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Antibacterial properties, corrosion resistance and mechanical properties of Cu-modified SUS 304 stainless steel

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Abstract

This investigation studies the effects of Cu content and ageing treatment on the microstructural, mechanical, corrosion and antibacterial properties of SUS 304 austenitic stainless steel. Cu was added respectively to SUS 304 stainless steels in proportions of 1.5, 2.5, 3.5, 4.5 and 5.5 wt.%. A vacuum arc remelting furnace was used to remelt SUS 304 stainless steel with various added Cu contents. These ingot alloys underwent hot rolling and various heat treatments, and were then cut into test specimens. A series of microstructural investigation, tensile tests, corrosion tests and antibacterial tests were conducted to study the properties of Cu-containing SUS 304 austenitic stainless steel. Microstructural observations reveal that the amount of retained δ-ferrite in the as-cast SUS 304 steel decreases as the Cu content increases. After hot rolling, the retained δ-ferrite disappears and α′-martensite forms in the austenitic matrix. The results of the tensile tests reveal that the ultimate tensile strength (UTS) declines as the Cu content increases below 2.5 wt.%. However, the ultimate tensile strength increases with the Cu content above 2.5 wt.%. X-ray diffraction analysis reveals that adding Cu suppresses the formation of strain-induced martensite (α′-martensite). The corrosion test indicates that the pitting potential declines as the Cu content in SUS 304 steels increases. The results of the antibacterial test reveal that adding a proper amount of Cu (such as 2 wt.%) gives SUS 304 stainless steel an excellent antibacterial property.

Keywords: SUS 304 stainless steel; Strain-induced martensite; Antibacterial property; Cu content; Stacking fault energy; *Staphylococcus*

1. Introduction

In modern life with scientific and technological advances, much attention is paid to the safety, sanitation and health of environments. Therefore, daily appliances are increasingly being designed with antibacterial features. Austenitic stainless steels, such as SUS 304, are widely used, because they exhibit superior corrosion resistance and workability. The development of austenitic stainless steels with excellent antibacterial property would expand the applications of such steels. In the past, some organic coatings have been used as antibacterial agents [1]. Those organic agents can inhibit the breeding of bacteria; however, their antibacterial effects can not last for a long time. During the past decade, for the sake of safety, an inorganic antibacterial method, such as adding copper or silver to the alloy [1], has replaced the coating of organic agents. Metallic ions from the alloy are strongly reductive and can destroy the cell walls and cell membranes of bacteria, inhibiting their breeding.

According to some reports [1–3], the *Staphylococcus aureus* is the common pathogen that causes the food poisoning. The probability of food poisoning would decrease by reducing the amount of the *S. aureus* on the stainless steel that people always touch. *S. aureus* is a sort of gram-positive bacterium and it has thick cell walls. If their cell wall can be destroyed by Cu-ions, the *S. aureus* can not survive. Therefore, the *S. aureus* is used as the testing bacteria in this research. The antibacterial rate of each specimen is calculated to access the relation between the antibacterial rate and Cu content in stainless steels.

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Three main factors are important in fabricating antibacterial stainless steel: (1) the amount of antibacterial element added, (2) the amount of antibacterial element precipitated upon the passivated oxide film, and (3) the temperature and duration of ageing treatment. This work investigates the effects of various Cu contents and different heat treatment conditions on the antibacterial property of SUS 304 steel to obtain the optimal parameters for making an effective antibacterial stainless steel.

2. Experimental method

2.1. Material preparation

The nominal 304 type alloys, containing 0 to 5.5 wt.% Cu, were melted in a non-consumable electrode arc furnace in an atmosphere of argon. The alloys were remelted seven times to ensure homogeneity and then cast into rectangular bars with dimensions 65 mm × 40 mm × 13 mm (thickness). The cast ingots were hot-rolled at 1150 °C to reduce their thickness from 13 to 3 mm. After hot rolling, the sheets were solution-treated at 1050 °C for 5 min, and then aged at 700 and 800 °C for 30, 60, 120 and 240 min, respectively. The heat-treated sheets were prepared for microstructural investigation, tensile, corrosion and antibacterial tests.

2.2. Microstructural investigations

Metallographical investigations were carried out using optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffractometry (XRD). The specimens were mechanically polished with wet SiC paper of 2000 grit and then finely polished with 0.05 μm Al_2O_3 powder to enable optical observations to be made. Finally, an etching solution consisting of 20 ml of HNO_3, 40 ml of HCl and 40 ml of glycerol was used to etch the specimens for 10 s. The precipitation of ε-Cu on the passivated film of SUS 304 steel and the fracture surfaces were examined by scanning electron microscopy. The amount of α'-martensite generated by deformation was evaluated by X-ray diffraction with Mo-Kα radiation from 40° to 120°. The chemical compositions of the alloys were determined by X-ray fluorescence analysis (XRF).

2.3. Investigations of mechanical properties

The heat-treated sheets were cut into tensile specimens with gauge dimensions 25 mm × 6 mm × 3 mm and were then mechanically polished. Room temperature tensile tests were conducted with an MTS testing machine at a strain rate of $1 \times 10^{-4}\,s^{-1}$. The hardness was measured using a Vickers hardness test machine with a load of 300 g.

2.4. Corrosion investigations

The heat-treated sheets were cut into corrosion specimens with dimensions 15 mm × l5 mm × 1 mm. These specimens were mechanically polished with wet SiC paper of 600 grit and then placed into an acetone bath for ultrasonic cleaning before they were tested. Potentiodynamic polarization tests were conducted in 3.5 wt.% NaCl solution under nitrogen gas. A saturated calomel electrode (SCE) was used as the reference electrode. The potentiodynamic polarization curve of each specimen was measured at a potential scan rate of 0.1 mV/s after the open circuit potential (OCP) was measured. Pitting nucleation potential (E_{np}) and pitting protection potential (E_{pp}) were obtained from the potentiodynamic polarization curve.

