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Effect of silicon content and aging time on density, hardness, toughness and corrosion resistance of sintered 303LSC–Si stainless steels

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Abstract

303LSC stainless steel powder was mixed with silicon powder; the powder mixture was then compacted and sintered at 1250 °C in bottle hydrogen. The sintered alloys were exposed to 800 °C to investigate the effect of silicon content and aging tome on density, hardness, toughness and corrosion resistance of the aged alloys. Experimental results show that the density and hardness of sintered alloys increase with increasing silicon content and aging time. σ-Phase precipitates during the aging treatment; the morphology and chemical composition of this precipitated phase vary markedly with the aging time. Variation of toughness is discussed as the consequence of two competition mechanisms σ-phase precipitation and porosity modification. Increasing silicon content and aging time decreases the corrosion resistance.

Keywords: Sintered 303LSC stainless steel; Silicon powder; σ-Phase precipitation; Toughness; Corrosion resistance

1. Introduction

The corrosion resistance of sintered stainless steels is inferior to that of either cast or wrought stainless steels. However, the use of powder metallurgy methods to manufacture stainless steel parts is of industrial interest as the production is economically more attractive. This is especially true when a large amount of identical pieces with small size and good dimensional accuracy are produced. There are no metal losses from machining and finishing [1–6]. The greater chemical activity of sintered materials can be reduced by applying various techniques. These are mainly based on a reduction in the volume content of porosity. The inferior corrosion resistance of sintered stainless steels is resulted from the interconnected open pores. This reduction of porosity can be achieved through the adjustment of processing parameters or by modification of the composition of the sintered material (through addition of alloying elements such as Sn, Cu or Si) [7–10]. High silicon contents can increase the sinter density and improve the mechanical properties of austenitic stainless steel powders [9,10]. Both the corrosion and oxidation resistance of conventional stainless steels can also be improved by the addition of silicon [11–13].

In a previous study [14] an attempt has been made to explore methods of improving the sinterability of atomized 304L stainless steel powders. Silicon powder was chosen as an additive to promote the densification rate because of its strong effect in introducing and stabilizing the ferrite-phase in the microstructure. The experimental results obtained showed that the austenitic stainless steel powder aggregates were sintered into duplex stainless steels with a mixed austenite/ferrite structure. The volume content of ferritic-phase increases with increasing silicon content. The density, mechanical properties, corrosion and oxidation resistances of the sintered alloys are improved markedly.

The stainless steels containing higher content of the elements Cr, Ni and Mo are apt to precipitate σ-phase during exposure to high temperature (700–1000 °C). Wilm investigated the effect of σ-phase precipitation at 800 °C on the corrosion resistance in sea water of a high alloyed duplex stainless steel [15]. A serious deterioration of the corrosion resistance is found after aging times longer than 7 min. Lopez studied the influence of σ-phase on mechanical properties and corrosion resistance of duplex stainless steels [16]. Precipitation of σ-phase reduces the ductility, and is harmful on the intergranular corrosion resistance. Hertzman found that the precipitation of σ-phase is very

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rapid and it has a strong influence on corrosion resistance [17]. Maehama also reported that σ-phase formation leads to serious embrittlement of stainless steels [18]. Li found that σ-phase precipitation greatly reduces the high temperature ductility of a super duplex stainless steel [19]. Adhe et al. studied the influence of σ-phase formation on the localized corrosion behavior of a conventional duplex stainless steel [20]. Nakade investigated the effect of σ-phase precipitation on hydrogen induced cracking of a duplex stainless steel. The σ-phase enhances hydrogen embrittlement; and the σ-phase itself and σ-/ferrite-phase boundaries are preferential hydrogen induced cracking sites [21].

In the present work silicon powder was mixed with the 303LSC austenitic stainless steel powder, and the compacts of powder mixtures were sintered into duplex stainless steels with a structure of austenite–ferrite. The sintered alloys were exposed to 800 °C for various periods. Effect of the silicon content and aging time on the density, hardness, morphology and chemical composition of σ-phase, toughness and corrosion resistance of sintered alloys was investigated.

