Investigations into the Transformation of Sigma Phase in Shot-peened Duplex Stainless Steel at Elevated Temperatures by Rietveld Method

F. Qiang[1], J. Chuanhai[1], H. Pan[2]

1 School of Material Science and Engineering, Shanghai Jiaotong University)
2 EPCO Testing Technology (Shanghai) Ltd.)

Abstract
Phase transformation and growth of sigma phase in shot-peened duplex stainless steel (DSS) S32205 was measured by X-ray diffraction during 64-min isothermal heat treatment at temperature between 600 °C and 700 °C. Quantitative analysis of phase in duplex stainless steel S32205 at elevated temperature was obtained by Rietveld method. Shot peening can facilitate the formation of sigma phase in tnear surface layers at elevated temperature, which is due to domain sizes refined. The content of sigma phase is most at layer depth of 10 μm rather than in surface layer at temperature of 700 °C and mechanism of formation was discussed. Sigma phase is known to adversely affect mechanical properties and corrosion resistance of DSS alloy. Therefore, it is important to assess phase composition and performance in shot-peened DSS subsurface layer at elevated temperatures.

Keywords: Intensity, fatigue, aluminium, anodised.

Introduction

As an effective and important surface treatment method, shot peening can introduce high residual compressive stress and microstructure refinements at near-surface layers, thus enhance fatigue properties of treated materials. With depth increasing, deformation variation decreases in deformation layers [1, 2]. DSS are superior to single phase austenitic or ferritic grades because of their improved corrosion resistance and increased strength. For this reason, DSS are considered as excellent choice for various industrial applications. Enhanced mechanical properties of DSS are partly due to fine-grained structure, where grain growth is restricted by two phases to certain degree [3-7]. However, owing to their susceptibility to formation of dangerous intermetallic phases, use of duplex stainless steels has to be restricted, especially when temperature is over 500 °C. Generally, this embrittlement is attributed mainly to the formation of austenite, but also to other intermetallic phases such as sigma phase and nitrides [8]. Therefore, formation of intermetallic phases and their influence on toughness of DSS has been extensively examined [9-11]. Sigma phase is more easily formed in high energy regions such as grain boundaries and interfaces, for example, the smaller the grain size, the greater the tendency towards sigma-phase formation [11]. Rietveld method was successfully applied for determination of quantitative phase abundances of composite materials containing several crystallographic phases [12]. The mechanism, time and temperature range of occurrence of sigma phase has been reported widely [8-11]. But little attention has been paid to the effect of shot peening on the formation of sigma phase in shot-peened samples at elevated temperatures. Therefore, influence of shot peening on the formation of sigma phase in near surface layers at elevated temperatures has been investigated with X-ray diffraction Rietveld method and formation mechanism of sigma phase was discussed.

Experimental procedure

The material used in this investigation was DSS S32205 provided by Shanghai Baosteel Group Corporation, and chemical composition is C (0.029), S (0.006), Si (0.42), Mn (1.27), Cr (22.10), Ni (5.17), Mo (3.10), N (0.18), P (0.021), and rest Fe (all in wt. %). Shot peening treatments were carried out on the samples by an air blasting machine (Shanghai, Carthing Machinery

Company). Shot peening intensity (0.35 mmA) was measured by arc height of Almen specimen (A type), which was controlled by jet pressure of nozzle, shot time and average ball diameter. Diameter of peening nozzle was 15 mm and distance between nozzle and samples was 100 mm. Coverage of shot peening was 100% in all samples. In order to investigate the translation phase of shot-peened DSS, isothermal annealing treatments were carried out at 600 °C, 650 °C and 700 °C, respectively. During annealing, samples were sunk in alumina powders for a even thermal environment. XRD investigation was conducted on the same zones of samples after cooling to room temperature. The reflection profiles of materials were measured by Rigaku Ultima IV X-ray diffractometer with D/tex 1D high-speed detector, which was operated at 40 kV/ 30 mA with Cu-Kα radiation (λ = 1.54056 Å). Samples for depth XRD examination were electrolytically etched in 10 N KOH. Quantitative analysis of phase in DSS S32205 was obtained with X-ray diffraction Rietveld method [13].

Method of analysis

In present investigation, Rietveld's structure refinement analysis [14-17] of X-ray diffraction data are adopted to fit accurately the whole X-ray pattern for micro-structural characterization of constituent phases, including lattice defects measurement in homogenized samples. A diffraction pattern is simulated from a series of structural parameters (cell, atomic co-ordinates, thermal vibration, etc.), micro-structural parameters (domain size and micro-strain), as well as specimen parameters (preferred orientations, eccentricity, thickness, transparency, absorptions, phase fractions, et al.), peak shape and width parameters and background parameters, etc. A Rietveld's software MAUD 2.33 [13] is specially designed to refine simultaneously both structural and micro-structural parameters through a least-squares method.

