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The effect of aging on heat-resistant cast stainless steels

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ABSTRACT

The effect of aging on four heat-resistant cast stainless steels heat treated for various durations at 820 °C was investigated and is described in this paper. The steels were examined in terms of their microstructure and mechanical properties. Microstructural characterization of the steels revealed complex microstructures with a large number of carbide precipitates in an austenitic matrix. The as-cast materials contained carbides as clusters or networks, which were almost fully dispersed in the specimens aged for 1200 h. The σ-phase was identified in each steel grade after only 100 h of aging, although in an austenitic–ferritic grade, it was identified already in the as-cast condition. Impact toughness results revealed the embrittlement of each studied steel grade after only 100 h of aging at 820 °C. The hardness values for the steels increased slightly and almost linearly with increase in the aging time. The results of this study indicate that the formation of the σ-phase is primarily responsible for the observed embrittlement, while the increase in hardness may be explained by the formation of the σ-phase and the dispersion of the carbides. These results are presented and discussed in this paper.

1. Introduction

Heat-resistant cast stainless steels are generally austenitic, ferritic, or austenitic–ferritic in microstructure and they may contain a variety of minor phases, such as different types of carbides. These steels typically have excellent properties, such as corrosion resistance and mechanical strength, that are also maintained at elevated temperatures above 650 °C. However, elevated temperature use may facilitate elemental diffusion and microstructural changes in the material. These changes include the precipitation of intermetallic phases, such as the σ-phase. The σ-phase is hard and extremely brittle at room temperature, and it may introduce dramatic embrittlement of the alloy [1,2]. Nevertheless, the ductility is preserved at elevated temperatures, and the embrittlement usually takes place only when the material is cooled to room temperature or at least below 600 °C [3]. Literature on the σ-phase formation has mainly concentrated on its formation in ferritic and duplex stainless steels [4–11]. Few studies have been published on the formation of the σ-phase in austenitic stainless steels [12–15]. Especially, studies on the σ-phase formation in cast stainless steels are scarce.

The σ-phase generally forms in the temperature range from 550 to 950 °C. In terms of kinetics, the formation of the σ-phase is typically fastest at temperatures in the range from 700 to 900 °C [16]. However, the presented temperature ranges have been under debate, since the exact temperatures for the σ-phase formation are highly dependent on the used alloying. As a whole, all microstructural changes resulting from aging, including the formation of the σ-phase in heat-resistant cast stainless steels, are highly dependent on the alloying. Alloying elements that are known to promote the σ-phase formation are also ferrite promoting elements, such as chromium, silicon, and molybdenum [8,9,17,18]. Also, tungsten, vanadium, and niobium are known for favoring the σ-phase [1]. Sometimes the phase development may be highly sensitive to the used alloying, as shown by Blachowski et al. [19]. They studied the effects of titanium alloying on the kinetics of the σ-phase formation in iron-chromium alloys as a result of isothermal aging at 700 °C. According to their study, titanium additions up to 1.5 at% accelerated the σ-phase formation, whereas the formation rate was decelerated at titanium additions over 1.5 at%. In addition to alloying, certain microstructural characteristics, such as chromium-rich primary carbides, like $Cr_{23}C_6$, may facilitate the σ-phase development during aging by acting as favorable nucleation sites [7].

Due to the rather high carbon content, even up to 0.75 wt%, heat-resistant cast stainless steels often contain various metal carbides in the austenitic, ferritic, or austenitic–ferritic matrix [20]. The chromium-rich carbide $M_{23}C_6$ (M standing for metallic elements), which forms at 600–950 °C, is the most common type of carbide detected in these alloys. The chromium carbide M_7C_3 typically precipitates at somewhat higher temperatures, at 950–1050 °C, and is therefore less common. It has been documented

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that, besides the formation of σ-phase, the networking of carbides adversely influences the mechanical properties [21,22]. Particularly the strength, i.e., the material's ability to resist plastic deformation, is reported to be strongly reduced when the carbides form continuous networks in the microstructure, for example, at grain boundaries, instead of being finely dispersed. In other words, the fine distribution of carbides, i.e., their dispersion due to aging, would lead to better mechanical properties, including the impact toughness, as compared to the networked carbides.

In this study, we report and discuss the influence of isothermal aging at the temperature of 820 °C on the microstructure and properties of four heat-resistant cast stainless steel grades; this aging temperature corresponds to, e.g., applications in industrial furnaces and elevated-temperature process equipment [20]. Here, the main interest is in the development and effects of the σ-phase. We emphasize that, although plenty of literature has been published on the development of the σ-phase in austenitic and duplex stainless steels, e.g., Lee et al. [15] and Chen et al. [23]. However, investigations concerning cast alloys have been extremely rare. In order to characterize the σ-phase, carbide structures were partly sacrificed in the sample preparation process. Therefore, carbides are of secondary interest, though they are dealt with whenever relevant.

