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Inconsistent evolvement of micro-structures and corrosion behaviors in cold/warm deformed austenitic stainless steel

Huimin Tao*, Mingming Ding¹, Cheng Shen¹ and Lin Zhang*  
1 Zhejiang University of Water Resources and Electric Power, Zhejiang Engineering Research Center for Advanced Hydraulic Equipment, Key Laboratory for Technology in Rural Water Management of Zhejiang Province, Hangzhou 310014, People’s Republic of China  
2 Institute of Material Forming and Control Engineering, Zhejiang University of Technology, Hangzhou 310014, People’s Republic of China  
* Authors to whom any correspondence should be addressed.

E-mail: 243508480@qq.com and zhlin@zjut.edu.cn

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**Abstract**

The effects of cold/warm deformation on the micro-structures and corrosion properties of type 304 stainless steel (SS) were studied by micro-structural analysis and electro-chemical tests. Strain-induced α’ martensite was produced by cold deformation but not by warm deformation at 100°C, and it significantly influenced the surface nanohardness of SS. The corrosion resistance of the cold deformed 304 SS continued to decrease as the deformation reduction increased, while the corrosion resistance of the warm deformed 304 SS first decreased and then increased. The increases in strain-induced α’ martensite and dislocation tend to promote corrosion, but the increases in low-∑ coincidence site lattice boundaries, low angle grain boundaries and the severely disrupted random grain boundaries tend to resist corrosion. Warm deformation may provide a possibility of obtaining type 304 SS with high-strength and corrosion resistance, which is attributed to the coupling effect of dislocation and grain boundary.

1. **Introduction**

Researches on stainless steel (SS) have been going on for many years due to their combination of high quality, diverse variety, rich reserves and moderate price, etc [1]. There is always a continued and strong interest in developing the SS with favorable properties for their further application in automotive, aerospace, marine and so on [2–4]. The properties of SS may be significantly improved by deformation processing which could change their micro-structures. A great amount of researchers have devoted significant effort to optimize the structural design of SS to acquire desired properties [5, 6]. To obtain desired properties of SS, many factors that govern material micro-structures including initial material (chemical composition and micro-structure), deformation conditions (method, rate and temperature) need to be taken into consideration [7].

The corrosion behavior of SS must be considered during their further application, and it was also easily to be affected by the application environment. Deng et al [8] reported that the corrosion behavior of an annealed duplex steel was significantly affected by the different phases and partitioning of elements. Mordyuk et al [9] found that the refined grain and the martensite induced by ultrasonic peening influenced the electro-chemical quantities of SS, and these micro-structural changes could increase the corrosion potential and decrease the passivated current. Moreover, it was revealed that the corrosion behavior of the peening treated SS was restrained because of the smooth surface and martensite induced by deformation [10].

Many mechanical processing methods have been used to change the micro-structures of SS to control their properties. Among those processing methods, rolling is known as an effective and convenient method to improve the properties of SS. Rolled steels may exhibit outstanding properties of high strength, high proportion by weight, wear resistance, etc. Some researches [11–14] have been performed on the changes of texture and micro-structure in the rolling deformed SS. Ravi Kumar et al [13] presented that the phase transformation...
\(\alpha\)’ martensite in SS was induced by strain rather than stress. It has also been reported that the oxidation film formed on 430 ferritic SS would be thicker and its surface would be smoother with decreasing hot-rolling deformation reduction [14]. These studies suggested that the microstructures of the rolled material may be significantly affected by the deformation conditions. SS shows a complex evolution of micro-structures depending on the deformation conditions and structural characteristics.

Cold or hot working has been widely used in steel processing while the warm working rarely attracted attention during production of SS [15]. Only limited studies have been carried out on the warm deformed SS. Chen et al. [16] reported that the mechanical properties of the warm deformed steel were significantly different from the cold/hot deformed steel. The properties of SS may be improved by the warm deformation due to the micro-structural changes induced by deformation. However, few studies have been conducted on the different effects of cold/warm deformation on the properties of metastable austenitic SS yet. The difference between the micro-structure and corrosion resistance evolution mechanism of cold and warm deformed SS has still not been clearly illuminated and thoroughly understood yet. Thus, systematic comparative studies are needed to research the influences of micro-structures on the corrosion properties of cold/warm deformed SS for expanding their application.

