A study on the microstructural evolution and subgrain size dependent constitutive equation of a type of maraging steel in the solid solution treatment process

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Abstract

00Cr12Ni9Mo4Cu2 is an ultra-high strength, maraging stainless steel. Optical microscopy, microhardness measurement, scanning electron microscopy (SEM), and transmission electronic microscopy (TEM) were used to quantitatively investigate the effect of the solid solution parameters on the grain size and the secondary phases of the steel. It was found that the grain size increased from 8.5 μm to 28 μm when the solid solution temperature was increased from 960 °C to 1040 °C. Meanwhile, the strength of the alloy increased from 822 MPa to 1054 MPa. However, when the temperature was increased from 1040 °C to 1100 °C, the grain size rose dramatically to 55 μm, and the strength of the alloy decreased from 1054 MPa to 782 MPa. Most of the original carbides were dissolved when the solid solution temperature increased up to 1040 °C. Finally, a constitutive equation based on the evolution of the subgrain size is proposed, clarifying the relationship between the mechanical properties and microstructures.

Introduction

Generally, a high strength is typically required for the industrial application of materials, whereas a low strength is necessary for their preparation. This contradiction is a challenge for scientists and engineers.

Recently, a type of material—maraging steel—was invented [1−3]. This material can be prepared in a low flow stress by a solid solution treatment. And its strength can be drastically enhanced by the following ageing treatment [4, 5]. This material has drawn the attention of materialists and designers in the industries of aerospace, nuclear energy, and other fields of engineering [6, 7].

The ultimate strength of the maraging steel can be as high as 3000 MPa [8, 9]. This ultra-high strength depends on the solid solution, martensite, and ageing strengthening process.

The solid solution strengthening process of the steel is the first and most important step in achieving ultra-high strength [10, 11]. If the duration of the solid solution process is not sufficiently long, or the temperature is not sufficiently high, the coarse and the original carbides will not be dissolved completely, leading to a deterioration of mechanical properties. A too high temperature or a too long duration in the solid solution process may also lead to the coarsened grains and the deterioration of the mechanical properties. A large number of researches on the heat treatment processes have been conducted [12−15]. However, few quantitative studies have been conducted on the grain growth and the dissolution of the secondary precipitates in the solid solution process, which would potentially be important references for materialists or engineers, in terms of improving the mechanical properties of this type of steel.

00Cr12Ni9Mo4Cu2 is a typical maraging steel which has a strength of more than 3000 MPa [16, 17]. The microstructure study will be performed on this steel in its solid solution process. The quantitative relationship between its microstructure and mechanical properties after the solid solution treatment process will be clarified in this paper.
The material and experimental procedure

The maraging steel used in the study is 00Cr12Ni9Mo4Cu2. Its chemical composition is listed in table 1. The as-received steel in this study is a hot-rolled strip with a thickness of 1 mm. The strip was cut into multiple pieces sizing in 5 mm × 5 mm for further solid solution treatment and microstructure measurement.

Because the content of Mo and Cr are 4% and 11.9% respectively, a relatively high temperature is needed for the solid solution of the steel. The specific solid solution treatment process used for the steel is shown in table 2. It was performed in a muffle furnace. Following the solid solution heat treatment, the steel samples were then removed from the furnace and placed directly into water at room temperature.

The Vickers hardness test was conducted. The average of the measured value of the 20 points for each sample is regarded as the hardness of the studied steel. The strength of the steel can also be measured using the hardness/strength relationship [18, 19].

The rolling surfaces of all samples were polished and then etched in a solution of 4%HNO₃ + 4%HF + 92%H₂O. The microstructure parallel to the rolling surface of the strip was then analyzed.

The SEM observation was undertaken using the field emission Sigma-300 system.

The disks in a diameter of 3 mm of the steels were polished using a twin jetter in an alcohol solution with a volume of 10% HClO₄, with a voltage of 30 V, at −20 °C. The microstructure of these prepared samples was further analyzed on the H-800 TEM system.

