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Effect of Tempering Temperature on the Microstructure and Hardness of a Super-bainitic Steel Containing Co and Al

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The effect of tempering temperature, within the range of 400 to 700 °C, on the microstructure and hardness of two super-bainitic steels, one as the control parent sample and the other with added Co & Al was investigated. Post-tempering examinations of the super-bainitic samples showed that low temperature tempering cycles (400–500 °C) resulted in carbides formation, and some increases in the hardness possibly due to precipitation strengthening in the Co & Al contained steel. Once the tempering temperature increased to 600 °C, the hardness plummeted in both steels due to the concurrent coarsening of the bainitic ferrite plates and more precipitation of carbides. At the higher tempering temperature of 700 °C, further reduction in the hardness occurred because of the accelerated recovery of ferrite and spheroidization of carbides. This work clearly showed that the super-bainitic steel containing Co & Al had a superior tempering resistance particularly at low tempering temperatures (<500 °C) due to reduced carbide precipitation in the presence of Co & Al.

KEY WORDS: tempering; carbide precipitation; retained austenite; bainitic steels.

1. Introduction

Super-bainitic steels are generated by isothermal transformation at low temperatures (125–300 °C) with relatively long processing times, e.g. up to 9 days at 200 °C. These steels have very high strength and toughness due to their nano-scale structure consisting of bainitic-ferrite and retained austenite.1–4) Reduction in the bainitic transformation time is highly desirable in order to make the application of these steels more viable. Pervious work showed that bainitic transformation could be accelerated by the addition of small amounts of Co & Al without compromising the microstructure and mechanical properties of the steel.5) Since some structural components are exposed to elevated temperatures, such as the main shaft of a jet engine, it is essential to assess the stability of these steels at elevated temperatures. Hence, the tempering resistance of super-bainitic steels has been widely studied.5,6) The effect of various elements such as Si, Mn, Cr, Mo and V on the tempering kinetics have also been studied.7) However, the effect of Co and/or Al on the tempering behavior of super-bainitic steels is not well understood. It must be noted that both Co & Al proved to accelerate bainitic transformation.8) In this work, the effect of tempering temperature and time on the microstructure and hardness of a super-bainitic steel with added Co & Al was investigated.

2. Experimental Procedure

Two bainitic steels, Alloy 1 without Co and Al and Alloy 2 with about 4 wt% Co and 1.5 wt% Al were prepared by vacuum induction remelting process. Table 1 shows the measured chemical composition of these two alloys. Both steels were homogenized at 1 200 °C for 2 days in a vacuum furnace then furnace cooled. All samples were austenitized at 1 000 °C for 30 min then kept at 200 °C to transform to bainite. Based on previous work, 192 hrs of isothermal transformation for Alloy 1 and only 78 hrs for Alloy 2 were needed to obtain a super-bainitic structure.9) The bainitic samples were then tempered at 400 to 700 °C for 2 to 8 hrs. Two types of specimens were prepared for transmission electron microscopy (TEM, JEM 2010 HT): thin foils and carbon replicas. The TEM foils were used to examine the microstructures and determine the thickness of the bainitic-ferrite.2) The replicas were used to identify the carbides using selected area electron diffraction patterns. The thin foils were cut from the bulk specimens, and then mechanically ground to about 50 mm thickness. The specimens were