This work contributed to illustrate the effects of cold/warm deformation (deformation reduction: 0 to 50%, deformation temperature: 25 °C or 100 °C) on the micro-structures and corrosion properties of 304 SS by micro-structural analysis and electro-chemical tests. The evolution of micro-structures and corrosion properties of the cold/warm deformed 304 SS was investigated, and the corrosion theory of SS was studied relying on the evolution of micro-structures caused by different deformation conditions.

2. Materials and methods

304 metastable austenitic SS (wt.%: 0.07 C, 0.33 Si, 1.13 Mn, 18.09 Cr, 8.06 Ni, 0.022 S, 0.039 P) was heat-treated at 1050 °C for 1 h and followed by water quenching. Heat-treated sheets were rolled multiple times in the same direction by using a two-roller mill with the heating system. Nearly 1% of the original thickness of the sheets was reduced after every deformation, and finally the thickness reduction from 10% to 50% was obtained after numerous continuous passes. Cold rolled samples were obtained by rolling at 25 °C ± 1 °C and warm rolled samples were obtained with the rollers and samples kept in a desired constant temperature of 100 °C ± 2 °C. Diagrammatic presentation of the rolling process was displayed in figure 1. The obtained samples will be hereafter referred to as the RXX-TYY sample which was rolled to acquire a XX% reduction of its original thickness at YY °C. The experimental sample was marked with rolling direction (RD) and transverse direction (TD).

Succedent annealing treatments of all samples were conducted in vacuum atmosphere. The samples were annealed at 400 °C (0.29 \(T_m\), \(T_m\): the melting temperature of 304 SS) for 4 h (cooled in furnace) and 950 °C (0.68 \(T_m\)) for 1 h (cooled in water), respectively. Nanohardness tests of the samples were measured using an Agilent G200 nanoindenter with a Berkovich diamond tip. All of 900 (30 × 30) indentation points were conducted on the samples, and the minimum distance between the points was 3 \(\mu\)m to avoid interaction. The tests were performed using the maximum load of 1 mN with the loading rate of 0.2 mN s\(^{-1}\).

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**Figure 1.** Diagrammatic presentation of the deformation process for 304 SS. (Deformation temperature: 25 °C and 100 °C; Deformation amount: 10%~50%).
The samples for electro-chemical experiments were processed into the sizes of 10 mm × 10 mm × 2 mm. Back of sample was linked with a copper wire and they were embedded in the epoxy to prevent crevice corrosion [17, 18]. These samples were sequentially polished with abrasive papers from #100 to #2000 and then polished into a mirror with 0.1 μm polishing paste. All the samples were ultrasonically cleaned with deionized water and alcohol before electro-chemical experiments. A standard IVIUMSTAT electro-chemical workstation was used for the tests, and it was equipped with a three-electrode cell system containing a platinum sheet (the counter electrode), a saturated calomel electrode (SCE) (the reference electrode) and the samples prepared above (the working electrode). All the measured potentials in the experiments were displayed referenced to the SCE. All the electro-chemical experiments were conducted in 3.5 wt.% NaCl solution at 25 ± 1 °C. Before these electro-chemical measurements, open-circuit potential tests were lasted for 30 min to stable the experimental environment. Potentiodynamic polarization measurements were performed in the potential range from −0.6 V_{SCE} to +1 V_{SCE} in a scanned rate of 1 mV s⁻¹. Each experiment was repeatedly conducted for many times with the same conditions to ensure the tests to be reproducible.