Results and discussion

Mechanical properties

The measured mechanical properties of the steel treated at different temperatures are illustrated in table 3 and figure 1. This shows that the strength of the steel increased in line with an increase in the solid solution temperature in the range of 960 °C–1040 °C. When the temperature was higher than 1040 °C, the strength of the solid solution treated steel decreased, in line with an increase in temperature.

The content of the residual austenite

The x-ray diffraction patterns of the steel treated at different temperatures are illustrated in figure 2. This shows that the major phase is martensite (α-Fe), and minor austenite was also detected in the treated steel. The intensity of the austenite diffraction peak decreases in line with an increase in temperature.

It can be seen in figure 2 that there are three phases detected in the steels. But the major two phases are austenite and martensite. The detected austenite has not been transformed into martensite, namely residual austenite. If only the two major phases, the residual austenite and the martensite are considered in the quantitative calculation, then the volume fraction of the residual austenite in the steel can be calculated.

| Elements | Cr | Ni | Mo | Cu | Ti | Al | Mn | Si | N + C | Fe |
|----------|----|----|----|----|----|----|----|----|-------|----|
| Content/Wt% | 11.9 | 8.99 | 4 | 1.95 | 0.87 | 0.3 | 0.23 | 0.11 | ≤0.05 | bal |

| Temperature/°C | 960 | 1000 | 1040 | 1060 | 1080 | 1100 |
|-----------------|-----|-----|------|------|------|------|

| Temperature(°C) | 960 | 1000 | 1040 | 1060 | 1080 | 1100 |
|-----------------|-----|-----|------|------|------|------|
| Micro-hardness(HV) | 247 | 243 | 317 | 308 | 274 | 233 |
according to the x-ray diffraction pattern using the following equation [20, 21]:

\[
\phi_\gamma = \frac{I_\gamma K_\alpha}{I_\gamma K_\alpha + I_\alpha K_\gamma}
\]

where \( \phi_\gamma \) is the volume fraction of the residual austenite, \( I_\gamma \) is the integral intensity of the austenite, and \( I_\alpha \) is the integral intensity of the martensite. \( K_\alpha \) and \( K_\gamma \) are the reflection constant of ferrite and the austenite, respectively.

The volume fraction of the residual austenite in treated steel is presented in figure 3. This shows that the volume fraction of the residual austenite is 7.16% at 960 °C. It decreases in line with an increase in the solid solution temperature. The volume fraction of the residual austenite in the steel was lowered to 0.42%, with the temperature increased to 1100 °C. This decrease in the residual austenite tended to enhance the hardness or the strength of the steel, which partly explains the increase in its strength, in line with an increase in the solid solution temperature from 960 °C to 1040 °C (seen in figure 1).

Grain size
The grain size of the steel treated at different temperatures is provided in figures 4. and 5. This suggests that the grain size of the steel increased with the increase of the temperature. However, the coarsening rate of the grains was different at different temperatures. For instance, the grain size increased only slightly in line with an increase
in the temperature, when the temperature was lower than 1040 °C. However, the grains coarsened rapidly when the temperature was higher than 1040 °C, resulting in a rapid decrease in the strength of the steel.

The microstructure of the treated steel

The microstructure of the steel was observed using the SEM system. The results are illustrated in figure 5. Grey/white regions are visible in the microstructure of the treated steel, especially in the steel treated at relatively lower temperatures, for example 960 °C and 1000 °C, respectively (seen in figures 5(a) and (b)). The residual austenite is found concentrated in these regions. Moreover, the amount of residual austenite decreases in line with an increase in temperatures. No obvious austenite can be seen in the steel treated at a temperature higher than 1080 °C, which is in coincidence with the x-ray measurement results (seen in figure 3). The decrease in the volume fraction of the austenite in line with an increase in temperature is one of the reasons for an increase in the strength of the steel treated at the temperatures ranging from 960 °C to 1000 °C.

It is also shown in figure 5 that the size of most of the carbides was smaller than 1 micron, partially leading to the high strength of the steel (figures 5(a) and (b)). The carbides became invisible in the steel when the solid solution temperature was higher than 1040 °C, implying that the carbides in the steel were dissolved at these temperatures. At the same time, a reduction in the strength resulted from the rapidly coarsened grains in the steel at the temperatures.