2.5. Antibacterial test

This experiment was conducted by Food Industry Research and Development Institute of R.O.C. The plain-plate dilute method was used to measure the number of live bacteria and to calculate the antibacterial rate of each specimen in this study. The heat-treated sheets were cut into squares with dimensions 50 mm × 50 mm × 1 mm. These specimens were mechanically polished with SiC paper of 800 grit and then cleaned with alcohol before they were tested. The bacterial solution was made by incubating the *S. aureus* on an agar plate at 37 °C for 24 h and then using distilled water to dilute the solution by a factor of five hundred. 0.4 ml of the bacterial solution was dripped onto the test specimen and the specimen was covered with an aseptic polyethylene film to ensure that the bacterial solution was in close contact with the surface of the specimen. The specimen with the bacterial solution was incubated at 25 °C for 24 h, and all of the bacterial solution was collected in 10 ml of SCDLP (soybean-casein digest broth with lectithin and polysorbate) broth.

3. Results and discussion

3.1. Microstructural analysis

After casting, austenitic stainless steels always retain some of the δ-ferrite that forms during solidification. This retained δ-ferrite is believed to dissolve some impurities, such as S, P, Se, and others preventing the formation of low melting point compounds which cause cracking under solidification stress. The morphology of the retained δ-ferrite depends not only on cooling rate but also on the compositions of the alloys [5], and makes the cast structure of the austenitic stainless steels more complex. The retained δ-ferrite in the casting of austenitic stainless steel can be divided into three categories, according to the morphology of ferrite and the Cr_{eq}/Ni_{eq} ratio, as described below [4,5]:

Type A, $Cr_{eq}/Ni_{eq} \leq 1.48$: The δ-ferrite is vermicular and located at the cell boundaries.
Type B, $1.48 \leq Cr_{eq}/Ni_{eq} \leq 1.95$: Both vermicular and lathy ferrite are observed in the microstructure, and the δ-ferrite is located at the cell axes.

Table 1
Chemical composition and Cr_{eq}/Ni_{eq} ratio of investigated alloys

wt.%	C	Si	Mn	P	Ni	Cr	Mo	Cu	Nb	Co	Cr_{eq}/Ni_{eq}
As-received	0.027	0.348	1.352	0.022	9.01	18.60	0.158	0.15	0.004	0.194	1.90
1.5 wt.% Cu	0.022	0.319	1.248	0.017	9.21	18.64	0.157	1.57	0.004	0.193	1.67
2.5 wt.% Cu	0.013	0.321	1.261	0.016	9.15	18.49	0.157	2.55	0.003	0.195	1.55
3.5 wt.% Cu	0.016	0.327	1.221	0.016	9.10	18.31	0.161	3.54	0.004	0.191	1.43
4.5 wt.% Cu	0.020	0.329	1.229	0.016	9.04	18.42	0.155	4.51	0.004	0.196	1.33
5.5 wt.% Cu	0.021	0.336	1.209	0.017	9.03	18.45	0.153	5.51	0.003	0.194	1.25

Type C, $Cr_{eq}/Ni_{eq} \geq 1.95$: The lathy δ-ferrite dominates the cast microstmcture.

Table 1 shows the chemical composition of investigated alloys. The chromium and nickel equivalents of the investigated alloys (in weight %) can be calculated from the following formulae [6].

$$\text{Ni equivalent} = \text{Ni} + 0.31\,\text{Mn} + 22\,\text{C} + 1\,\text{Cu} + 14.2\,\text{N}$$

$$\text{Cr equivalent} = \text{Cr} + 1.5\,\text{Si} + 1.4\,\text{Mo} + 2\,\text{Nb} + 3\,\text{Ti}$$

The Cr_{eq}/Ni_{eq} ratio of each alloy is listed in Table 1. The Cr_{eq}/Ni_{eq} ratio of specimen decreases with the increasing of Cu content. In this investigation, the Cr_{eq}/Ni_{eq} ratios of the as-received SUS 304 steel and the SUS 304 steel that contains 2.5 wt.% Cu are 1.90 and 1.55, respectively. Therefore, according to the solidification mode of austenitic stainless steel [5], the vermicular and lathy ferrite would be formed in the as cast microstructure of both 0% and 2.5% Cu austenitic stainless steels. Fig. 1(a) and (b) show as-cast images of the as-received SUS 304 steel and the SUS 304 steel that contains 2.5 wt.% Cu, respectively. Figures reveal that the δ-ferrite morphology of as-cast SUS 304 steel is complex, and depends strongly on the composition. When the Cu content of as-received SUS 304 steel is 0.15 wt.% and its Cr_{eq}/Ni_{eq} ratio is 1.90, the microstructure consists of lathy ferrite and small amounts of vermicular ferrite distributed in the austenitic matrix, as shown in Fig. 1(a). When the Cu content of SUS 304 steel increases to 2.5 wt.% and its Cr_{eq}/Ni_{eq} ratio decreases to 1.55, the microstructure shows that the vermicular ferrite embedded in the austenitic matrix and the lathy ferrite almost disappears, as shown in Fig. 1(b).

As the Cu content of SUS 304 steel increases to 3.5 wt.% or more, such as 4.5 or 5.5 wt.%, the lathy ferrite in austenite matrix would completely disappear and were displaced with vermicular ferrite. Additionally, the amount of δ-ferrite decreased as the Cu content increased because the Cu element is the γ-phase stabilizer. Therefore, the formation of retain δ-ferrite appears to be reduced as the Cu content increases.

The cast ingots were hot-rolled at 1150 °C in order to eliminate voids, dendritic structure and macrosegregation of the castings. Fig. 1(c) and (d) show the morphology of the as-received SUS 304 steel and the SUS 304 steel containing 2.5 wt.% Cu after hot rolling at 1150 °C. Fig. 1(c) reveals that the retained δ-ferrite in the as-cast SUS 304 steel is eliminated after hot rolling. Meanwhile, dark, stripe-like α′-martensite is formed parallel to the direction of hot rolling in the austenite grain. However, no α′-martensite is observed in the specimen that contain 2.5 wt.% Cu, as shown in Fig. 1(d), because adding 2.5 wt.% Cu not only enlarges the γ-phase field but also increases the stacking fault energy [17]. Additionally, some mechanical twins are observed in the austenitic matrix.

