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Mechanical and Antibacterial Properties of Copper-added Austenitic Stainless Steel (304L) by MIM

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Abstract For the austenitic stainless steel (304 L) manufactured by metal injection molding (MIM), the effects of copper content and sintering temperature on the mechanical properties, antibacterial activities, corrosion resistance, and electric resistances were investigated. The specimens were prepared by injection molding of the premixed powders of water-atomized 304 L and Cu with poly-acetyl binders. The green compacts were prepared with various copper contents from 0 to 10 wt.% Cu, which were debound thermally at 873 K for 7.2 ks in N_2 gas atmosphere and subsequently sintered at various temperatures from 1323 K to 1623 K for 7.2 ks in Ar gas atmosphere. The relative density and tensile strength of the sintered compacts showed the minimum values at 5 and 8 wt.% Cu, respectively. Both the relative density and the tensile strength of the specimen with 10 wt.% Cu sintered at 1373 K showed the highest values, higher than those of copper-free specimen. Antibacterial activities investigated by the plastic film contact printing method for bacilli and the quantitative analysis of copper ion dissolved in water increased as the increase of the copper content to stainless steels. It was also verified by the measurement of pitting potential that the copper addition in 304 L could improve the corrosion resistance. Furthermore the electric conductivity increased with the increase of copper content.

Keywords: Metal injection molding, Copper-added stainless steel, Mechanical property, Antibacterial activity

1. Introduction

Austenitic chromium-nickel stainless steels exhibit a passivity in wide range of corrosive environments, and have been widely used as corrosion-resistant materials. Among them, low carbon stainless steels (such as 304L) have been paid an attention mostly for the usages with the excellent corrosion-resistance. Copper-added SUS304 steel, namely XM7 (18Cr-9Ni-3Cu), is one of the corrosion-resistant materials with improved cold workability. Recently, the copper-added stainless steels have been attracting attentions due to the antibacterial activity along with the excellent corrosion-resistant properties of austenitic stainless steels. The stainless steel exhibits the high-functional characteristics since copper ion is easy to dissolve into the ambient water from the passive surfaces of steel.[1,2] Duration of antibacterial activity depends on the total amount of dissolved copper ion. It is expected that the amount of dissolved copper ion is proportion to the copper content added to stainless steels. In contrast to such advantages, however, the addition of copper may cause deteriorating the mechanical properties by segregation. There have been few reports on the high copper content austenitic stainless steels (Cu-304L) manufactured by metal powder injection molding (MIM) process.[2]

One of the aims in this study is to obtain the fundamental database necessary for industrial production of high copper content stainless steels by powder injection molding. In this paper, the effects of copper content and sintering temperature on the density and the tensile strength are discussed in association with the microstructures. Furthermore antibacterial activity, corrosion-resistance, and electric resistance were evaluated experimentally. The effects of copper content on these

Table 1. Characteristics of 304L water-atomized powder

Chemical composition [mass%]										Mean particle size [μm]	Tap density [g/cm^3]
C	Si	Mn	P	S	Ni	Cr	Mo	Cu	O(ppm)		
0.03	0.82	0.77	0.02	0.01	11	18.2	0.03	0.03	3860	8.05	4.30

properties were discussed.

2. Experimetal Procedure

2.1. Preparation for specimens

The metallic powders used in this experiment were 304L powders (8.05 μm in average diameter, Atmix Co., Ltd. Japan) and pure copper powders (8.95 μm in average diameter, Atmix Co., Ltd. Japan), both of which were produced by water-atomization. The chemical compositions are listed in Table 1 and Table 2. These powders were mixed mechanically in a stainless steel container, where the copper contents varied from 0 to 10 wt.%. The mixed metallic powders were compounded with poly-acetyl based binders as feedstock materials for MIM with the volume fraction of the metal powders set to be 65%. The powders and the binders were premixed at 443 K for 3.6 ks using the high-pressure kneader (Toshin Co., Ltd., Japan, TD1-3M), and granulated at 423 K using the plunger-type extruder (Toshin Co., Ltd., Japan, TP80-2). Tensile specimens (Figure 1) were made with the plunger-typed injection molding machine (Sodick Plustech Co., Ltd. Japan, TR40S3, 40 ton), where the molding condition was optimized as the injection pressure of 100 MPa and the injection speed of 50 mm/s. The green compacts were debound at 873 K for 7.2 ks in N_2 gas atmosphere, and sintered for 7.2 ks in Ar gas atmosphere using the vacuum debinding and sintering furnace (Shimadzu Mectem Inc. Japan, VHSgr, 40/40/100-M). The sintering temperature was selected at 6 levels from 1323 K to 1623 K.