To identify the carbides in the steel, EDS mapping analysis was conducted on the typical carbides in the steel treated at 1000 °C. The results are given in figure 6. They indicate that the size of the carbides is several
nanometres, which is in coincidence with the SEM observations (seen in figures 5(a) and (b)). The shape of the carbides was sphere-like. The EDS analysis results show that the carbides are composed of chrome, molybdenum and titanium. These types of composite carbides were stable at temperatures as high as 1000 °C. The grains grew rapidly when these types of carbides were dissolved (seen in figure 5).

For further investigation of the evolution of the carbides in a smaller size, TEM observation was conducted on the steel treated at different temperature. Attention was paid to the transitional temperatures, for instance, 1000 °C and 1040 °C. The TEM micrographs are given in figure 7. They show that obvious carbides were seen in the steel, when treated at 1000 °C. The carbides were distributed in clusters or dispersed. Their size ranged from tens, to hundreds, of nanometres. No bigger carbides were observed in the steel. No carbides were visible in the TEM micrographs of the steel treated at 1040 °C, indicating that they were dissolved. The presence and the size of the carbides would directly affect the growth of grain in the steel at the elevated temperatures. The dissolved or partially dissolved carbides resulted in the different grain growth rate at the different temperatures. Moreover, obvious plates of martensite were detected in the steels treated at 1000 °C and 1040 °C. The thickness of the martensite was about 50um, and a high density of dislocations within the martensite were also seen in both steels. However, it seems that the distribution of dislocation in the steel treated at 1040 °C was more homogeneous than that treated at 1000 °C.

The solid solution process of the steel would probably lead to a change in grain size, the dissolution of carbides, and the reduction of dislocations, which would affect the mechanical properties of the steel.
Constitutive equation considering the microstructure evolution
The strength of the crystalline materials depends on the barriers against the motion of the dislocations. The barriers include the grain boundaries, the secondary precipitates, and the dislocation tangling etc. Grains coarsening, precipitates dissolving, and dislocation annihilation may occur in the solid solution process of the materials. The strength $\sigma$ of the crystalline material is the function of the grain size, the volume fraction $v$ of the secondary precipitates and the density $\rho$ of the dislocations. Then it can be expressed in following equation:

$$\sigma = f(r, v, \rho).$$

(2)

where $\sigma$ is the strength of the material, $r$ is the average grain radius, $v$ is the volume fraction of the secondary precipitates, and $\rho$ is the density of the dislocations.

If there was no secondary precipitates and dislocation tangling in the steel, the strength could be calculated according to the Hall-Petch equation directly:

$$\sigma_y = \sigma_0 + KR^{-1/2}$$

(3)

where $\sigma_y$ is the actual strength of the material, $\sigma_0$ is the initiate strength, $R$ is the radius of the grains, and $K$ is the constant. It is well-known that the strength of the crystalline material is the result of the motion of the dislocations, which depends on the average distance from the mobile dislocations to the adjacent barriers in the material. When the carbides and the dislocation tangling are present within the grains, the strength of the material is difficult to be calculated by the Hall-Petch equation. But if the grain boundaries, the carbides and the
dislocation tangling are all regarded as the barriers to the dislocations’ motion, then domains are generated by these adjacent barriers, which are substantially subgrains in the material. Moreover, the size of the subgrains can be easily measured by the x-ray diffraction. Actually, secondary precipitates and dislocation tangling are of presence in most of the industry materials. Thus, the subgrain size may become a more accurate parameter to evaluate the average distance from the mobile dislocations to the adjacent barriers in the material. If the subgrain size is used to substitute the grain size, the Hall-Petch equation as equation (3) still works as:

$$\sigma_y = \sigma_0 + Kr^{-1/2}$$

where $\sigma_y$ is the strength of the steel, $\sigma_0$ and $K$ are constant, and $r$ is the subgrain size. The growth of the subgrain size depends on the diffusion of atoms in the steel. The size of the subgrain is the function of the time and the temperature, as the following equation [22]:

$$r = tR_0e^{-(Q/RT)}$$

where $r$ is the subgrain size, $t$ is the time, and $T$ is the temperature. $R_0$ and $R$ are constant. $Q$ is the activation energy.