X-ray diffraction (XRD), optical microscope (OM), electron backscatter diffraction (EBSD) and scanning kelvin probe force microscopy (SKPFM) were utilized to illustrate the micro-structures of the samples. The X-ray diffraction (XRD) tests were conducted using the XRD-7000 SL equipment, and the X-ray beam energy was 86.70 keV, the beam size was 0.5 × 0.5 mm², and the scanning angle was from 30° to 100°. The microstructures of the samples, such as grains, grain boundaries, misorientation, and dislocations, were observed using NordlysMax II EBSD system. EBSD tests were conducted with the acceleration voltage of 20 kV, the collection speed of 637.76 Hz, and the scanning step of 0.75 μm. The SKPFM measurement were conducted in a flowing nitrogen atmosphere using a Nanoscope IIIa scanning probe microscope, and the measurements were carried out in the tapping/lift mode with a lift height of 50 nm at 301 ± 0.5 K.

3. Results

3.1. Micro-structural analysis
To explore the inclusions and pores in the used material, the 304 SS sample without deformation was polished to observe the inclusions or pores in SS. The surface of the polished sample is observed by a metallographic microscope, and the tests were carried out many times. The surface morphologies of polished SS and the SEM-EDS (Scanning Electron Microscope-Energy Dispersive Spectrometer) test of an inclusion was shown in figure 2. As can be seen, there are a few inclusions and almost no big pores in the SS used in this work. Among them, the elements of S and Mn in one inclusion are significantly higher, indicating that the inclusion may be MnS.

Inverse pole figure (IPF) images and XRD patterns of the 304 SS samples are displayed in figure 3. The as-received sample showed polygonal grains with some lathy twins in austenite grains, as observed in figure 3(a). R20-T25 and R20-T100 samples had the similar polygonal grains like the as-received sample, while a slightly disorder of grain orientation along the deformation direction was observed, as displayed in figures 3(b) and (d). As the deformation reduction increased to 50%, a distinctly disorder of grain orientation and fragmentation of
grains occurred in the samples, as shown in figures 3(c) and (e). Accumulative dislocation induced by deformation surrounded the grain boundaries would limit the deformation of grains and lead to the grain fragmentation [19]. In addition, a great amount of heterogeneous subgrains occurred in some original grain interiors in the 50% rolled samples, and the number of subgrains in the R50-T100 sample was greater than in the R50-T25 sample.

The XRD patterns for 304 SS samples are displayed in figure 3(f). Only $\gamma$-austenite diffraction peaks are seen in the as-received and warm deformed samples, while $\alpha'$ (110), $\alpha'$ (200) and $\alpha'$ (211) diffraction peaks appeared in the cold deformed samples. The XRD analysis suggested that warm deformation at 100 °C can restrict the martensite transition in 304 SS. Besides, the intensity of the diffraction peaks weakened as the deformation reduction increased, which may be owing to the more chaotic micro-structures caused by increasing the deformation reduction.

The grain boundary distribution and relative percentages of different grain boundaries in the 100 °C warm deformed samples were displayed in figures 4 and 5, respectively. Grain boundaries are categorized into the high angle or the low angle grain boundaries according to the orientation difference was greater or less than 15 degrees. Among the coincidence site lattice boundaries, the $\Sigma \leq 29$ are categorized as the low-$\Sigma$ coincidence site lattice boundaries, which are also called the special grain boundaries because they may be beneficial to the properties of the material [20]. In addition, the other grain boundaries are classified as the random grain boundaries in this study. As can be seen in figure 4, the low angle, special and random grain boundaries are displayed in green, red and black lines, respectively. A crowd of low angle grain boundaries was observed in the warm deformed sample, and they surrounded the original grain boundaries for the R20-T100 sample (figure 4(a)) while they observed almost throughout the all scope for the R50-T100 sample (figure 4(b)). The low angle grain boundaries of the R50-T100 sample was much greater than that of the R20-T100 sample. Besides, the random grain boundaries of the R50-T100 sample were severely disrupted compared with that of the R20-T100 sample. The special grain boundaries increased from 1.62% to 2.29% as the deformation increased from 20% to 50%.