Solid solutioning and ageing treatments were performed to precipitate the ε-Cu phase in the passivated film and, thus, give SUS 304 steel the antibacterial property [1–3]. Fig. 1(e) and (f) show the optical micrographies of the as-received SUS 304 steel and the SUS 304 steel that contains 2.5 wt.% Cu after solid solutioning and ageing treatments. Fig. 1(e) shows that the α′-martensite remains and the grain size of the austenitic matrix is coarser after the solid-solutioning treatment at 1050 °C for 5 min and then ageing at 800 °C for 60 min. Microstructural observations revealed that adding 2.5 wt.% Cu or more to austenitic stainless steel can eliminate the α′-martensite and reduce the formation of retain δ-ferrite.

Because the ε-Cu precipitates upon the passivated oxide film are too small to be observed by optical microscopy, Fig. 2 shows the back-scattering electron images (BEIs) of the as-received SUS 304 steel, the SUS 304 steel that contains 1.5, 2.5 and 4.5 wt.% Cu after the solid-solutioning at 1050 °C for 5 min and ageing treatment at 800 °C for 120 min, respectively. Since the atomic number of Cu (29) is larger than that of Fe (26) and Cr (24), the bright area in the back-scattering electron images represents the ε-Cu phase, whereas the dark region represents the austenitic matrix. Moreover, the ε-Cu is fcc structure and its lattice parameter is 0.363 nm. The composition of ε-Cu is close to pure copper [18]. Fig. 2(a) reveals that no ε-Cu precipitates on the passivated film of SUS 304 steel because the Cu content of the as-received material is only 0.15 wt.% (Table 1). In this case, the Cu content is too low to precipitate on the passivitated film after ageing treatment. However, little ε-Cu can be observed on the passivated film of SUS 304 steel after ageing treatment, as the Cu content increases to 1.5 wt.%, as shown in Fig. 2 (b). Fig. 2(c) and (d) reveal that the amount of ε-Cu precipitated on the passivitated film increases as the Cu content increases to 2.5 or 4.5 wt.%. The tiny precipitation of ε-Cu phase which is smaller than lum, gives the SUS 304 steel antibacterial property, as discussed in Section 3.5.

3.2. *Mechanical test*

SUS 304 stainless steel has an austenitic phase at room temperature, and so cannot be hardened to any great extent

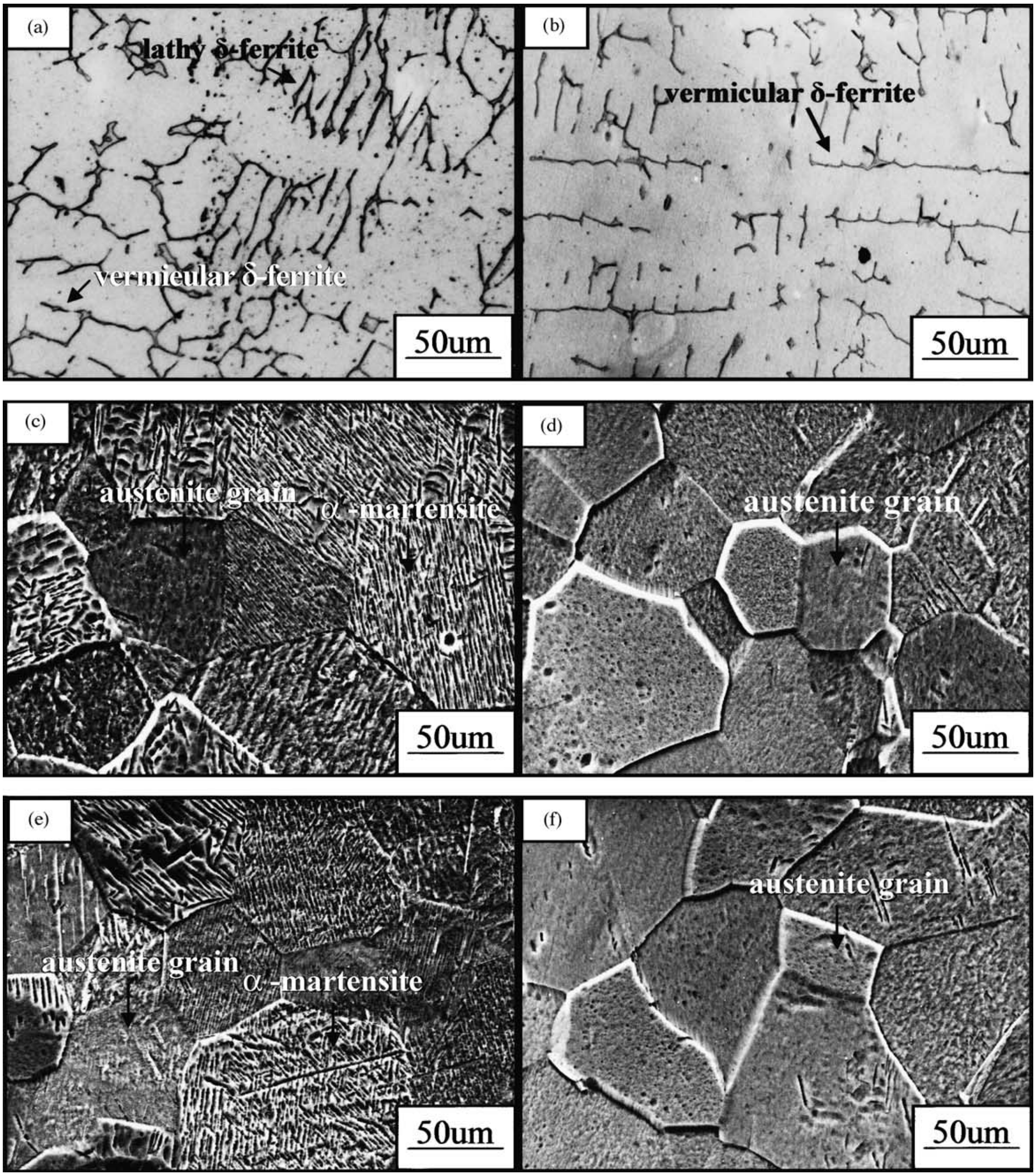

Fig. 1. Micrographs showing OM images of SUS 304 steels containing Cu at various conditions: (a) The as-cast SUS 304 steel without Cu addition and (b) with 2.5 wt.% Cu. (c) The as-cast SUS 304 steel without Cu addition and (d) with 2.5 wt.% Cu after hot rolling at 1150 °C. (e) The rolled SUS 304 steel without Cu addition and (f) with 2.5 wt.% Cu after solid-solutioning treatment at 1050 °C for 5 min and then ageing treatment at 800 °C for 60 min.