2. Experimental

The 303LSC stainless steel powder used was water-atomized with a particle size of −100 mesh, its chemical composition is Cr 18.9 wt.%, Ni 12.8 wt.%, C 0.03 wt.%, Sn 0.8 wt.%, and Cu 2.0 wt.%. The matrix powder has been admixed with the compacting lubricant that is composed of 0.3 wt.% lithium stearate and 0.7 wt.% Acrawax. The particle size of silicon powder is −325 mesh. The specimens containing 0, 1, 2, 3, 4 and 5 wt.% Si were designated as S0, S1, S2, S3, S4 and S5, respectively. After mixing the powder mixtures were consolidated with a pressure of 500 Mpa. The compacts were then sintered at 1250 °C for 40 min in bottle hydrogen (with a dew point of −30 °C). Precipitation of the σ-phase was carried out at 800 °C for 30–1500 min, and protected by the bottle hydrogen. The diameter, thickness and weight of specimens before and after aging treatment were measured. The sintered and aged densities were calculated to investigate effect of the aging time on the density of sintered specimens. The impact energy absorbed by a specimen during failure is expressed in joule, which is used to describe the toughness of aged alloys. The dimension of impact test specimens is 10 mm × 10 mm × 55 mm without notch.

Effect of σ-phase precipitation and aging time on the corrosion resistance of sintered alloys was studied by the immersion test. The aged specimens were immersed in the 10% $FeCl_3$ solution for 15 days, then water-rinsed and dried. The erosion solution was slowly stirred. The lab was air-conditioned to keep the room temperature at 25 °C when the experiment was conducted. During immersion the rust did not accumulate on the specimen surface, but detached and suspended in the solution. The weights of specimens before and after immersion were measured with a balance with a precision of 0.1 mg. The weight loss rate (mg/cm^2 day) was calculated.

The morphology change of σ-phase with the aging time was examined with a scanning electron microscope. The intensity of the composition elements in the austenite-, ferrite- and σ-phase of the sintered and aged alloys was measured by point counting. The acceleration voltage was 15 kV.

3. Experimental results and discussion

3.1. Effect of silicon content and aging time on the density of sintered alloys

Influence of the silicon content and the aging time on the density of sintered alloys is shown in Fig. 1. The density is expressed by the percentage value, which is calculated by sintered density/theoretic density. For the as-sintered alloys the density increases with increasing silicon content. The density increases markedly as the silicon powder is added more than 3 wt.%. The densities of aged alloys increase pronouncedly as being aged for 300 min, but no significant density variation is found after the aging time is longer than 600 min.

As being aged at 800 °C intense diffusion of atoms occurs in the specimens. Eight hundred degree Celsius is close to the Tamman temperature (half of the melting point) of stainless steels. At this temperature the lattice structure of a crystal becomes loose slightly, some atoms in the crowded lattice may obtain enough energy and jump into the neighboring vacant sites. Large volume of atoms migrates toward the region with higher surface energy (such as the surface of small pores) through the volume and grain boundary diffusion [22]. The small pores in the sintered specimens will be preferentially filled. Densification continues to proceed during the aging treatment. During further aging the small pores will be filled out gradually, at the same time large pores grow. These large pores are very difficult to eliminate, therefore, the density of aged specimens hardly increases after the aging time being longer than 600 min.