Being a linear combination of a Cauchyian and Gaussian functions, Pseudo-Voigt function is the most reliable peak-shape function and is widely used in the Rietveld structure refinement software [13-17]. Rietveld method was also successfully applied for determination of quantitative phase abundances of composite materials containing several crystallographic phases [18-20]. There is a simple relationship between individual scale factors determined, considering all refined structural parameters of individual phases of a multiphase sample, and phase concentration (volume/weight/molar fraction) in the mixture. Weight fraction (Wi) for each phase was obtained from the refinement relation:

$$W_i = S_i(ZMV)_i / \sum_j S_j(ZMV)_j \qquad (1)$$

where i is value of j for a particular phase among N phases present, Si is a refined scale factor, Z is number of formula units per cell, M is atomic weight of formula unit and V is the volume of unit cell [16-20].

Considering the integrated intensity of peaks as a function of structural and micro-structural parameters, a Marquardt least-squares procedure is adopted for minimizing difference between observed and simulated diffraction patterns and minimization is monitored using reliability index parameter, Rwp (weighted residual error), and Rexp (expected error) defined respectively as

$$R_{wp} = [\sum_i w_i(I_o - I_c)^2 / \sum_i w_i(I_o)^2]^{1/2} \qquad (2)$$

$$R_{exp} = \left[(N - P) / \sum_i w_i(I_o)^2\right]^{1/2} \qquad (3)$$

where Io and Ic are experimental and calculated intensities, wi = (1/Io) and N are the weight and number of experimental observations and P is the number of fitting parameters. This leads to the value of goodness of fit (GoF) [14-17]:

$$GoF = R_{wp} / \mathrm{R}_{exp} \qquad (4)$$

Refinement continues till convergence is reached with value of the quality factor, GoF very close to 1 (varies between 1.1 and 1.4), which confirms the goodness of refinement. Microstructural

parameters like domain size values of samples are also obtained from this analysis along with all structural parameters.

Results and discussions

XRD profiles of shot-peened DSS S32205 annealed for 64 minutes at temperatures ranging from 600 to 700 °C are shown in Ref. [2]. It is clear that the peak intensity of ferrite is weakened with increasing annealing temperatures while that of austenite becomes stronger, which is attributed to the transform of ferrite into austenite at temperatures range of 600 and 650 °C. However, a new phase appears under annealing temperature of 700 °C. Analysis data of new phase (sigma phase, space group: P42/mnm, a=8.802 Å, c=4.586 Å) are obtained by Maud software with Retvield method [2]. Sigma phase is an inter-metallic compound, rich in Cr and Mo, with tetragonal structure and non-magnetic. It is hard and brittle and its occurrence also has deleterious effects on corrosion resistance [8-11]. The sigma phase appears only at temperature of 700 °C after annealing 64 minutes, which indicates that the formation of sigma phase depends on annealing temperatures. At initial annealing stage (0 - 16 minutes) at 700 °C, it is found on the surface layer that ferrite phase content decreases with increasing annealing time, as shown in Fig. 1 (b), however, sigma phase appears after 32 minutes annealing and its content increases with prolonged annealing time. It can be concluded that the formation of sigma phase at 700 °C takes a significantly long time (more than 16 minutes).

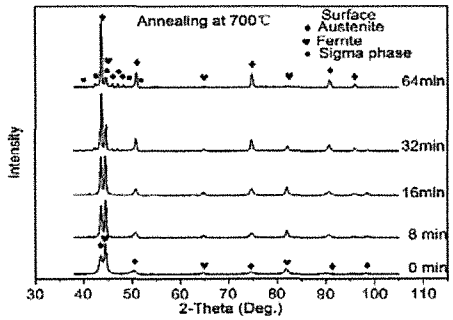

Fig. 1 XRD patterns of surface layer of shot-peened DSS under different annealing time at 700 °C.

XRD profiles of shot-peened DSS (annealed at 700 °C for 64 mins) with different depths are shown in Fig. 2. It can be obtained that formation of sigma phase appears only in the near surfaces (within depth of 75 μm), which can be attributed to shot peening facilitated formation of sigma phase. In near surface layers, shot peening can introduce microstructure refinements and results in sharp increase of dislocation density.