by heat treatment. However, it can be considerably strengthened by strain-induced martensite (α′-martensite), low stacking fault energy, and precipitation hardening or solid-solution strengthening [10]. The deformation mode of austenitic stainless steel generally involves a sequence of planar slip to ε-martensite then to α′-martensite. As the stacking fault energy of austenitic stainless steel increases, the dominant deformation mode is shifted from α′-martensite formation to the formation of deformation twins and then to cross slip [6,8]. The results of tensile testing shown in Fig. 3(a) reveal that the ultimate tensile strength (UTS) declines evidently as the Cu content increases from 0 to 2.5 wt.%, for two reasons. Firstly, Cu is one of the elements that effectively increase the stacking fault energy (SFE) of austenitic stainless steel and stablizes the austenitic structure. The increase of the SFE due to the addition of Cu reduces the width between the partial dislocations that contain the stacking faults, so that two partial dislocations are more likely to combine to form a perfect dislocation, which can cross-slip to another slip plane to prevent the pile up of a large number of dislocations on the same

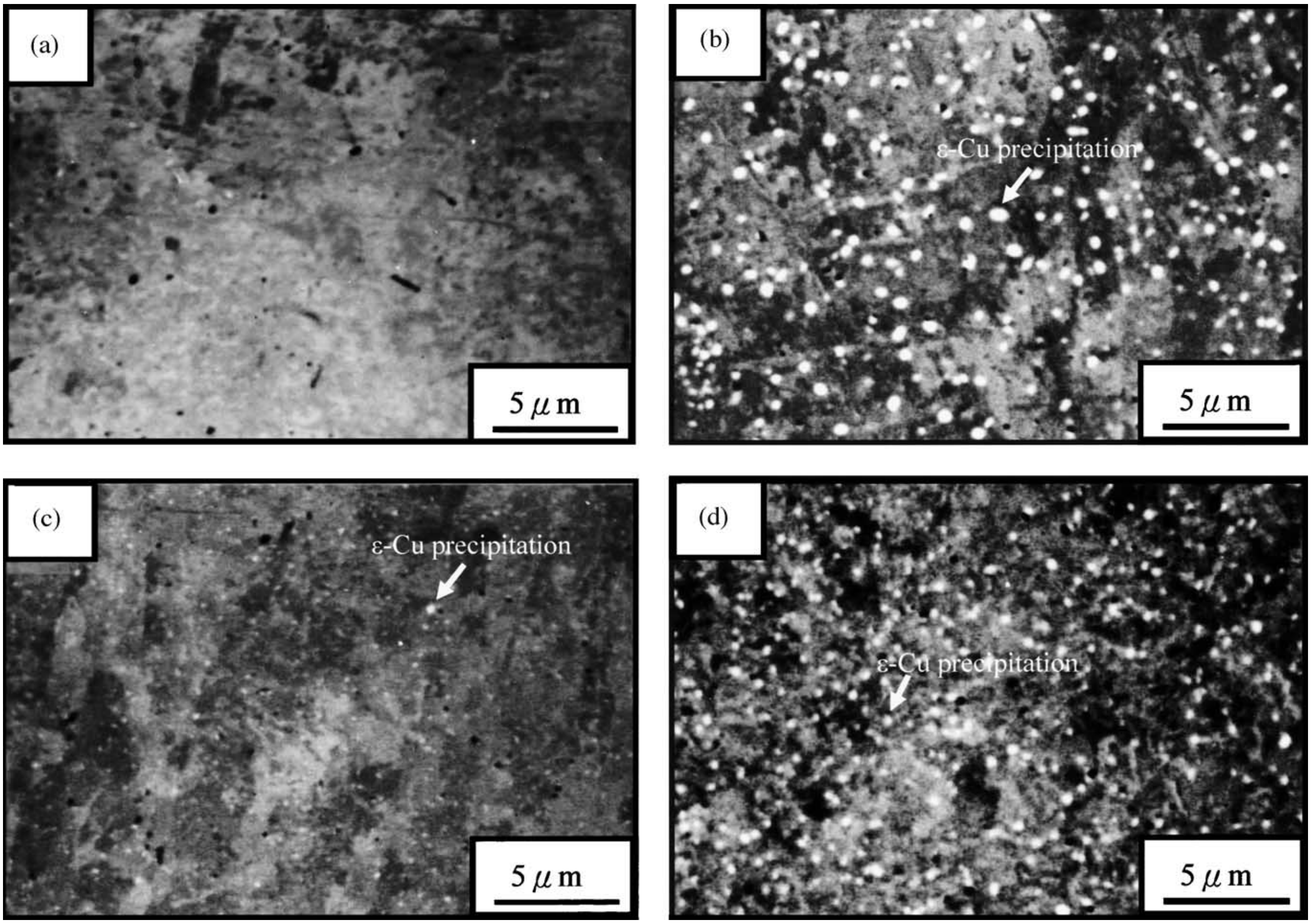

Fig. 2. The back-scattering electron images (BEIs) of SUS 304 steels containing Cu. (a) The rolled SUS 304 steel without Cu addition and with (b) 1.5 wt.% Cu, (c) 2.5 wt.% Cu, (d) 4.5 wt.% Cu, after solid-solutioning treatment at 1050 °C for 5 min and then ageing treatment at 800 °C for 120 min.

slip plane. Secondly, the addition of Cu can suppress the formation of strain-induced martensite (α′-martensite) during tension testing to prevent strain hardening.