The actual content of $\alpha'$ martensite of the deformed steel was detected by the ferritescope and the results were shown in figure 6. The volume fractions of $\alpha'$ martensite of the R50-T25 sample (53.27%) was much higher than that of the R20-T25 sample (21.71%) in the cold deformed samples. Thus, the actual contents of $\alpha'$
Martensite considerably increased with the increase of cold deformation. However, there is almost no $\alpha'$ martensite in the warm deformed specimen. This result is consistent with the XRD result.

### 3.2. Electrochemical tests

Electrochemical behaviors of cold/warm deformed 304 SS samples were analyzed by potentiodynamic polarization tests, and the results are shown in figure 7. In the potentiodynamic polarization plots, several related parameters (corrosion potential: $E_{cp}$, passivation current density: $i_{pc}$, pitting potential: $E_{pp}$, and length of the passive region: $\Delta E (\Delta E = E_{pp} - E_{cp})$) were acquired by polarization plots and Tafel extrapolation method [21, 22]. The $i_{pc}$ represented the current in the middle of the passive region of the polarization plot. The acquired related parameters of cold and warm deformed 304 SS samples were recorded in tables 1 and 2, respectively.

A significant difference was observed in the potentiodynamic polarization plots of 304 SS samples, indicating the distinctly different effects of cold/warm deformation on the corrosion properties of 304 SS. The $E_{cp}$ of all the deformed samples were lower than that of the undeformed samples. For the cold deformed samples, the $E_{cp}$ value continued to decrease from $-131.4$ mV$_{SCE}$ (as-received) to $-244.5$ mV$_{SCE}$ (R50-T25) with increasing the deformation; however, for the samples deformed at $100$ °C, the $E_{cp}$ value decreased from $-131.4$ mV$_{SCE}$ (as-received) to $-183.5$ mV$_{SCE}$ (R20-T25) and then increased to $-177.3$ mV$_{SCE}$ (R50-T25) with increasing the deformation. The $E_{cp}$ of the warm deformed sample was higher than that of the cold deformed sample with the same deformation reduction. Theoretically, the sample with the higher $E_{cp}$ reflects the better corrosion resistance.
Resistance in the corrosive medium \[23\]. Thus, cold deformation weakened the general corrosion resistance of 304 SS as the deformation reduction increased, while warm deformation first decreased and then improved the general corrosion resistance. In addition, an obvious passivation area presented in these polarization curves, indicating a protective passivation film produced on the sample. The \(i_{pc}\) and \(E_{pp}\) could reflect the status of the passivation film to reveal the corrosion resistance ability of the material \[24, 25\]. The sample with smaller \(i_{pc}\) and greater \(E_{pp}\) indicate the slower reaction and better pitting resistance of the passivation film, respectively. The \(i_{pc}\)