According to equations (4) and (5), the following equation can be given:

$$K_1t\Delta\sigma^2 = e^{Q/RT}$$

where $K_1$ is constant, $\Delta\sigma$ is the strength increment of the steel from the original state, $T$ is the temperature, and $R$ is the Planck’s constant. Equation (6) can be further simplified as:

![Figure 7. The TEM bright field micrograph of the treated steel (a), (b)1000 °C, (c), (d)1040 °C的TEM (b), (d) are the magnification of (a) and (c), respectively.](image-url)
where C1, C2, and C3 are constant. Equation (7) can be used to calculate the strength, changing with the solid solution temperature of the crystalline material.

In the case of the maraging steel in this experiment, the time is 1 h, the equation can be rewritten as:

\[ C_1 T + C_2 T \ln t + C_3 T \ln \Delta \sigma = 1 \]  

where \( C_1, C_2, \) and \( C_3 \) are constant. Equation (7) can be used to calculate the strength, changing with the solid solution temperature of the crystalline material.

In the case of the maraging steel in this experiment, the time is 1 h, the equation can be rewritten as:

\[ K_2 T \ln t + K_3 T \ln \Delta \sigma = 1 \]  

The constants of \( K_2 \) and \( K_3 \) can be calculated using the least square method according to the figures listed in table 1. The calculated \( K_2 \) and \( K_3 \) are \(-1.8263\) and \(-890.224\), respectively. Thus, the strength of the steel treated at different temperatures can be predicted using equation (7). The results are shown in figure 8. They show that the strength of the steel increases in line with an increase in the solid solution temperature when the temperature was lower than 1040 °C. A temperature higher than 1040 °C resulted in a decrease in the strength of the treated steel. The predicted strength results are in negative correlation with the measured subgrain results as shown in figure 9. This proposed equation for calculation of the strength in solid solution process according to the subgrain domain size is physically precise, which is possibly a reference for materialists to study the heat treatment of the crystalline materials.

The strength of the steels changing with the changes in the temperature (seen in figure 1) owes to the changes in the subgrain size of steel. When the temperature is lower than 1040 °C, the carbides have not been dissolved completely (seen in figure 7(a)). The grain grows very slowly at this stage. However, the partially dissolved carbides lead to not only a solid solution strengthening of the matrix but also a more homogeneous distributed
carbide, resulting in an increase in the martensite in the quenched steel (seen in figure (3)). Thus, the subgrain size decreases, leading an increase in the strength of the steel. When the temperature is higher than 1040 °C, the softening resulting from grain growth is the governing mechanism in the steel.

Conclusions

The solid solution process for a type of maraging steel was studied in this paper. The following conclusions can be drawn:

1. The secondary precipitates are dissolved frequently in line with an increase in temperature from 960 °C to 1040 °C. Meanwhile, the strength of the steel also increased in line with an increase in temperature.
2. The grain size coarsened rapidly when the temperature was higher than 1040 °C, and the mechanical properties of the steel also deteriorated.
3. The residual austenite in steel decreased from 7.16% down to 0.42% with the quenching temperature increasing from 960 °C up to 1100 °C.
4. Finally, the constitutive equation to calculate the strength of the solid solution treated steel is proposed based on the subgrain size.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Oliveira A R, Jardini A L and Del Conte E G 2020 Effects of cutting parameters on roughness and residual stress of maraging steel specimens produced by additive manufacturing Int. J. Adv. Manuf. Technol. 111 2449–59
[2] Krol M, Snaponski P and Czech A 2020 The phase transitions in selective laser-melted 18- NI (300-grade) maraging steel Journal of Thermal Analysis and Calorimetry 142 1011–8
[3] Nandwana P, Kanman R and Leonard D N 2020 Leveraging solute segregation in laser powder bed fusion to achieve superior strength and ductility via single-step heat treatment in ti-free grade 300 maraging steel JOM 72 4221–31
[4] Ebrahimi A, Kenny S and Mohammadi M 2021 Failure mechanisms of equal and unequal wall thickness hybrid maraging steel-P20 tubular joints: effects of welding residual stresses J. Offshore Mech. Arct. Eng. -Transactions of the ASME 143 011705
[5] Wang B, Zhang P and Duan Q Q 2017 Optimizing the fatigue strength of 18Ni maraging steel through ageing treatment Materials Science and Engineering A: Structural Materials Properties Microstructure and Processing 707 674–88
[6] Li H, Lu Q, Zhang D and Huang S 2019 Study on hot deformation behavior and applications in aerospace of ultra-high-strength and HIGH-toughness steel Aerospace Shanghai 36 111–7
[7] Goedl M, Eder H and Prestl A 2020 Diffusion Bonding of High-Alloyed Tool Steels with Maraging and Precipitation Hardening Steels Metals 10 1622
[8] Sun Y Q, Yang Z Y and Liang J X 2009 Progress and prospect of high strength stainless steel for civil airplanes in china J. Iron Steel Res. 21 1–5
[9] Sun L, Simm T H and Martin T L 2018 A novel ultra-high strength maraging steel with balanced ductility and creep resistance achieved by nanoscale beta-NiAl and laves phase precipitates Acta Mater. 149 285–301
[10] Pandey C, Mohan Mahapatra M, Kumar P and Sainia N 2018 Some studies on P91 steel and their weldments J. Alloys Compd. 743 332–64
[11] Pandey C, Giri A and Mahapatra M M 2016 Effect of normalizing temperature on microstructural stability and mechanical properties of creep strength enhanced ferritic P91 steel Mater. Sci. Eng. A 657 173–84
[12] Pandey C, Giri A and Mahapatra M M 2016 Evolution of phases in P91 steel in various heat treatment conditions and their effect on microstructure stability and mechanical properties Mater. Sci. Eng. A 664 58–74
[13] Pandey C 2019 Effect of heat treatment on mechanical behavior and microstructure feature of the thermal aged P91 steel Mater. Res. Express 6 096541
[14] Ozer G and Karaaslan A 2020 A study on the effects of different heat-treatment parameters on microstructure-mechanical properties and corrosion behavior of maraging steel produced by direct metal laser sintering Steel Res. Int. 91 2000195
[15] Elangeswaran C, Gurung K and Koch R 2020 Post-treatment selection for tailored fatigue performance of 18Ni300 maraging steel manufactured by laser powder bed fusion Fatigue Fract. Eng. Mater. Struct. 43 2359–75
[16] Ju L, Qiaolian D and Xiaoxiang W 2007 Age-hardening behaviour and the factors of 00Cr12Ni9Mo4Cu2 maraging stainless steel and its factors Rare Met. Mater. Eng. 36 273–6
[17] Tang L and Yang S 2013 Experimental investigation on the electrochemical machining of 00Cr12Ni9Mo4Cu2 maraging stainless steel and multi-objective parameters optimization International Journal of Advanced Manufacturing Technology 67 2909–16
[18] Walley S M 2012 Historical origins of indentation hardness testing Mater. Sci. Technol. 28 1028–44
[19] Banerjee S, Chakraborti P C and Saha S K 2019 An automated methodology for grain segmentation and grain size measurement from optical micrographs Measurement 140 142–50
[20] Liu P 2000 Relationships between microstructure and properties of stainless steels — A few working examples Mater. Charact. 44 413
[21] Hou H, Qi L and Zhao Y H 2013 Effect of austenitizing temperature on the mechanical properties of high-strength maraging steel Materials Science and Engineering A 587 209–12
[22] Zhu Y Z 2014 Grain growth and microstructure evolution based mechanical property predicted by a modified Hall-Petch equation in hot worked Ni76Cr19Al1Co alloy Mater. Des. 55 456–62