2. Experimental

Four heat-resistant cast stainless steel grades, with the compositions shown in Table 1, were tested in this study. The four alloys included three austenitic grades, HHa, HHb, and HI, and one austenitic–ferritic grade HD. The austenitic grades HHa, HHb, and HI were essentially standard alloys. The grade HD was slightly modified with respect to the standard alloy in terms of increased nitrogen and silicon contents. All alloy grades were received in as-cast ingots with minimum dimensions being 130 mm × 110 mm × 30 mm. The specimens were then cut from such ingot areas where the densest specimens were obtained. The specimens were aged in a laboratory chamber furnace (Lenton EF 11/8) in an ambient atmosphere at 820 °C. The aging times were 100, 300, 600, and 1200 h.

All four alloys were examined in terms of their microstructure in the as-cast condition and after aging for 100 and 1200 h. The specimens for microstructural characterization were wet ground and polished down to 1 μm. We tried several etching procedures suggested by Michalska and Sozańska [24], such as electrolytic etching in oxalic acid ($C_2H_2O_4$) and sodium hydroxide (NaOH), and found that the use of 20% NaOH and the voltage of 3.0 V reveal the overall microstructure and give good contrast between the σ-phase and the matrix phases. Hence we applied electrolytic etching in 20% NaOH in the examination of the specimens included in this study, with the etching times varying from five to ten seconds in order to reach a sufficient staining of the σ-phase. An optical microscope (Leica DM 2500M) was used to examine the microstructures of the as-cast and 100 and 1200 h aged specimens after the etching. Optical microscopy images were then edited using a thresholding technique, which enables quantitative analysis of the areas with different contrasts. In this study, image analysis of the optical microscope images presented in this paper was used to determine the amount of the σ-phase in the specimens. The obtained results, however, are approximations rather than exact numbers, but they enable the comparison between the specimens of different aging times. The microstructures of the specimens in the as-cast condition and aged for 100 h were also investigated by the X-ray diffraction technique using a PANalytical Empyrean diffractometer operated at 40 kV and 45 mA with CuKα radiation.

Both unetched and etched specimens were subjected for further microstructural examinations. However, for a systematic approach, we report here only the results obtained using the specimens electrolytically etched in 20% NaOH. These specimens were studied and analyzed using a scanning electron microscope (SEM) Philips XL-30 and an energy dispersive spectroscope (EDS) EDAX DX4 to verify the obtained results. The SEM studies were conducted using both secondary (SE) and back-scattered electrons (BSE) at the accelerating voltage of 20 kV. The fracture surfaces of the impact test bars (as-cast and 100 h aged conditions) were also examined using SEM and EDS.

The mechanical properties of particular interest in this study were ductility, defined and examined as impact toughness, and hardness. Specimens of as-cast and aged alloys were machined into standard Charpy V-notch impact bars [25]. The size of the impact bars was 55 mm × 10 mm × 10 mm, and they contained a V-notch with the root radius of 0.25 mm. Impact testing of as-cast and 100 h aged bars was performed using a WPM Leipzig Charpy impact test device with the impact energy scale up to 300 J, whereas the bars aged for 300, 600, and 1200 h were tested using a corresponding Zwick tester with the scale up to 50 J. Impact tests were performed for three replicate bars under ambient conditions. Hardness tests were carried out using a Struers Duramin-A300 tester with a Vickers diamond indenter and a load of 3 kg. Ten measurements were conducted for each combination of the alloy and aging time.

Table 1
The test materials and their chemical composition (wt%).

Material	Alloying element							
	Cr	Ni	C	Mn	Si	Mo	N	Fe
HD	27.00	6.40	0.47	1.06	2.86	0.37	0.42	61.32
HHa	25.51	12.68	0.30	1.48	1.27	0.28		58.16
HHb	24.92	12.16	0.41	1.15	1.22	0.37		59.73
HI	25.70	16.50	0.38	1.03	1.37	0.21		54.32

3. Results

3.1. Microstructure

The optical microscopy images in Figs. 1–4 disclose the overall microstructure of the studied steel grades HD, HHa, HHb, and HI. Fig. 1 shows the microstructure of the grade HD in the as-cast and 100 and 1200 h aged conditions. The austenite phase was the main phase particularly in the as-cast condition and after a short (100 h) aging time and was retained uncolored in the etching. In the examination by optical microscopy, a phase of dark gray contrast appeared in all conditions; this was the ferrite phase. The ferromagnetic behavior, essentially due to the presence of ferrite, was verified with a magnet. Furthermore, in the as-cast alloy, the carbides and their lamellar networks, seen in gray contrast, surrounded the ferrite islands. The areas of light gray contrast were identified as the σ-phase in the microstructure already in the as-cast state. Aging introduced notable changes in the microstructure of the grade HD, particularly in the distribution and amount of ferrite, the carbide networks and the σ-phase. The amount of ferrite somewhat decreased in aging. The lamellar carbide networks were clearly dispersed after both 100 and 1200 h of aging, as compared to the distinct carbide areas in the as-cast state. The σ-phase areas were more evenly distributed throughout the microstructure and had a more angular shape in the aged than