the Cu-Zn-Al shape memory alloy in the symmetrical relationship, should try to cluster Lun calculated Cu-Zn-Al alloy martensitic metamorphosis. The application of cluster theory to martensitic transformation crystallography remains to be extended and deepened.

5. Conclusion

Martensite from its birth has been to many years of history, but people's understanding of martensitic transformation is not enough depth, there are many problems to be solved. Recently, will be published by the Science Press, Liu

Zongchang et al. monograph 'Martensitic Transformation' a book covering the metal integration system, phase change process of atomic movement, phase change thermodynamics dynamic histology crystallography, phase change the mechanism, performance and quenching applications such as the use of inheritance and innovation combined with the latest research results at home and abroad, complement the updated content to meet the construction of innovative society in the 21st century, due to the martensitic transformation of the important prospect of science, science should continue to pay attention to, and constantly improve China's phase change research work to develop China's materials science.

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