However, the ultimate tensile strength increases with the Cu content over 2.5 wt.%, because the effect of solution strengthening caused by the addition of Cu exceeds the softening effect due to the increase of stacking fault energy. When the Cu content of the alloy exceeds 4.5 wt.%, the increase in the ultimate tensile strength tends to be small, indicating that the contribution of Cu to the increase of UTS has reached

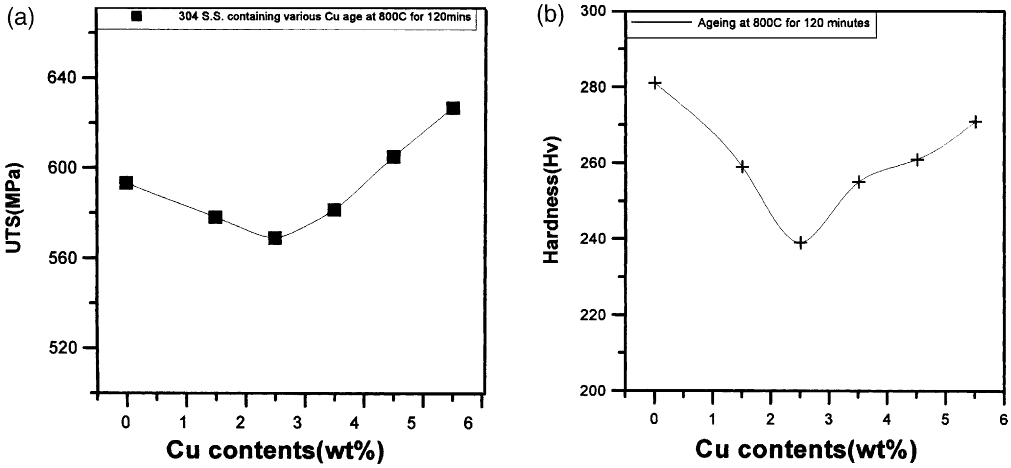

Fig. 3. The (a) UTS and (b) Vicker hardness of Cu-modified 304 stainless steel are functions of Cu content after solution-treatment at 1050 °C for 5 min and then ageing at 800 °C for 120 min.

a maximum. Fig. 3(b) plots the hardness of SUS 304 steel varies against Cu content. The hardness decreases as the Cu content increases below 2.5 wt.%, but increases with the Cu content above 2.5 wt.%, implying that when the Cu content is 2.5 wt.%, the softening effect of Cu on SUS 304 steel matrix tends to be mitigated. As the Cu content increases further, the saturated Cu atoms in the matrix precipitate and harden the SUS 304 steel.

Fig. 4 shows fractographs of the SUS 304 steel with various Cu contents, after tensile testing at room temperature. The ductile fracture surfaces of all of the SUS 304 steels, with and without Cu, are similar. These figures reveal that adding Cu does not change the deformation behavior leading to the final failure of the stainless steel. It may be attributed to that the matrix of SUS 304 steel is always in a stable state of austenitic phase, instead of transforming into ferrite or martensite, as Cu content increasing from 0 to 5.5 wt.%.

3.3. X-ray diffraction test

Fig. 5 shows the results of the XRD of the specimens solution-treated at 1050 °C and then ageing-treated at 800 °C

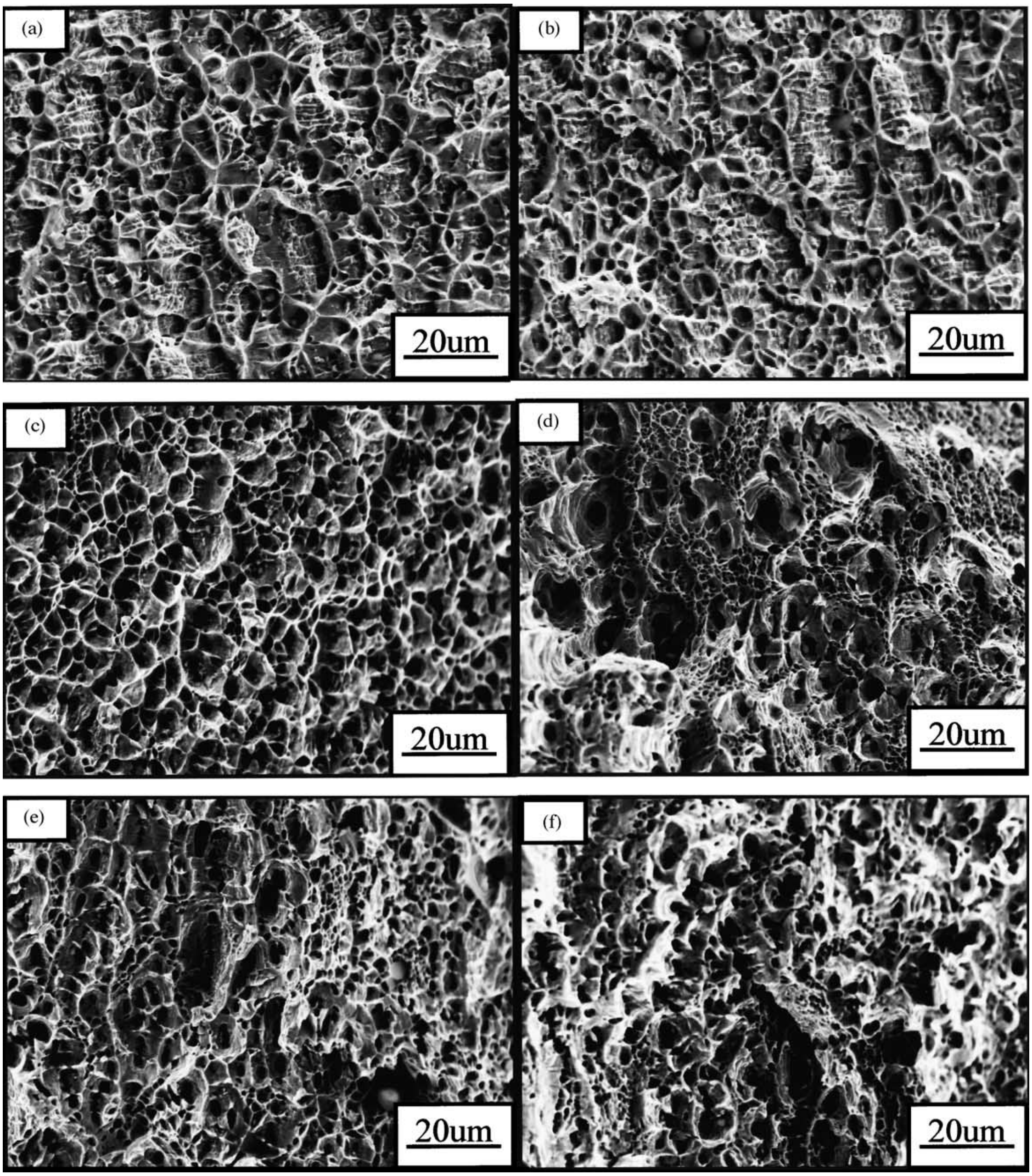

Fig. 4. SEM fractographies of the SUS 304 steel containing various Cu contents after room temperature tensile testing: (a) without Cu addition, (b) 1.5 wt.% Cu, (c) 2.5 wt.% Cu, (d) 3.5 wt.% Cu, (e) 4.5 wt.% Cu, (f) 5.5 wt.% Cu. The specimens were solution-treated at 1050 °C for 5 min and then ageing treated at 800 °C for 120 min.