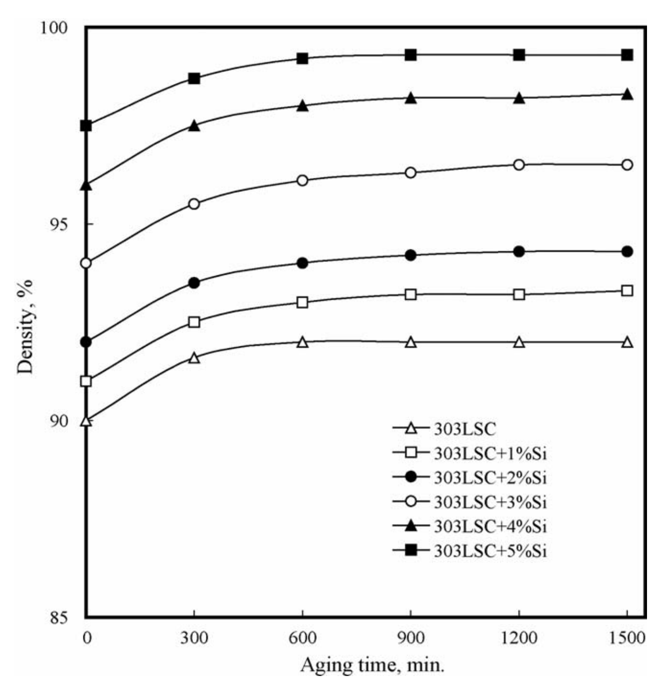

Fig. 1. Variation of density with silicon content and aging time of sintered 303LSC alloys.

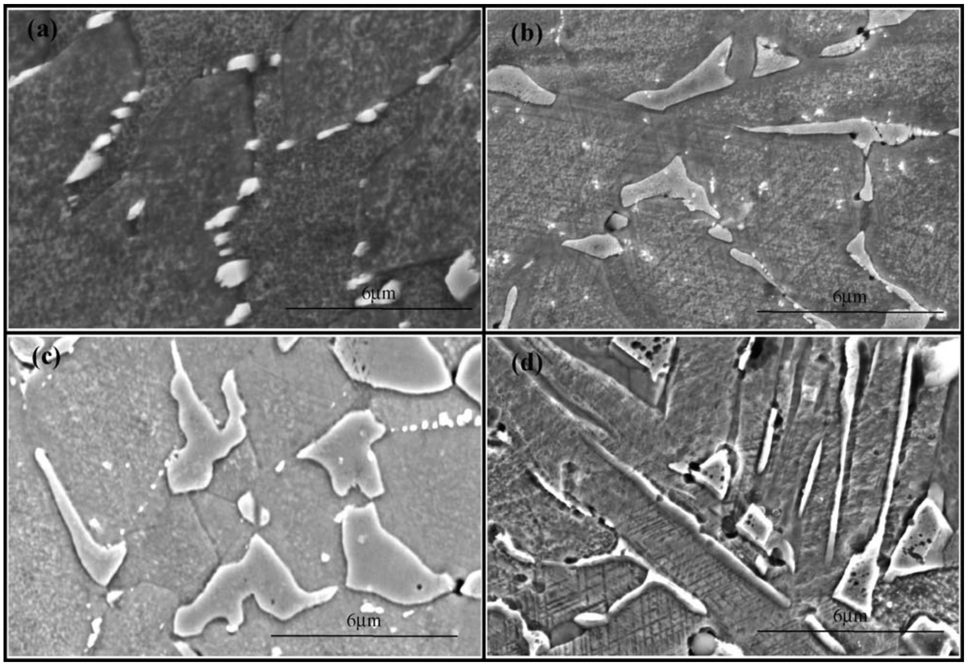

Fig. 2. Morphology of the σ-phase precipitated in the S5 alloy aged at 800 °C for: (a) 30 min, (b) 300 min (c) 600 min and (d) 1500 min.

3.2. Morphology evolution of σ-during aging at 800 °C

σ-Phase precipitates during the aging treatment, and its morphology evolution in the S4 sintered alloy is shown in Fig. 2. Fig. 2(a) is the specimen aged for 30 min, most of σ-phase particles nucleates on the grain boundaries, and some induced in the ferritic-phase. After aging for 300 min this phase changes its morphology, many particles grow into the bar shape as shown in Fig. 2(b). Part of the precipitates continues to grow and thicken as revealed in Fig. 2(c) after aging for 600 min. When the aging time increases to 1500 min, the morphology of σ-phase changes significantly. Most of this phase becomes a filament, and some filaments are parallel to each other.

Table 1 shows the chemical compositions of σ-phase induced in the sintered S4 alloys after exposing at 800 °C from 30 to 1500 min. Studying Fig. 2 and Table 1 it can be found that both the morphology and the chemical composition vary with the aging time. Chromium and silicon atoms continuously migrate into the σ-phase during further aging. The iron and nickel contents decrease with increasing aging time. Chromium content can attain a level of 35 and 43 wt.% after aging for 600 and 1500 min. The chromium enrichment in this phase decreases the chromium content of the neighboring regions, and may lead to degradation of the corrosion resistance of Cr-depleted zones.