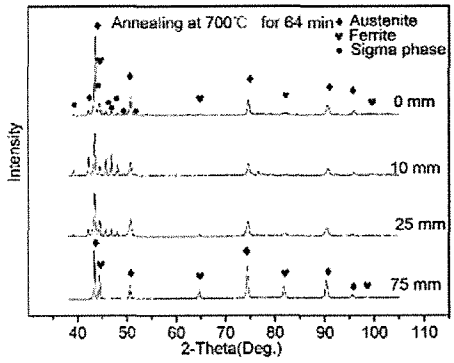

Fig. 2 XRD patterns of distribution of depth for shot peened DSS annealed for 64mins at 700°C

The maximum of microstructure refinement lies in shot-peened surface layer and then decreases as depth increases [2]. It is interesting that the maximum peak intensity of sigma phase exists at depth of 10 μm on the shot-peened surface. It can be obtained from a typical Rietveld plot shown in Fig. 3 that weight fraction of sigma phase is 0.562 at depth of 10 μm, this will be discussed later in this work.

After annealing at temperature of 700 °C for 64 minutes, quantitative phase analysis of shot-peened DSS was carried out by Rietveld method and weight fraction along depth for each phase are shown in Fig. 4. It can be found that (1) ferrite disappears at depth of 10 μm, (2) weight fraction of sigma phase increases from 0.162 at surface to 0.562 at depth of 10 μm, then decreases. Sigma phase disappears at depth of 75 μm. From data of Rietveld plot, it also can be obtained that shot peening facilitate the formation of sigma phase at elevated temperatures due to microstructure refinements. However, it is amazing that the maximum weight fraction of sigma phase exists at subsurface but shot-peened surface.

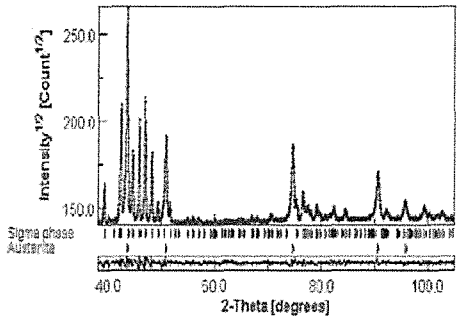

Fig. 3 Rietveld plot depth of 10μm of DSS annealed at 700°C for 64 minutes; Rwp:0.0612, Rp: 0.0985.

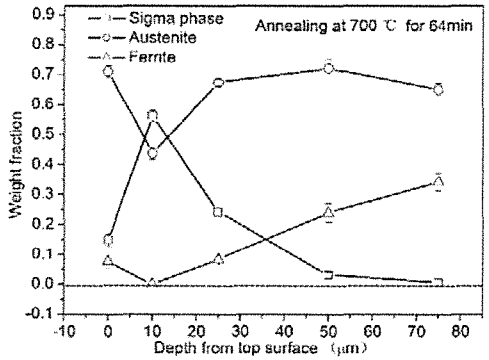

Fig. 4 Distributions of weight fraction of DSS annealed at 700 °C for 64 minutes obtained by Rietveld method.

According to description above, it can be obtained that the formation of sigma phase depends both on annealing temperatures and annealing time. Sigma phase transition only happens in the near-surface layers (less than 75 μm from surface layer) after shot peening, which is due to the microstructure refinement of surface layers. The smaller the grain size is, the greater the tendency towards the sigma formation. Sigma phase is more easily formed in high energy regions such as grain boundaries and interfaces [9, 21, 22]. The most content of sigma phase exists at the sub-surface (depth of 10 μm) but the shot-peened surface in present study, which can be attributed to the direction of heat transfer and time of sigma phase transition. In the process of annealing, whole heat is always conducted across from surface to subsurface, in theory, the growth rate of grain size in surface is faster than that in subsurface. What is more, the formation of sigma phase needs

a long annealing time. Grain sizes in surface have enough time to increase, which results in the bigger grain size in the surface than that in subsurface, therefore, the tendency towards sigma phase formation in surface is reduced.
Sigma phase is known to adversely affect the mechanical properties [23] and corrosion resistance [23] of DSS alloy. Content of sigma phase is most in the subsurface rather than in the surface layer for shot-peened DSS in this work, which may degrade severely the performance of surface. Therefore, to assess the phase composition and performance of shot-peened DSS S32205 applied at elevated temperatures, it is worth noting that not only the surface but also subsurface layer should be paid attention to.

Conclusions

Phase transformation analysis in shot-peened DSS S32205 under isothermal annealing was obtained using Rietveld method. It can be concluded that the formation of sigma phase depends not only on annealing temperatures but also on annealing time. After shot peening, microstructure refinements in near surface layers (less than 75 μm) facilitate the formation of sigma phase. However, the most content of sigma phase exists at the subsurface (depth of 10 μm) but the shot-peened surface. This can be attributed to the bigger grain size in surface than that in subsurface, which hinders the tendency towards sigma phase formation.

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