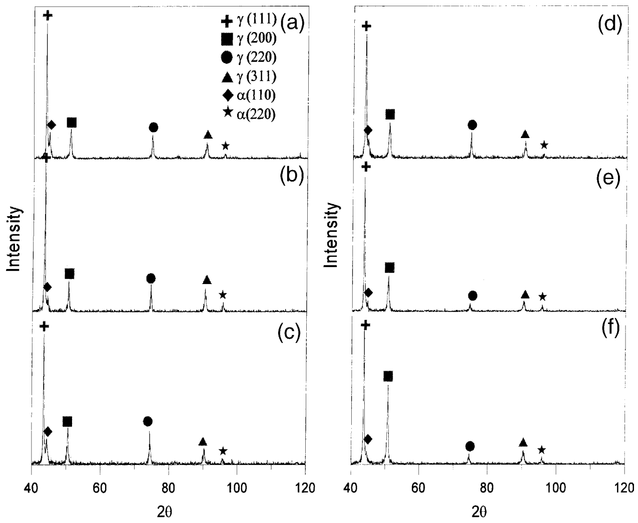

Fig. 5. X-ray diffraction intensity -2θ curves for the SUS 304 steels containing various Cu contents before tensile testing: (a) without Cu addition, (b)1.5 wt.% Cu, (c)2.5 wt.% Cu, (d) 3.5 wt.% Cu, (e) 4.5 wt.% Cu, (f) 5.5 wt.% Cu. The specimens were solution-treated at 1050 °C for 5 min and then ageing treated at 800 °C for 120 min.

for 120 min before tensile testing, where the peak intensity of strain-induced martensite (α′-martensite) are very low, thus, little α′-martensite exists prior to testing. Fig. 6 shows the results of XRD analysis of the tensile test specimens solution-treated at 1050 °C and then ageing-treated at 800 °C for 120 min. The peak intensity of α′-martensite of the specimens after the tensile test are higher than those of the specimens before the tensile test. The peaks intensity of α′-martensite decline as the Cu content increases because the addition of Cu can effectively increase the stacking fault energy of SUS 304 steels, reducing the formation of strain-induced martensite (α′-martensite). Adding Cu from 0 to 3.5 wt.% effectively suppresses the formation of strain-induced martensite (α′-martensite). However, when the Cu content exceeds 4.5 wt.%, the amount of strain-induced martensite no longer changes with the Cu content, implying that the suppression of the formation of the strain-induced martensite (α′-martensite) by Cu addition tends to mitigated when the Cu content reaches 3.5 wt.%.

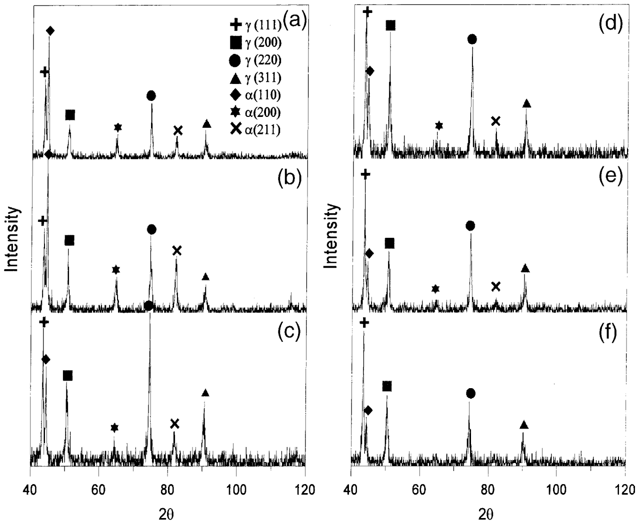

Fig. 6. X-ray diffraction intensity -2θ curves for the SUS 304 steels containing various Cu contents after tensile testing: (a) without Cu addition, (b) 1.5 wt.% Cu, (c) 2.5 wt.% Cu, (d) 3.5 wt.% Cu, (e) 4.5 wt.% Cu, (f) 5.5 wt.% Cu. The specimens were solution-treated at 1050 °C for 5 min and then ageing treated at 800 °C for 120 min.

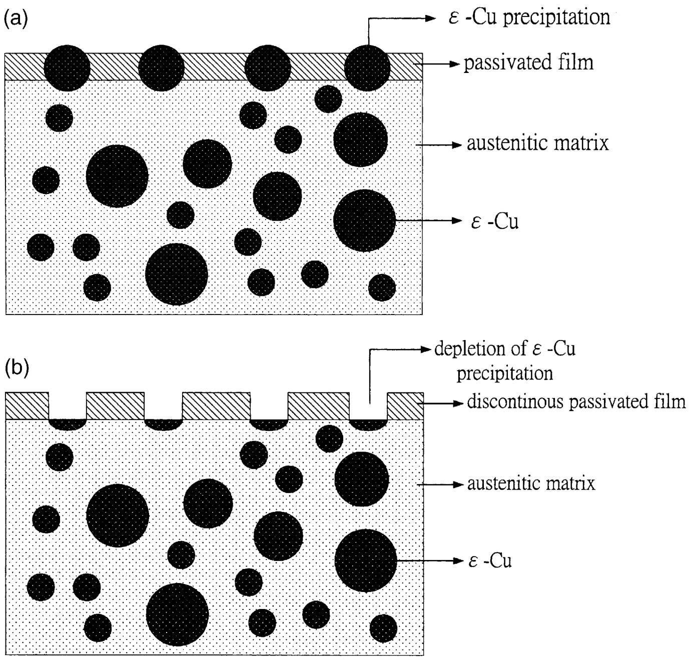

Fig. 7. A schematic illustration of (a) the precipitation of ε-Cu on the SUS 304 steel specimen; and after the galvanic corrosion, it shows (b) the depletion of ε-Cu and discontinuous passivated film.