Table 1
Variation of the chemical composition (wt.%) of σ-phase with the aging time (min)

Aging time	Fe	Cr	Ni	Si
30	67.8	20.2	6.9	5.1
300	60.7	27.6	6.4	5.3
600	52.2	34.8	6.2	6.9
1500	44.1	42.6	5.8	7.5

Fig. 3 shows the variation of hardness of sintered alloys with the silicon content and aging time. Hardness increases profoundly with increasing Si content owing to better densification and silicon hardening. For the groups of low-silicon alloys S0, S1 and S2 the hardness increases slightly with increasing aging time. As to the high-Si groups of S3, S4 and S5 harden-

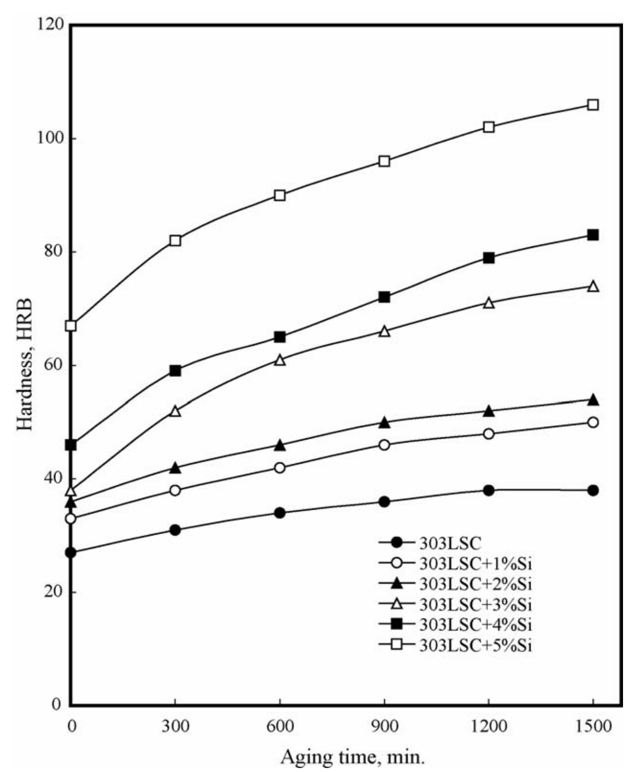

Fig. 3. Variation of hardness with silicon content and aging time of sintered 303LSC alloys.

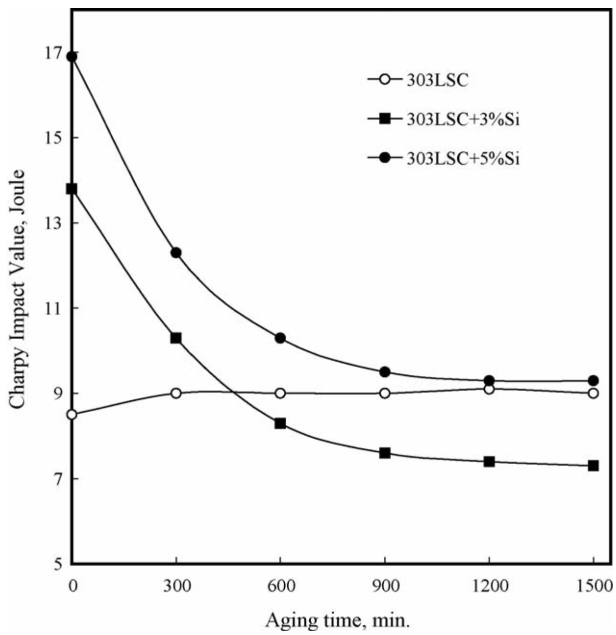

Fig. 4. Variation of impact value with silicon content and aging time of sintered 303LSC alloy.

ing proceeds profoundly with the increase of aging time. Further densification resulted from the aging treatment and precipitation of σ-phase contributes to hardening of the aged alloys. As referring to Fig. 1 the effect of σ-phase precipitation on hardening seems to be predominant.