2.2. Density measurement and tensile test

Densities of the specimens were measured in order to investigate the effects of copper content on the packing ratio of metal powders or apparent density in green compacts and sintered compacts. The weights of green compacts and sintered compacts were measured in air and water using the electronic balance (Shimadzu Co., Ltd, AY220, minimum displayed value = 0.1 mg), and the density was calculated based on the Archimedes' principle (JIS Z 2505(1989)). The tensile test of sintered compacts was carried out using the universal testing machine (Shimadzu Co., Ltd, Autograph®, AG-10TD) at a constant crosshead speed of 5 mm/min.

Table 2. Characteristics of pure copper water-atomized powder

Chemical composition [mass%]		Mean particle size [μm]	Tap density [g/cm^3]
Cu	O(ppm)		
Bal.	600	8.95	5.34

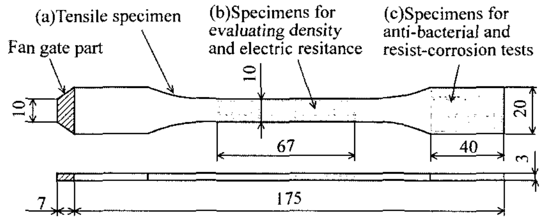


Fig. 1. Geometry of specimens(Unit: mm).

2.3. Cross-sectional observation

The cross-sectional observation of the specimens was carried out with the scanning electron microscope (SEM, Hitachi Co., Ltd. Japan, S-2460N). The samples were prepared by polishing with Al_2O_3 powder (0.02 μm in average diameter), without etching. The number of pores on the cross-sectional area was evaluated by the image analysis processor (Media Cybernetics Inc., Image-Pro Plus®). Micro-elemental analysis on the cross-section has been done by Energy Dispersive X-ray analyzer (EDX, Horiba Co., Ltd. Japan, EMAX-5770) for the qualitative analysis of the chemical composition of the precipitated phase.

2.4. Evaluation of antibacterial activity

2.4.1 Film contact printing method

Film contact printing method is one of the testing methods for evaluating antibacterial activity, which is recommended in the Society of Industrial-technology for Anti-microbial Articles (SIAA).[1] The experimental procedure is done as following; 1) a drop of liquid including bacteria on the surface of specimens, and 2) cover the specimen surface with the plastic film such as Polyethylene. In such a way, the film inoculates the viable bacilli from the specimen surface. The number of viable bacilli was counted for an evaluation of antibacterial activity of the sample. The experimental bacterial strain used was the colon bacillus (*Escherichia coli* IFO-3972), which was cultured at 308 K for 24 hr. The numbers of sample were 6 for the well verification in reappearance of the testing result. The wrought stainless steel XM7 (solution heat-treated, and skin-pass finish) was also used as the reference in comparison with the injection molded parts. The chemical composition of XM7 is listed in Table 3.

2.4.2 Quantitative elemental analysis of copper ion dissolved in water

The amount of copper ion soluble in distilled water was evaluated by the quantitative elemental analysis. The result can give the quantitative index how long the antibacterial activity of the material is in effect in its ambient. It is generally thought that approximately 50% of colon bacillus cannot survive in the copper ion concentration of 40 p.p.b. (= 40 μg/l).[3] The effect of copper on antibacterial activity was evaluated by measuring the amount of copper ion dissolved from the specimen into distilled water with the Inductively Coupled Argon Plasma (ICAP) analyzer (Nippon Jarrell-Ash Co., Ltd. IRIS ADvantaged™ ICMP). The wrought stainless steel XM7 (solution heat-treated, and skin-pass finish) was also used as the reference. The chemical composition of 304L is listed in Table 4.