3.4. Corrosion test

The ε-Cu must precipitate on the passivated oxide film of stainless steels to form Cu ions to extract the electrons from bacteria, as shown in Fig. 7(a) and, thus, provide stainless steels with the excellent antibacterial property. Unfortunately, the precipitation of ε-Cu negatively affects the corrosion property of stainless steels.

Copper dissolved in austenite solid solution does not detrimentally affect the stability of the passivated oxide film. However, after ageing treatment, ε-Cu precipitates on the passivated film and reduces the corrosion resistance of steels in NaCl solution [11,13]. This effect is related to the galvanic corrosion which occurs between the ε-Cu precipitates on the passivated film. The corrosion potential of ε-Cu is known to exceed that of austenite stainless steel in NaCl solution [12,14]. Once the active ε-Cu precipitates on the passivated film, the corrosion rate of ε-Cu precipitates will exceed that of the passivated film. The ε-Cu phase is not resistant to pitting corrosion in a solution that contains chlorides [12]. The precipitations of the ε-Cu phase are the “weak points” of the passivated film, susceptible to local attack. Once the ε-Cu has

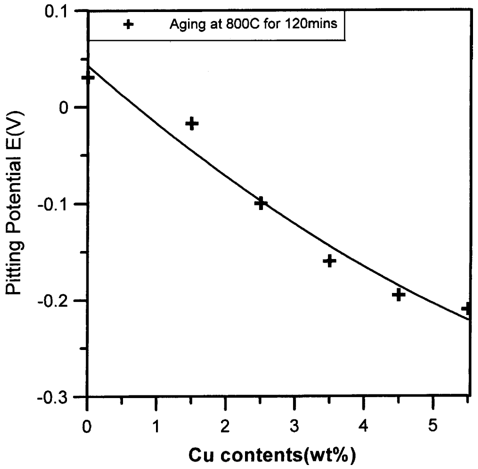

Fig. 8. Effect of Cu addition on the pitting potential of SUS 304 steel after solution-treating at 1050 °C for 5 min and then ageing at 800 °C for 120 min.

been depleted by galvanic corrosion, the passivated film of stainless steel will be discontinuous, as shown in Fig. 7(b). These discontinuities of the passivated film reduce the resistance of stainless steel to pitting corrosion. Fig. 8 reveals that pitting potential of the SUS 304 steel after ageing at 800 °C for 120 min declines as the Cu content increases. The passivated oxide film of SUS 304 steel without any Cu is continuous and dense, effectively resisting the pitting corrosion caused by chloride ions. The pitting potential declines to 0.05 V as the Cu content increases from 0 to 1.5 wt.%. When the Cu content exceeds 3.5 wt.%, the pitting potential declines more obviously. The Cu content in those steels is enough to cause the ε-Cu phase to precipitate upon the passivated film during the ageing treatments. These ε-Cu precipitates will cause passivated film to become discontinuous and unable to resist the pitting corrosion, reducing the pitting potential.

3.5. Antibacterial test

The *S. aureus* is used as the testing bacteria in this test. The specimens with *S. aureus* were incubated at 25 °C for 24 h. The number of the live bacteria and the antibacterial rate were measured by the plain-plate dilute method.

The precipitation of the ε-Cu phase on the surface of stainless steel enables the Cu-ions to be dissolved from it and, thus, come into contact with the bacteria on the surface of steel [1–3]. These Cu-ions can kill bacteria by destroying their cell walls and cell membranes because Cu-ions that have the strong reduction can extract the electrons from the bacteria, causing their cytoplasm to run off and oxidizing their cell nucleus [1–3]. A large amount of ε-Cu precipitates on the passivated film corresponds to more Cu-ions can be dissolved on the surface of the stainless steel, and better antibacterial ability.

Table 2 states the antibacterial rate of SUS 304 steel that contains Cu. The results reveal that after ageing treatment at 700 or 800 °C for 30 to 120 min, the SUS 304 steels that

Table 2
The antibacterial rates of SUS 304 steel with various Cu contents

Heat treatment conditions (all specimens were solution-treated at 1050 °C for 5 min before ageing treatment)	The number of cultivated bacterial	The number of cultivated bacterial after 24 h	Antibacterial rate (%)
SUS304 steel + 0 wt.% Cu ageing at 700 °C for 240 min	4.1×10^5	2.8×10^5	0
SUS304 steel + 0 wt.% Cu ageing at 800 °C for 240 min	2.8×10^5	1.7×10^5	0
SUS304 steel + 1.5 wt.% Cu ageing at 700 °C for 30 min	4.6×10^5	5.1×10^4	30.04
SUS304 steel + 1.5 wt.% Cu ageing at 700 °C for 120 min	4.1×10^5	9.2×10^3	81.72
SUS304 steel + 1.5 wt.% Cu ageing at 700 °C for 240 min	4.1×10^5	<10	99.99
SUS304 steel + 1.5 wt.% Cu ageing at 800 °C for 30 min	2.8×10^5	3.6×10^4	23.40
SUS304 steel + 1.5 wt.% Cu ageing at 800 °C for 120 min	4.6×10^5	5.1×10^4	30.04
SUS304 steel + 1.5 wt.% Cu ageing at 800 °C for 240 min	4.1×10^5	<10	99.99
SUS304 steel + 2.5 wt.% Cu ageing at 700 °C for 30 min	4.6×10^5	3.8×10^4	41.54
SUS304 steel + 2.5 wt.% Cu ageing at 700 °C for 240 min	4.1×10^5	<10	99.99
SUS304 steel + 2.5 wt.% Cu ageing at 800 °C for 30 min	2.8×10^5	1.3×10^4	64.80
SUS304 steel + 2.5 wt.% Cu ageing at 800 °C for 240 min	2.8×10^5	<10	99.99
SUS304 steel + 3.5.wt.% Cu ageing at 700 °C for 30 min	4.6×10^5	1100	99.00
SUS304 steel + 3.5 wt.% Cu ageing at 700 °C for 240 min	4.1×10^5	<10	99.99
SUS304 steel + 3.5 wt.% Cu ageing at 800 °C for 30 min	2.8×10^5	<10	99.99
SUS304 steel + 3.5 wt.% Cu ageing at 800 °C for 240 min	2.8×10^5	<10	99.99
SUS304 steel + 4.5 wt.% Cu ageing at 700 °C for 30 min	4.6×10^5	<10	99.99
SUS304 steel + 4.5 wt.% Cu ageing at 700 °C for 240 min	4.1×10^5	<10	99.99
SUS304 steel + 4.5 wt.% Cu ageing at 800 °C for 30 min	2.8×10^5	<10	99.99
SUS304 steel + 4.5 wt.% Cu ageing at 800 °C for 240 min	2.8×10^5	<10	99.99
SUS304 steel + 5.5 wt.% Cu ageing at 700 °C for 30 min	4.6×10^5	<10	99.99
SUS304 steel + 5.5 wt.% Cu ageing at 700 °C for 240 min	4.1×10^5	<10	99.99
SUS304 steel + 5.5 wt.% Cu ageing at 800 °C for 30 min	2.8×10^5	<10	99.99
SUS304 steel + 5.5 wt.% Cu ageing at 800 °C for 240 min	2.8×10^5	<10	99.99