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\begin{array}{cccc}
\text{Samples} & E_{cp} (\text{mV SCE}) & i_{pc} (\mu\text{A cm}^{-2}) & E_{pp} (\text{mV SCE}) & \Delta E (\text{mV}) \\
\hline
\text{As-received} & -131.4 \pm 3.5 & 0.37 \pm 0.02 & 404.6 \pm 5.2 & 536.0 \\
\text{R10-T25} & -185.2 \pm 10.3 & 2.73 \pm 0.07 & 269.4 \pm 13.1 & 454.6 \\
\text{R20-T25} & -217.3 \pm 14.7 & 3.65 \pm 0.14 & 193.3 \pm 12.4 & 410.6 \\
\text{R30-T25} & -222.4 \pm 14.5 & 7.66 \pm 0.31 & 176.2 \pm 11.2 & 398.6 \\
\text{R50-T25} & -244.5 \pm 10.6 & 8.11 \pm 0.29 & 138.7 \pm 12.2 & 383.2 \\
\end{array}
\]
value continued to increase from 0.37 μAcm⁻² (as-received) to 8.11 μAcm⁻² (R50-T25) with increasing the deformation for the cold deformed sample, while, the \( i_{pc} \) increased from 0.37 μAcm⁻² (as-received) to 6.19 μAcm⁻² (R20-T25) and then decreased to 4.05 μAcm⁻² (R50-T25) with increasing the deformation for the samples deformed at 100 °C. The \( E_{pp} \) of the cold deformed samples continued to decrease from 404.6 mV SCE (as-received) to 138.7 mV SCE (R50-T25) with increasing the deformation; however, the \( E_{pp} \) decreased from 404.6 mV SCE (as-received) to 181.3 mV SCE (R20-T25) and then increased to 293.1 mV SCE (R50-T25) with increasing the deformation for the samples deformed at 100 °C. Moreover, the \( \Delta E \) of the cold deformed samples continued to decrease with increasing the deformation, while they decreased first and then increased for the samples deformed at 100 °C. As a result, the pitting resistance continued to decrease with increasing the deformation for the cold deformed 304 SS, while it first decreased and then increased with increasing the deformation for the 304 SS deformed at 100 °C. The pitting resistance of the warm deformed sample was better than that of the cold sample with the same deformation reduction.

Annealing technology can control the micro-structures in the samples to investigate the influence of different micro-structures on the corrosion properties of 304 SS. 304 stainless steel samples were annealed at 400 °C and 950 °C to study the effect of residual stress and dislocation on corrosion resistance. The potentiodynamic polarization plots of 400 °C annealed and 950 °C annealed samples are displayed in figures 8(a) and (b), respectively. The electro-chemical results of 400 °C annealed samples have changed little in comparison with the unannealed samples, as displayed in figure 8(a). Therefore, the corrosion resistance of 304 sample was not influenced by annealing at 400 °C, indicating that the residual stress caused by deformation had little effect on the corrosion properties of 304 SS. However, annealing at 950 °C had obviously changed the corrosion properties of the deformed samples, as displayed in figure 8(b). For the sample deformed at 100 °C, the \( E_{cp} \) increased from −177.3 mV SCE (R50-T100) to −98.4 mV SCE (R50-T100–950), the \( i_{pc} \) decreased from 4.05 μAcm⁻² (R50-T100) to 1.58 μAcm⁻² (R50-T100-950) and the \( E_{pp} \) increased from 293.1 mV SCE (R50-T100) to 452.6 mV SCE (R50-T100-950). In addition, for the sample deformed at 25 °C, the \( E_{cp} \) increased from −244.5 mV SCE (R50-T25) to −214.7 mV SCE (R50-T25-950), the \( i_{pc} \) decreased from 8.11 μAcm⁻² (R50-T25) to 1.77 μAcm⁻² (R50-T25-950) and the \( E_{pp} \) increased from 138.7 mV SCE (R50-T25) to 192.3 mV SCE (R50-T25-950). Above results indicated that the corrosion resistance ability of the 950 °C annealed sample was significantly improved in comparison with the sample without annealing treatment.
3.3. Nanohardness measurement

Contour plots of the measured nanohardness distribution of cold/warm deformed 304 SS samples were shown in figure 9. Plastic deformation can change the micro-structure of metal materials such as vacancies, dislocations, boundaries or phase transitions. The distribution of measured nanohardness of the samples depends heavily on these micro-structures. The measured nanohardness of the as-received sample was approximately 4-5 GPa in most of the measured areas, which was much lower than that of the deformed samples. The changes of dislocations, residual stress and other micro-structures were inevitably produced in the samples during deformation process, which would increase the nanohardness of the sample. The measured nanohardness distinctly increased with increasing the deformation whether in the cold deformed samples or the warm deformed samples, which was caused by the changes of micro-structures induced by different deformation reductions. Generally, the hardness of martensite with BCC structure is obviously higher than that of austenite with FCC structure. There were a great number of higher measured nanohardness (greater than 7 GPa) areas in the cold deformed samples, which may be caused by the presence of strain-induced \(\alpha'\) martensite. The areas of the higher measured nanohardness of the R50-T25 sample were much greater than that of the R20-T25 sample, which may be attributed to the increase in the content of \(\alpha'\) martensite. Few higher measured nanohardness existed in the warm deformed sample, indicating no \(\alpha'\) martensite produced in 304 SS which was deformed at 100 °C. The result above was consistent with the XRD analysis (figure 3(f)). The typical load versus displacement curve of the as-received sample confirmed the credibility of the nanohardness measurements, as shown in figure 9(f).