3.3. *Influence of silicon content and aging time on the toughness*

Effect of aging time on the toughness of sintered S0, S3 and S5 alloys is shown in Fig. 4. It can be seen that precipitation of the σ-phase is detrimental to the toughness of Si-containing sintered alloys. The Charpy impact value of S3 and S5 alloys decrease markedly with increasing aging time due to the increasing σ-phase formation. Then the toughness of aged alloys does not vary significantly as the aging time is longer than 900 min. However, due to the inferior impact strength of sintered materials the effect of precipitation of σ-phase on the toughness is not so drastic as that in the conventional duplex stainless steels [23,24].

In the as-sintered state the toughness of S3 alloy is lower than that of the S5 alloy because of its higher content of porosity. During impact testing pores are apt to initiate fracture. After aging at 800 °C for various time intervals the S5 alloy is always tougher than the S3 ones, though the S5 alloy contains more ferritic-phase and precipitates more σ-phase during aging. As shown in Fig. 1 the S5 alloy can densify to a density of 99% after aging, but the density of aged S3 alloy is 96% only. The density of the S5 alloy is always higher than that of the S3 alloy. Comparing the toughness of S3 and S5 alloys before and after aging, it can be found that for the same batch of specimens the volume content of σ-phase precipitated is predominant in determining the toughness. However, the porosity modification plays an important role in determining the impact value of sintered alloys with different silicon content.

As regards the S0 alloy, the impact value is much lower than that of the S3 and S5 alloys in the as-sintered state because of its lower density and higher porosity. But variation of the impact value of the S0 alloy with the aging time is completely different from that of S3 and S5 alloys. The impact value increases slightly with increasing aging time. Metallographic observation of the aged S0 alloy showed that only few amount of σ-phase particles precipitate on the grain boundaries and pore surface of this sintered austenitic stainless steel during aging. These σ-phase particles seem to have little influence on the toughness, and the effect of density increasing is dominant. There is a coincidence between variations of the impact value and density of the aged S0 alloy with the aging time. After being aged for 300 min the large gain in density as shown in Fig. 1 leads to an increase of the impact value. Then the impact value and density vary slightly during the prolonged aging time.

3.4. *Effect of silicon content and aging time on the corrosion resistance*

Influence of the silicon content and aging time on the corrosion resistance is shown in Fig. 5. Corrosion resistance is expressed by the weight loss rate of aged alloys after immersing in the 10% $FeCl_3$ solution for 15 days. The weight loss rate of sintered 303LSC alloy decreases monotonously with increasing aging time due to the density increasing resulted from the aging treatment.

For the Si-added alloys in the as-sintered state the weight loss rate decreases with increasing silicon content. The corrosion resistance is improved by addition of the silicon powder. To investigate the corrosion resistance of austenitic- and ferritic-phase in the duplex structure the sintered S4 specimens were sectioned, polished and immersed in the $FeCl_3$ solution for 5

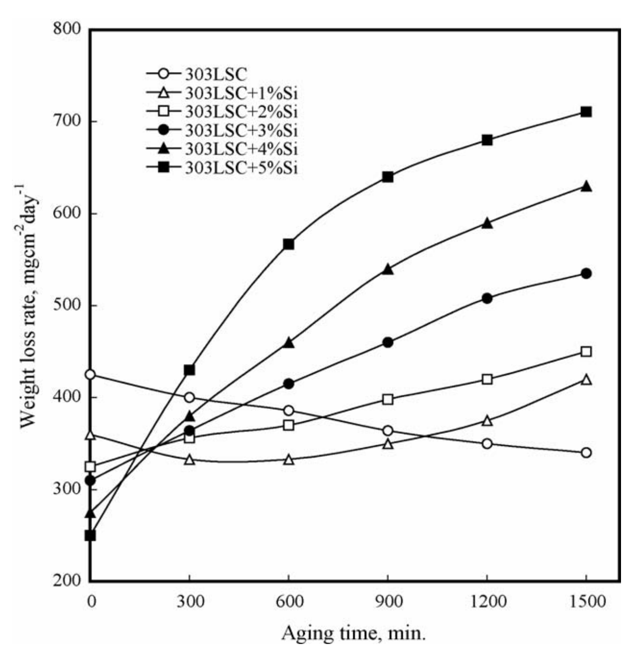

Fig. 5. Variation of weight loss rate with silicon content and aging time of sintered 303LSC alloys immersed in 10% $FeCl_3$ solution for 15 days.