This experiment was conducted by Food Industry Research and Development Institute of R.O.C. in Taiwan.

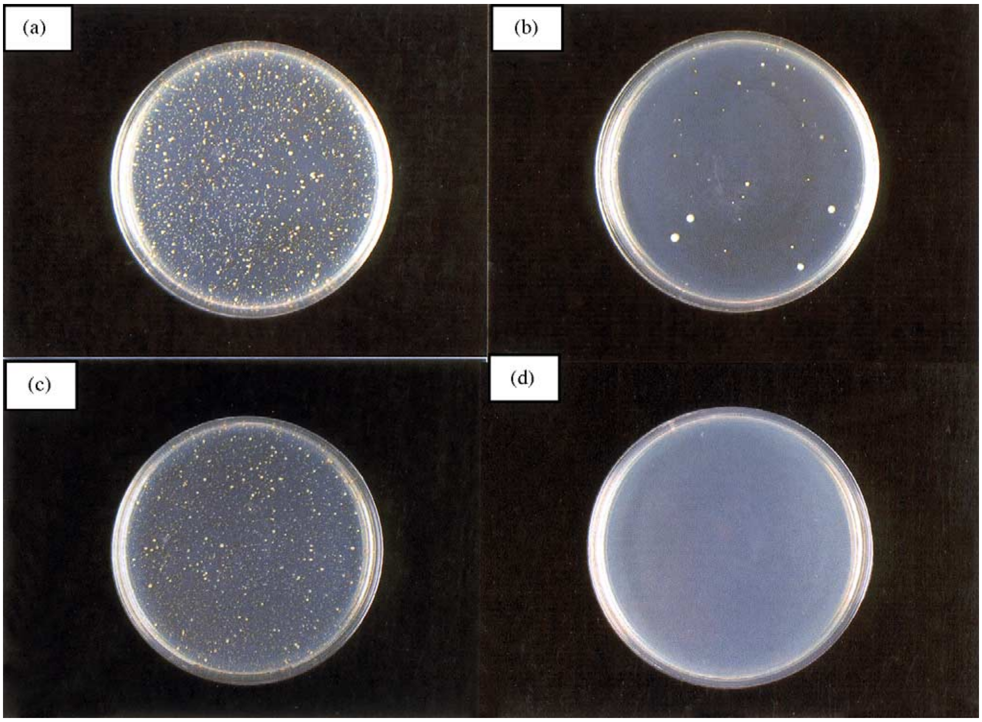

Fig. 9. The breeding status of *Staphylococcus aureus* on SUS 304 steel: the SUS 304 steel: (a) without Cu addition and (b) with 2.5 wt.% Cu addition, ageing-treated at 800 °C for 30 min. The SUS 304 steel (c) without Cu addition and (d) with 2.5 wt.% Cu addition, ageing-treated at 800 °C for 240 min.

contain either 1.5 or 2.5 wt.% Cu do not exhibit good antibacterial ability, because the amount of added Cu is too little to be precipitated effectively on the passivated film by ageing treatment, so the antibacterial rate is quit low. However, when the ageing time is extended to 240 min, adding even 2.5 wt.% or less Cu generates enough ε-Cu precipitates by long-time diffusion, to make the antibacterial rate reach 99.99%. When the Cu content exceeds 3.5 wt.%, the antibacterial rates of all stainless steels can be as high as 99.99% for all the ageing times.

Fig. 9 presents the breeding status of *S. aureus* which are cultivated on the surface of the as-received SUS 304 steel and the SUS 304 steel that contains 2.5 wt.% Cu. After the *S. aureus* had been cultivated for 24 h, many fewer bacteria present on the surface of the SUS 304 steel that contains 2.5 wt.% Cu (Fig. 9(b)) than on that of as-received SUS 304 steel (Fig. 9(a)). This result reveals that adding Cu provides SUS 304 steels with the antibacterial property. Fig. 9(c) and (d) reveal that when ageing treatment is prolonged from 30 min to 240 min, the bacteria cultivated on the SUS 304 steel surface are all extinguished by ε-Cu precipitates.

4. Conclusion

(1) The microstructures of the as-received SUS 304 steel and the SUS 304 steel that contains 2.5 wt.% Cu are retained δ-ferrite distributed in an austenitic matrix. The retained δ-ferrite morphology strongly depends on the composition of the SUS 304 steel. After hot rolling and heat treatment, the δ-ferrite disappears and the α'-martensite formes in the austenite grain.
(2) Microstructural observations reveal that adding 2.5 wt.% or more Cu to the austenitic stainless steel can eliminate the α'-martensite and reduce the formation of retain δ-ferrite.
(3) The ultimate tensile strength declines as the Cu content in the stainless steels increases when less than 2.5 wt.% Cu is added. However, when more than 3.5 wt.% Cu is added, the UTS increases with the Cu content due to severe solid-solution strengthening.
(4) The ε-Cu precipitated on the passivated oxide film causes the film to become discontinuous, reducing the pitting potential.
(5) When the amount of added Cu exceeds 3.5 wt.%, even if the ageing time is as short as 30 min, the antibacterial rate is 99.99%. However, Cu addition should not exceed 3.5 wt.% to ensure that SUS 304 steels that contain Cu exhibit a balance among formability, corrosion resistance and antibacterial properties.

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