4. Discussion

Above experimental results indicated that cold/warm deformation has significantly different effects on the micro-structures of 304 SS, which will further affect the properties. The corrosion resistance of the cold deformed 304 SS continued to decrease with increasing the deformation reduction, while it first deceased and then increased for the 304 SS deformed at 100 °C. The corrosion properties of material heavily rely on its component and micro-structures. The distinctly different evolvement of the corrosion resistance of 304 SS with different deformation conditions was particularly interesting and the micro-structural relevance was considered necessary.

First, the structure of the SS itself should be analyzed to study the corrosion behaviour. It was reported that inclusions or pores in SS are an important factor affecting the corrosion behavior. As can be seen in figure 2, there are a few inclusions and almost no big pores in the SS used in this work. Inclusions in SS lead to the depletion of Cr in the surrounding materials, which caused the pitting corrosion to be more easily initiated at the...
inclusions [26]. Generally, inclusions are easy to form at the grain boundary of stainless steel, which are seriously sensitive to corrosion [27]. However, the inclusions will dissolve after pitting corrosion [28], and it was not easy to observe whether the pitting corrosion occurs at the position of the inclusions. In previous study, it was found that corrosion pits preferentially appeared at the grain boundary during the potentiodynamic polarization tests of deformed 304 SS. Therefore, it was reasonable to think that pitting corrosion was more likely to preferential occur at inclusions on the grain boundary. However, several studies [29, 30] demonstrated that some of the inclusions in SS may not trigger pitting corrosion, which determined by the chemical composition, size, and shape of inclusions. In this study, there are few inclusions in the used SS, and a small part of inclusions may be attacked during the pitting of SS. Moreover, it was proposed that the corrosion behavior of SS will be influenced only when the porosity exceeds 1% [31]. Thus, the effect of pores on the corrosion behavior of SS is not considered in this study. In this work, the micro-structures of deformed 304 SS significantly affected by the different deformation conditions, which may cause the difference of corrosion behavior. Therefore, the micro-structures of 304 SS with different deformed conditions should be further considered to analyze the evolution of corrosion behavior.

Some researchers have reported that grain refinement of stainless steel can improve the corrosion resistance of stainless steel [32]; meanwhile, it has also been reported that the corrosion resistance of stainless steel is not influenced by the grain size [33]. The effects of grain size on the corrosion behaviour of stainless steel has always been controversial. The structural analysis in figure 3 displayed that the grains of 304 SS with different deformed conditions were severely damaged by large deformation (50%), while small deformation (20%) did not. The average grain size distinctly decreased with increasing deformation in both cold and warm deformed steel. The decreased grain size of the sample at 50% deformation was attributed to the formation of many fine grains. In this study, the grain size of both cold and warm deformed 304 SS decreased with increasing deformation, while their corrosion behaviour evolutions were different. Thus, there may be no definite correlation between grain size and corrosion behaviour. The grains of the material were divided by grain boundaries; thus, the grain sizes of the materials were determined by the grain boundary distribution. More attention should be paid to the change of grain boundary distribution in cold and warm deformed 304 SS.