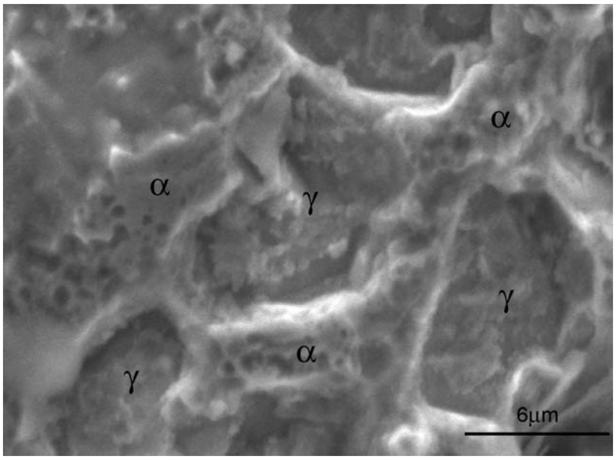

Fig. 6. Preferential erosion of austenitic-phase (γ) of sintered S4 alloys immersed in 10% $FeCl_3$ solution for 5 days.

days. Fig. 6 shows the surface morphology of this specimen after immersion. It can be seen that the austenitic-phase was preferentially eroded during the immersion test. The phase identification is ascertained by its chemical composition, which is examined by the EPMA attached on the SEM. The alloying element of the ferritic-phase is Cr 20.48 wt.%, Ni 6.57 wt.% and Si 6.76 wt.%; the austenite is Cr 16.48 wt.%, Ni 12.26 wt.% and Si 0.86 wt.%. Chromium and silicon are enriched in the ferritic-phase. The ferritic-phase in the duplex structure is more corrosion resistive than the austenite. Introducing more silicon powder induces higher volume content of ferritic-phase in the sintered alloys. Therefore, the alloys with higher sintered density and containing more ferritic-phase exhibit better corrosion resistance in the $FeCl_3$ solution.

For the aged Si-added alloys the weight loss rate increases with increasing silicon content. As shown in Table 1 the σ-phase precipitated from the ferrite of S4 alloy contains about 28 wt.% of Cr as being aged for 300 min. The Cr-enrichment in this phase will result in many neighboring chromium-depleted zones and lead to impairing of the corrosion resistance of the ferritic-phase. Adhe et al. has found that the regions adjacent to σ-phase are depleted of chromium and susceptible to intergranular corrosion and pitting corrosion [20]. The alloys with higher silicon content possess more volume fraction of the ferritic-phase, and more σ-phase particles will precipitate upon aging. Chromium enrichment in the σ-phase continues to proceed during further aging. Table 1 also reveals that the Cr content of σ-phase attains a level of 43 wt.% after aging for 1500 min. Therefore, the weight loss rate of Si-added alloys increases markedly with increasing silicon content and aging time. Here, σ-phase precipitation and the subsequent Cr-depletion are predominant in determining the corrosion resistance of the aged alloys, and effect of density increasing resulted from aging is insignificant.

4. Conclusions

(1) Density of the sintered alloys increases with increasing silicon content and aging time due to more efficient densification and continuous porosity elimination during aging at 800 °C.
(2) Hardness of the aged alloys also increases with increasing Si content and aging time owing to higher sintered density, silicon hardening, further densification upon aging and precipitation of σ-phase.
(3) Aging treatment at 800 °C is detrimental to the toughness of the Si-added 303LSC sintered alloys; the impact strength decreases markedly with the increase of aging time, but increases with increasing silicon content. Porosity is the major parameter influencing the toughness of sintered alloys with different silicon content.
(4) Both of the morphology and the chemical composition of σ-phase markedly change with the aging time.
(5) Precipitation of the σ-phase is harmful to the corrosion resistance of the Si-added 303LSC sintered alloys. The weight loss rate of the aged alloys increases with increasing silicon content and aging time.

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