Each specimen kept separately in the distilled water (200 ml) for 24 hrs at room temperature, and a part (60 ml) of the water was used for testing. The quantitative elemental analysis was done at the conditions of high wave frequency output 1150 W and wavelength Cu I 324.7 nm{103}.

2.5. Evaluation of corrosion resistance by pitting potential measurement

The corrosion resistance of sintered compacts[4] was evaluated by the pitting potential measurement. 304 L wrought material was used as the reference in comparison with the injection molded specimens. The test was performed in accordance with the Japanese Industrial Standard, JIS G 0577. For the anodic electrodes the specimens embedded in epoxy resin were used, which were polished using abrasive paper, #800 and degreased using alkali immersion degreaser (Dipsol Chemicals Co., Ltd. Japan, #44S). The polished surface was passivated by immersing in 30 wt.% H_2NO_3 solution at 323 K for 72 ks. The specimen surface was coated by silicon resin except testing area (10 mm^2) and polished again using abrasive paper, #600 just before testing and rinsed. The pitting potential measurement was done in 3.5 wt.% NaCl solution kept at 303 K under degassing by N_2 gas bubbling.

Table 3. Chemical compositions of XM7 wrought steel

Chemical composition [mass%]							
C	Si	Mn	P	S	Ni	Cr	Cu
0.037	0.48	1.64	0.028	0.003	8.88	18.42	3.11

Table 4. Chemical composition of 304L wrought steel

Chemical composition [mass%]						
C	Si	Mn	P	S	Ni	Cr
0.015	0.63	1.50	0.025	0.004	10.09	18.06

2.6. Measurement of electric resistance

Electric resistance is one of the interesting characteristics of the sintered compacts£ÆThe specimen surface was polished using abrasive paper, #220. The electric resistance of specimen surface was measured at room temperature by a 4-terminal conductivity meter (Sumitomo metal Co., Ltd. Japan).

3. Results and Discussions

3.1. Density of green compacts

When the feedstock was prepared by mixing 304 L and pure copper powders with the volume fraction of V_S and V_C, respectively. The premixed metal powders were mixed with a specific binder to make a feedstock with the volume fraction of V_M and V_B, respectively. The theoretical density of the green compacts (ρ_T) is determined by Equation (1) according to the rule of mixture:[5]

$$\rho_T = (\rho_S V_S + \rho_C V_C)V_M + \rho_B V_B \tag{1}$$

Where ρ_S, ρ_C and ρ_B represent the theoretical densities of 304L, pure copper and the binder, respectively, where $\rho_S = 7.80$ g/cm^3, $\rho_C = 8.93$ g/cm^3 and $\rho_B = 0.97$ g/cm^3, $V_M = 0.65$, $V_B = 0.35$. Substituting these values in Equation (1), the theoretical density of green compacts ρ_T can be presented as a function of copper content. Figure 2 shows the calculated and experimentally measured densities, and the relative density of the green compacts. The theoretical density of the green compacts increases as the copper content. The measured density of the green compacts is slightly lower than the theoretical one. The relative density of the green compacts is higher than 99% and tends to increase slightly with the increase of the copper content.

From these results, it could be found that there were no packing loss for mixed metal powders, i.e. the high content of copper added to 304 L powders did not make any problem for full packing in both mixing and molding processes.

3.2. Sintered density and mechanical properties

3.2.1. Relative density of sintered compacts

The relative density of the sintered compacts with various added copper contents, which have been processed at various sintering temperatures, are shown in Figure 3. It is obvious that the relative sintered density tends to decrease for 0 to 5 wt.% Cu specimens at any sintering temperature, and exhibits the minimum value when the copper content is 5 wt.%. The relative sintered density decreases by lower sintering temperatures, but tends to increase significantly as the copper content increases more than 5 wt.%, where the effect of sintering temperature on the relative sintering density is minimal. Such tendency appears clearly in the cases of sintering temperature higher than 1373 K, whereas the relative sintering density shows no significant change with copper content in the case of 1323 K below the melting temperature of copper 1355 K.

