Age-hardening kinetics and microstructure of PH 15-5 stainless steel after laser melting and solution treating

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Microstructural characterization and the kinetics of ageing of 15 PH stainless steel is studied in the fusion zone and in solution-treated and quenched (as-quenched) samples. Fusion zone had a finer structure than the as-quenched samples due to melting and subsequent solidification. This had a major effect on the amount of the hardness received in the fusion zone. The ageing structure of both samples was essentially the same, except for the smaller solidification cell size of the fusion zone. Strengthening was achieved by the formation of coherent precipitation of copper in the bcc martensite. Copper precipitates were found to be related to the parent martensite with a Kurdjumov–Sachs orientation relationship in both samples. Precipitates were spherical in shape and they nucleate and grow both on the dislocations and in the matrix. No incubation period was observed in the hardening curves. Kinetics of precipitation was studied from an Arrhenius type equation for both samples. It was found that, at high ageing temperatures, the activation energy for precipitation hardening was approximately the same as that of the activation energy for substitutional diffusion in bcc ferrite. At lower ageing temperatures, the calculated activation energy was consistent with the activation energy for short circuit diffusion of substitutionals in bcc structure. Microstructural characterization and the activation energy calculations showed that precipitation of copper in both samples was controlled by the diffusion of copper in bcc martensite. At high ageing temperatures, mass transport of copper was through the lattice. At low temperatures, the contribution of high dislocation density to the apparent diffusivity was large.

1. Introduction

In the last decade, lasers have found extensive applications in metallurgy and material science. Their major use in metallurgy involves welding, followed by laser surface modification (either by melting or heat treating to obtain martensite) and laser surface alloying. Depending on the sample scan velocity and the heat input, cooling rate may be varied in the molten zone. As the cooling rate increases, dendritic structure and the size of the solidification grains become finer. At the highest cooling rate, depending on the thermodynamics of the alloy system, a massive transformation may become possible, producing a surface alloy with the same composition of the liquid from which it forms, without any segregation at the cell or solidification boundaries. Therefore, processing of metallic materials with lasers can be called a rapid solidification technique, depending on the processing parameters used which may eventually produce a high cooling rate at the surface if properly designed. Accordingly, highly supersaturated structures can be achieved after melting and solidification at the surface which, through increasing driving force for nucleation and growth, may increase the kinetics of ageing in precipitation hardening systems.

Precipitation of intermetallic compounds in a martensitic matrix is known as an effective method of producing low-carbon, high-strength and high-ductility marage steels. However, marage steels suffer from a low resistance to corrosion and accordingly several marage steels were developed with additions of 13%–17% chromium to increase corrosion resistance [1].

PH stainless steels can be either austenitic, semi-austenitic or martensitic depending on the alloying element additions to the composition. Martensitic PH stainless steels usually contain 4%–7% nickel to keep the Ms temperature above room temperature. Elements added to form precipitates are copper, molybdenum, aluminium, titanium and niobium [2]. The alloys are solution treated, quenched and aged at temperatures between 400 and 500°C. The precipitation-hardening agents are copper, Ni3Ti, Ni3Al and NiAl [3].

Several studies have been reported in the literature generally concerning the microstructural characterization and mechanical behaviour of PH stainless and marage steels. Among the PH stainless steels, 17-4 PH grade [4] is strengthened by the precipitation of ε-copper phase, which is nearly pure copper. Reverted
austenite has been observed in this steel at ageing temperatures above 550 °C. This study assumed that the precipitation-hardening sequence is similar to those of Fe–Cu and Fe–Cu–X alloys [5–9]. Briefly, this involves the initial clustering of coherent copper-rich zones which later transforms to fcc e-copper precipitate with further ageing. The above studies on the precipitation-hardening mechanism involving copper as the precipitate, conclude that the hardening phase has an fcc structure and is coherent with the bcc, low-carbon martensite.

The precipitation-hardening mechanism and the kinetics of ageing as well as aged microstructure of the 15-5 PH stainless steel has not been studied in detail. It is known that the fast kinetics of ageing in maraging steels is due to the high defect density of martensitic matrix [10–13]. The studies listed above do not explain clearly the factors that affect the kinetics of ageing. The present study was concerned with the kinetics and the microstructure of the aged 15-5 PH stainless steel following laser melting, as well as after solution treatment.