The internal state of metallic materials was inevitably changed during mechanical deformation process, including grain shape, lattice orientation, grain boundaries, dislocation, residual stress, etc. The degree of micro-structural disorder of the deformed sample increased with the deformation reduction, as shown in figure 3. Deformation induced changes in the internal state of the 304 SS will lead to strain hardening, which was confirmed by the results of the nanohardness tests. As the deformation reduction increased, the measured nanohardness of 304 SS increased due to the generation of the chaotic micro-structure in the samples, as displayed in figure 9. Although the reactivity of the various micro-structure may be greatly different due to their crystallographic structures, all of these structures are more active compared with the grain matrix. Generally, the chaotic structures have disordered atomic arrangement, which are difficult to be passivated and could promote ion adsorption, resulting in accelerating the corrosion of material in the corrosive medium. The increase in chaotic structures which have the poor corrosion resistance in the deformed 304 SS resulted its poor corrosion resistance compared with the undeformed SS.

According to the potentiodynamic polarization results of the annealed samples, the corrosion resistance of 304 sample was not influenced by annealing at 400 °C, indicating that the residual stress caused by deformation had little effect on the corrosion properties of 304 SS. However, the corrosion resistance ability of the 950 °C annealed sample was significantly improved in comparison with the sample without annealing treatment. Generally, the dislocation density of the steels increased with the deformation reduction, which weakened the corrosion resistance of steels because of the reduce of energy barrier and the increase of sensitive areas [34, 35]. The corrosion resistance ability of the deformed sample after 950 °C annealing distinctly improved which was thought to be caused by the decreased dislocations. Thus, the dislocations induced by deformation increased as the deformation reduction increased, which would accelerate the corrosion of 304 SS.

Moreover, the corrosion resistance ability of the warm deformed sample was improved in comparison with the cold deformed sample with the same deformation reduction, as displayed in figure 7. Significantly different micro-structures were induced by cold/warm deformation in 304 SS, which will further affect the corrosion properties. Strain-induced α′ martensite was found in the cold deformed sample while it was not found in the sample deformed at 100 °C, as displayed in figure 3(f). And the actual content of α′ martensite considerably increased with the increase of cold deformation (figure 6). From figures 9(b) and (c), a remarkably higher measured nanohardness was observed in the cold deformed 304 SS, and that was caused by α′ martensite which has much higher hardness than that of austenite. Plastic strain may result in adiabatic heating during the deformation progress due to the dislocation pile-ups, and the local overheating could depress the martensite transformation [36–38]. Thus, all results show that there was almost no α′ martensite transformation in 304 SS deformed at 100 °C.
To further analyze the effect of $\alpha'$ martensite on the properties of SS, SKPFM technology was used in this work. SKPFM technology is effective to investigate the micro-structures in the metals by measuring the variation of work function of the micro-structures [39–42]. Contact potential difference (CPD) is usually defined as 

$$\text{CPD} = \frac{\varphi_{\text{tip}} - \varphi_{\text{sam}}}{e},$$

where $\varphi_{\text{tip}}$ represents the work function of the measured tip, $\varphi_{\text{sam}}$ represents the work function of the sample and $e$ represents the electronic charge [43]. When $\varphi_{\text{tip}}$ is constant, the CPD will increase as the $\varphi_{\text{sam}}$ decreases. In this work, SKPFM was conducted at the room temperature to study the different micro-structures in the deformed 304 SS, the CPD map of sample was shown in figure 10. Obviously lower CPD regions compared with that of the matrix were found in the R50-T25 sample (figure 10(a)) which was attributed to the $\alpha'$ martensite induced by cold deformation, while the CPD equally distributed in the R50-T100 sample (figure 10(b)). The result matches better with above results of XRD, nanohardness distribution and the content of $\alpha'$ martensite. The CPD of the $\alpha'$ martensite was much lower than that of austenite, as shown in figure 10(c), which was also observed in previous researches [39, 41]. Significantly large CPD between martensite and austenite in SS will promote the formation of micro-galvanic cells to accelerate the corrosion process [44].