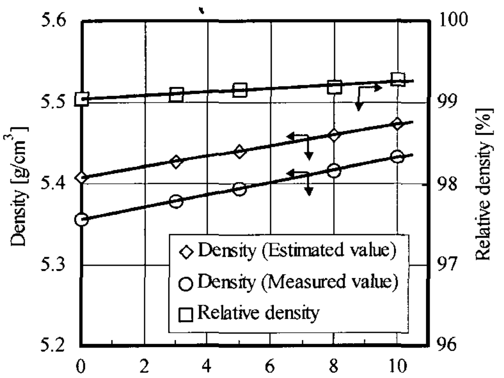


Fig.2. Density and relative density of green compacts as a function of Cu content.

The solubility of copper in 304 L at this temperature range is about 5 wt.%, thus it is suspected that the decrease of relative sintered density is due to the result of rapid solid-solutioning of copper leaving pores behind. For 8 and 10 wt.% Cu specimens, the tendency of increasing in sintered density is due to reducing the number of pores. The over-saturated copper filled the small pores and the number of pores decreased when copper had been added above the solubility limit in 304 L. These evidences will be shown by the experimental results, i.e. the cross-sectional observation and the pore counting by the image processing technique as shown in the following section. The relative density of 10 wt.% Cu specimen sintered at 1373 K shows the highest value.

3.2.2. Tensile strength of sintered compacts

The tensile strengths of the sintered compacts with various copper contents, processed at various sintering temperatures, are shown in Figure 4. When the copper content increases to 8 wt.%, the tensile strength

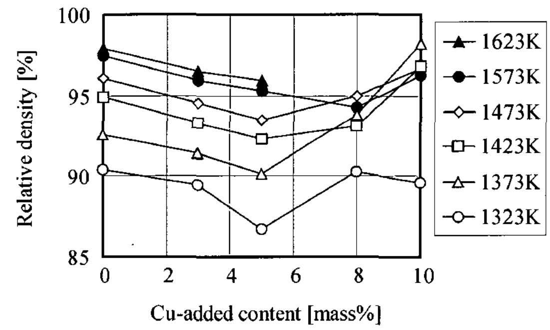


Fig.3. Effect of Cu content on relative density of sintered compacts.

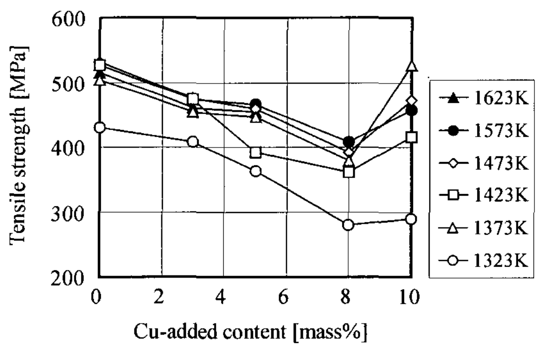


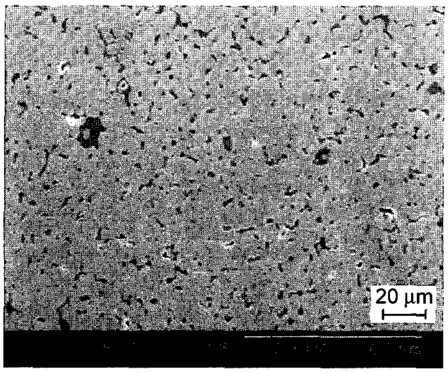
Fig.4. Effect of Cu content on tensile strength of sintered compacts.

of the sintered compacts decreases significantly at any sintering temperature. When the copper content is more than 8 wt.%, however, the tensile strength of the sintered compacts tends to increase. Particularly, 10 wt.% Cu specimen sintered at 1373 K shows the highest tensile strength, similar to that of copper-free specimen