Solidification of stainless steels has received a great deal of attention in the welding as well as casting literature [13–20]. It has been found that the most important parameter in preventing the so-called “hot cracking” in stainless steel weldments is the control over the composition as well as the solidification mode. Stainless steels that solidify in the primary austenite mode were found to be less resistant to hot cracking than the primary ferrite solidified alloys, due to extensive segregation of harmful elements (i.e. sulphur, phosphorus, niobium, silicon, etc.) to cell and solidification boundaries; these form low melting point eutectics. Primary-ferrite solidified welds, on the other hand, were found to be resistant to hot cracking due to higher solubility of these harmful elements in ferrite.

The results of fusion-zone microstructural characterization as well as a thermodynamic analysis of segregation of iron, nickel and chromium were reported in detail in a previous publication for laser welding of 15-5 PH stainless steel [21]. However, kinetics of ageing in the molten zone (henceforth called the fusion zone) is related to the structure and the laser processing parameters. Therefore, this study summarizes important aspects of the microstructure of the fusion zone with the main emphasis being on ageing structure and precipitation-hardening mechanism in the fusion zone and in the as-quenched alloy.

2. Experimental procedure

Laser-welding experiments were conducted on specimens of 15-5 PH whose composition is given in Table 1, as supplied by the manufacturer. The alloys were in the as-quenched condition prior to laser welding. Austenizing treatment was carried out at 1040 °C before laser treatment as well as on the as-quenched samples. Following austenizing, specimens were quenched in water.

Autogenous laser welding was carried out with a 5 kW continuous wave CO2 laser. The travel speed of the specimens was 4.3 mm s⁻¹. A 254 mm focusing lens was used. All welding experiments were made on samples of 25.4 × 25.4 mm² with a thickness of 11.2 mm under argon shielding gas.

After laser welding and ageing, specimens were sectioned and metallographic examinations were made on top and transverse sections. Final polishing was made with 0.06 μm alumina. Etching was conducted in a two-step procedure. First, the specimens were etched with Fry’s reagent [22] and then dipped in Murakami’s reagent for a few seconds until a good etching contrast was achieved.

The as-quenched and laser-welded samples were cut into the sizes of ¼ in × ¼ in × ¼ in (1 in = 2.54 cm) with a water-cooled saw. The surface oxide after laser welding was removed with 600 SiC paper prior to ageing. After this procedure, the specimens were aged in a liquid-lead bath at temperatures between 400 and 525 °C for 1–20000 min. It was observed that liquid lead did not wet the samples. The heating rates of the samples to the required ageing temperatures were determined by embedding a chromel–alumel thermocouple into the centre of a sample of the same size. Ageing time was determined after the samples reached the respective ageing temperature. Temperature of the baths were controlled within ± 2 °C, with a chromel–alumel thermocouple shielded with stainless steel. The samples were quenched in water immediately after they were taken out of the liquid-lead bath.

Electron microscopy investigations were carried out on the as-quenched and on the precipitation hardened samples from the fusion zone and base metal. TEM samples were prepared by electropolishing in an electrolyte containing 10% perchloric acid and 90% acetic acid with a fischione jet polisher at room temperature, 50 V and 80 mA. These samples were then examined in a Jeol 100C electron microscope operated at 100 kV. A Leco 400 microhardness tester was used to determine the age-hardening response of both the base metal and the fusion zone. Hardness in the as-welded samples varied as a function of the location in the fusion zone. To be consistent in the age-hardening study, hardnesses in the fusion zone were recorded at a depth of 50 μm from the surface. Samples for age-hardening study of the fusion zone were prepared from the samples with welding speeds of 4.3 mm s⁻¹.

3. Results

Fig. 1 is a representative micrograph of the overall microstructure in the fusion zone. A microscopic examination of the welds revealed that they are free of hot cracks. Fig. 2 shows a higher magnification optical micrograph of the fusion zone where the solidification structure can be seen in detail. The dark-etched vermicular phase is primary ferrite which forms at the axes of the primary solidification cells. The roundish dark phase that is located at the cell boundaries (arrowed in Fig. 2) is eutectic ferrite which forms at the final stages of solidification.

The determination of the solidification path and characterization of the fusion zone was given in detail.