Besides, the martensite transformation may impede the process of passivation or repassivation of the steel, which is not good for the formation of dense film on the steel [45]. Thus, $\alpha'$ martensite induced by cold deformation could significantly decrease the corrosion resistance ability of 304 SS. As a result, the corrosion resistance ability of the cold deformed 304 SS was weakened in comparison with the warm deformed sample with the same deformation reduction; and the actual contents of $\alpha'$ martensite and the dislocation density distinctly increased as the deformation reduction increased, leading to an evident decrease in the corrosion resistance ability of the cold deformed 304 SS as the deformation reduction increased.

For the warm deformed 304 SS, there was no strain-induced $\alpha'$ martensite produced during deformation progress. Distinctly changed trend of the corrosion behavior evolution of 950 °C annealed samples verified that the corrosion properties of the warm deformed 304 SS was significantly affected by the dislocation and grain boundary, which was also confirmed by previous work [46]. Dislocation density of the warm deformed 304 SS increased as the deformation reduction increased, which decreased the corrosion resistance of 304 SS. Moreover, grain boundary also plays the vital role in the corrosion behavior of the steels. According to the results of grain boundary distribution in figures 3 and 4, the low angle grain boundaries distinctly increased with the deformation increased from 20% to 50%. The random grain boundaries of the R50-T100 sample were severely disrupted compared with that of the R20-T100 sample. And the special grain boundaries also increased as the deformation increased. The highly regular and coherent atomic arrangement of the special and low angle grain boundaries lead to their lower energy [47, 48], and they will have better corrosion resistance ability in comparison with the random grain boundaries. Thus, the increased special and low angle grain boundaries, and the severely disrupted random boundaries will improve the corrosion resistance ability of the grain boundary. As the warm deformation increased from 20% to 50%, the special and low angle grain boundaries of sample increased, and the random grain boundaries were severely disrupted; thus, the corrosion resistance ability of grain boundary of the R50-T100 sample improved compared with the R20-T100 sample. The improved corrosion resistance ability of the grain boundary in 304 SS will increase the corrosion resistance of steel by hindering the pitting corrosion progress. Therefore, the increased dislocation density decreased the corrosion resistance as the warm deformation reduction increased, while the increased corrosion resistant grain boundaries improved the corrosion resistance, which resulted that the corrosion resistance of the warm deformed 304 SS first decreased and then increased.

The corrosion properties of the deformed 304 SS is determined by the coupling effect of micro-structural changes induced by different deformation conditions. Evolution of the corrosion susceptibility of the cold/ warm deformed 304 SS is summarized in figure 11. As the deformation reduction increased, the corrosion
resistance of cold deformed 304 SS continued to decrease, while it first decreased and then improved for the warm deformed 304 SS. The considerably different evolvement of the corrosion properties of cold/warm deformed 304 SS is attributed to the various micro-structural development during deformation progress. Relevant work may be helpful to illustrate the mechanism of corrosion properties of stainless steels and it will be valuable for further development of stainless steels with high-strength and corrosion resistance.

5. Conclusions

The effects of cold/warm deformation on the micro-structures and corrosion properties of 304 stainless steel were investigated by micro-structural analysis and electro-chemical tests. Relevant results can be summarized as follows:

1) As the rolling deformation gradually increases to 50%, the corrosion resistance of cold deformed 304 stainless steel gradually decreases, while the corrosion resistance of 304 stainless steel deformed at 100 °C decreases first and then increases.

2) Strain-induced $\alpha'$ martensite was produced by cold deformation but not by deformation at 100 °C, and the $\alpha'$ martensite in 304 stainless steel could significantly increase its surface nanohardness.

3) The inconsistent evolvement of corrosion behaviors of cold/warm deformed austenitic stainless steel was caused by the coupling effect of the micro-structures. Strain-induced $\alpha'$ martensite and dislocation in austenitic stainless steel may weaken the corrosion resistance, while the low angle, special and the disrupted random grain boundaries may improve the corrosion resistance.

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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).
Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors declare that the research did not involve Human Participants or Animals.

ORCID iDs

Huimin Tao https://orcid.org/0000-0002-7279-5215
Lin Zhang https://orcid.org/0000-0001-9647-8110

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