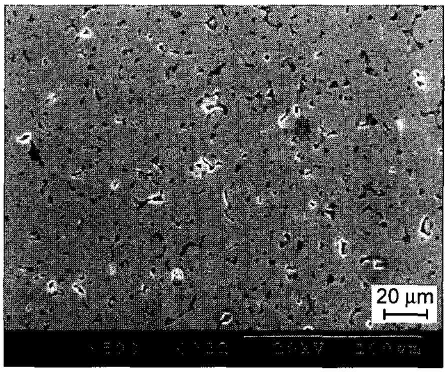
3.3. Microstructures in cross-section

3.3.1. Formation and number of pore

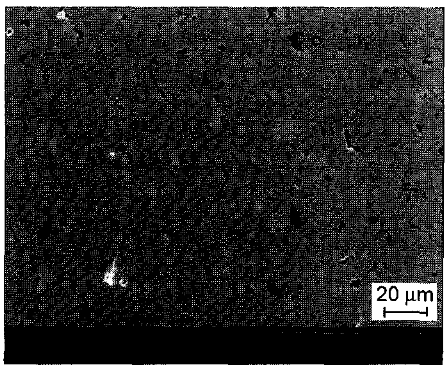
Cross-sectional SEM images of the sintered compacts sintered at 1373 K and 1573 K are shown in Figure 5 and 6, respectively. In the case of 1373 K (Figure 5), many fine pores are visible on the cross section of 0 and 5 wt.% Cu specimens, but the number of pores



(a) 0 wt.%Cu

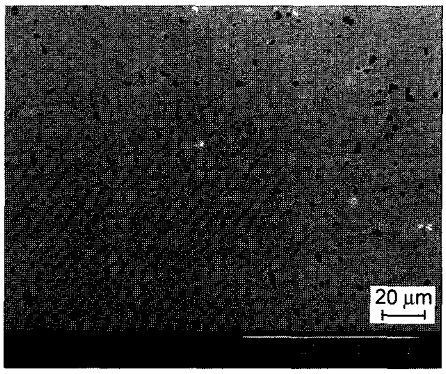


(b) 5 wt.%Cu

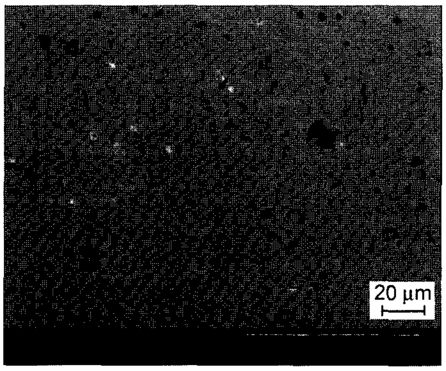


(c) 10 wt.%Cu

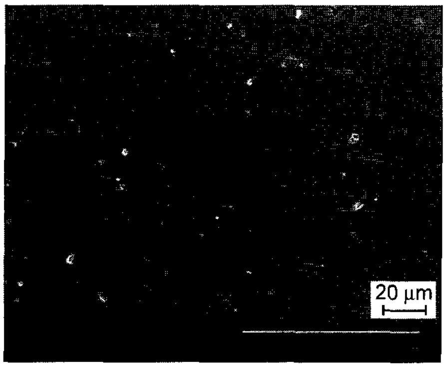
Fig.5. SEM images of polished cross section of Cu-added 304L sintered at 1373 K.



(a) 0 wt.%Cu



(b) 5 wt.%Cu



(c) 10 wt.%Cu

Fig.6. SEM images of polished cross section of Cu-added 304L sintered at 1573 K.

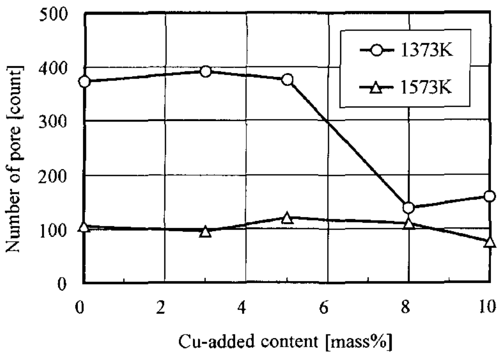


Fig. 7. Effect of Cu-added content and sintering temperature on the number of pore.

decreases significantly in the case of 10 wt.% Cu specimen. In the case of 1573 K (Figure 6), the number of pores is remarkably reduced compared to the case of 1373 K.

Figure 7 shows the number of pores as a function of copper content, which was obtained from the SEM image processing of the cross-section. When the copper content ranges from 0 to 5 wt.%, the number of pores of 1373 K specimen is 4 times more than that of 1573 K specimen. However, when the copper content is more than 8 wt.%, the number of pores decreases remarkably.

3.3.2. Elemental analysis of precipitated phase

As shown in the cross-sectional SEM images (Figure 5 and 6), massive segregated phases were observed in the case of 10 wt.% Cu. Table 5 shows the chemical composition obtained by EDX analysis for 10 wt.% Cu specimen sintered at 1373 K. The area analysis of the cross-section was carried out with the magnification of 500 (Table 5(a)), and the point analysis of the segregated phase was carried out with the magnification of 1500 (Table 5(b)). The result of the area analysis shows that the fraction of copper in the whole region is 10.29 wt.%, which is nearly the same as the added copper content. On the other hand, the fraction of copper in the precipitate is 87.00 wt.%, much higher than the other region. The segregation phase can be recognized as a copper compound.

3.4. Antibacterial activity

3.4.1. Count of viable bacilli

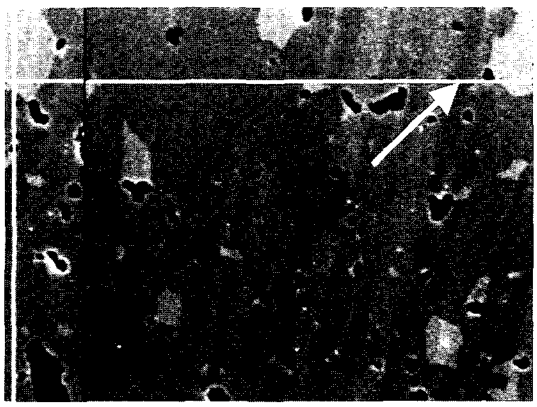
The result of the evaluation of antibacterial activity by the film contact printing method is shown in Table 6. The number of viable bacilli in the contrast ward increased remarkably from 4×10^5 to 1.8×10^7 after 24 hrs. While the number of viable bacilli was 5.4×10^5 in the Cu free specimen, it reduced remarkably to less than 10 for any specimens with more than 3 wt.% Cu or XM7 which contained approximately 3 wt.% Cu.

Table 5. EDX analysis for 10 wt.% Cu-added 304L sintered at 1373 K.

(a) Area analysis

Chemical composition [mass%]				
Fe	Si	Ni	Cr	Cu
64.52	2.13	9.08	14.00	10.29

(b) Point analysis



Chemical composition [mass%]				
Fe	Si	Ni	Cr	Cu
6.66	1.33	3.37	1.63	87.00

Table 6. Effect of copper addition on antibacterial activity. (304L compacts sintered at 1573 K)

Specimens	Count of viable bacilli	
	Immediately after the inoculation	After 24 hours
Contrast area	4.0×0^5	1.8×0^7
0 mass%Cu	-	5.4×0^4
3 mass%Cu	-	less than 10
5 mass%Cu	-	less than 11
8 mass%Cu	-	less than 12
10 mass%Cu	-	less than 13
XM7	-	less than 10

Table 7. Effect of copper addition on the amount of Cu ion dissolved in distilled water (304 L compacts sintered at 1473 K)

Specimens	Amount of dissolved Cu ion [μg/L]
Contrast area	less than 5
0 mass%Cu	less than 5
3 mass%Cu	5.9
5 mass%Cu	100
8 mass%Cu	240
10 mass%Cu	220
304L	9.3
XM7	19

From these experimental results, it is verified that copper addition to 304 L has remarkable effects on the antibacterial activity. However, the effects of the amount of copper content on the number of viable bacilli was not distinguishable in the film contact printing method.

3.4.2. Amount of copper ion dissolved in water

The antibacterial activity was evaluated indirectly by measuring the copper ion dissolved in distilled water, summarized in Table 7. The amount of copper ion dissolved in water for the Cu free specimen was less than 5 μg/l, same as that of the reference distilled water. The amount of dissolved copper ion of the specimens with the copper content more than 5 wt.% exceeded 100 μg/l. It is expected that 304 L with a proper copper addition exhibits enough antibacterial activity when immersed in water for 24 hrs. On the other hand, the antibacterial activity for 304 L and XM7 specimens was expected to be rather poor because dissolved copper ion was very small, i.e. 9.3 μg/l and 19 μg/l, respectively after 24 hrs immersion period. It is concluded that high content of copper addition is effective to improve the antibacterial activity of 304 L steel.

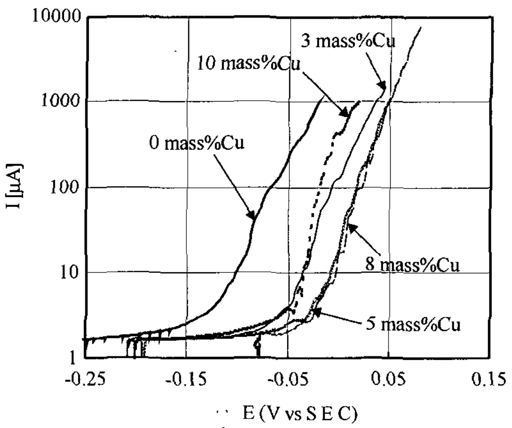


Fig. 8. Difference in pitting potential according to Cu content. (304L compacts sintered at 1573 K)

3.5. Corrosion resistance

The anodic polarization curves were obtained by the pitting potential measurement of copper added 304 L compacts sintered at 1573 K, shown in Figure 8. Specimens with 3 to 8 wt.% Cu show higher corrosion-resistance compared to Cu free sintered compacts. It has been known that corrosion resistance of steel can be improved by the addition of Cu, N, Si along with the major alloying elements such as Cr, Ni, Mo.[7] Thus it is expected that a certain amount of copper addition to 304 L steel can improve the corrosion resistance. However, the corrosion resistance of 10 wt.% Cu specimen shows lower than that of 3 to 8 wt.% Cu specimen. In the case of 304 L specimen with 10 wt.% Cu, large amount of precipitated copper phases were observed along the boundaries between the coarse grains as shown in Figure 6. When the adjacent two phases have a large difference in corrosion potential, a galvanic corrosion can be enhanced. An excessive addition of copper to 304 L, causing a massive precipitates of copper, has canceled the improvement of corrosion resistance obtained by copper addition.

3.6. Electric conductivity

Electrical resistivity as a function of added copper content in the 304 L compacts sintered at 1373 K and

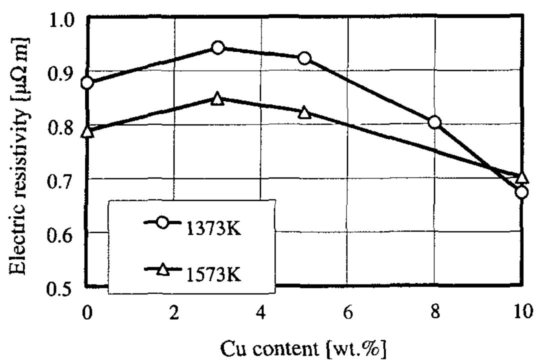


Fig. 9. Effect of Cu content on electric resistivity.

1573 K are shown in Figure 9. The electrical resistivity showed the maximum value when the copper content is 3 wt.%, and then decreased with the increase of copper content. It was higher at lower sintering temperature, where the relative density is lower. Therefore the electric resistivity of the sintered compact is significantly dependent on the density and the microstructure of the specimen. The electric conductivity of 10 wt.% Cu added 304 L sintered compact has been improved remarkably comparing to that of copper-free or low content copper-added specimen. The electrical resistivity of 304 L wrought steel is known as 0.72 μm.

4. Conclusions

The effects of copper content and sintering temperature on the mechanical properties, antibacterial activities, corrosion resistance and electric resistance of the austenitic stainless steel (304 L) produced by metal injection molding process were investigated. The experimental results obtained in this study are summarized as follows:

1) The relative density and tensile strength of the sintered compacts tend to decrease with the increase of the added copper content and showed the minimum values at 5 and 8 wt.% Cu, respectively. Both of the properties were improved up to the value of copper-free specimen by the addition of 10 wt.% Cu when the sintering temperature was 1373 K.

2) The results of antibacterial test based on the plastic film contact printing method for bacilli and the quantitative analysis of copper ion dissolved in distilled water exhibited that antibacterial activity can be improved effectively by copper addition to stainless steels.

3) It was also confirmed from the measurement of pitting potential that the copper addition improved corrosion resistance.

4) Furthermore the electric conductivity was improved with the increase of the added copper content.

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