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>Cr</th>
<th>Co</th>
<th>Al</th>
<th>P</th>
<th>S</th>
<th>V</th>
<th>Ni</th>
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<tbody>
<tr>
<td>1</td>
<td>0.79</td>
<td>1.59</td>
<td>1.94</td>
<td>0.30</td>
<td>1.33</td>
<td>0.013</td>
<td>&lt;0.002</td>
<td>0.11</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.78</td>
<td>1.60</td>
<td>2.02</td>
<td>0.24</td>
<td>1.01</td>
<td>3.87</td>
<td>1.37</td>
<td>0.002</td>
<td>0.002</td>
<td>–</td>
<td></td>
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</tbody>
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further thinned using a twin-jet electro-polisher operating at 40 V. The electrolyte consisted of 5 vol.% perchloric acid, 15 vol.% glycerol and 80 vol.% methanol. To make carbon extraction replicas, some 3 mm diameter steel samples were hot-mounted, ground, polished (final stage using an Al₂O₃ suspension solution to a particle size of 0.5 μm) and etched in 4 vol.% nital. A 20–30 nm thick carbon coating (brown gold color) was deposited onto the etched surface in vacuum. The thin film was then scored with a sharp blade and gold color) was deposited onto the etched surface in vacuum. In 4 vol.% nital. A 20–30 nm thick carbon coating (brown gold color) was deposited onto the etched surface in vacuum. The thin film was then scored with a sharp blade and divided it into several square shape pieces (~1 mm²), followed by etching in a solution of 8 vol.% nital in order to detach the carbon replica from the base sample. All samples were washed in methanol and rinsed in distilled water before inserting them in the TEM (using a copper grid to hold the replicas).

Plate-shape samples with approximate dimensions of 10 mm×10 mm×2 mm were used for X-ray diffractometry (XRD, Xpert Pro MPD), operating at 40 kV and 45 mA, with a Cu Kα radiation. The 2θ scanning angles varied from 20° to 100°, with a stepping angle of 0.03342°. The volume fraction of retained austenite was calculated by measuring the integrated intensities of the (111), (200), (220) and (311) in austenite peaks, and (110), (002), (112) and (022) in bainite peaks.9,10 The error in measuring the volume fraction of retained austenite was expected to be about 1.5 vol.%. The carbon concentration in austenite was estimated by measuring the volume fraction of retained austenite was calculated by measuring the integrated intensities of the (111), (200), (220) and (311) in austenite peaks, and (110), (002), (112) and (022) in bainite peaks.9,10 The error in measuring the volume fraction of retained austenite was expected to be about 1.5 vol.%. The carbon concentration in austenite was estimated by measuring the lattice parameters10,11 with an estimated error of about 0.10 wt.%. The XRD and neutron diffraction work published by Bigg et al.12,13 showed that the XRD technique understimates the volume fraction of austenite due to surface transformation during preparation by grinding even when the samples are chemically polished. In order to minimize such errors, all samples were prepared using the same preparation procedure.

Each hardness value, reported in this work, is the average of at least ten Vickers tests (1 kg).

3. Results

3.1. Microstructures Prior to Tempering

Figure 1 shows the TEM micrographs illustrating typical microstructures of the super-bainitic steels studied in this work. The microstructures of both steels consist of extremely fine bainitic-ferrite and film-like retained austenite. The average thickness of the bainitic-ferrites in Alloy 2 (with a holding time of 78 hrs) was 33 nm, which is substantially less than 47 nm in Alloy 1 (with a holding time of 192 hrs). X-ray analysis revealed that about 26.8 and 16.2 vol.% of retained austenite were present in Alloy 1 and Alloy 2, respectively. It must be noted that both steels were transformed to bainite at the same temperature, i.e. 200°C.

3.2. Post Tempering Microstructures

In Alloy 2, when tempering at 400°C for 2 hrs had no obvious effect on the microstructure, which still consisted of fine plates of bainitic-ferrite and retained austenite (Fig. 2(a)). The retained austenite began to decompose into fine particles of carbide and ferrite when the tempering time was increased to 8 hrs (Fig. 2(b)). With a higher tempering temperature of 500°C, most of the retained austenite decomposed into fine particles of carbide and ferrite within only 2 hrs (Fig. 2(c)). The retained austenite was entirely decomposed at 500°C after 8 hrs of tempering (Fig. 2(d)). As expected, further increase in the volume and size of carbides occurred when the tempering temperature increased to 600°C for 2 and 8 hrs (Figs. 3(a) and 3(b)). As the tempering temperature was further increased to 700°C for 2 and 8 hrs the bainitic ferrite grains were fully recovered and carbides were coarsened and spheroidized (Figs. 3(c) and 3(d)).

Carbides in the Alloy 1 were easier to be precipitated and coarsened, compared that in the Alloy 2. For instance, the retained austenite was decomposed into ferrite and fine carbides when the tempering temperature was increased to 500°C for 2 hrs (see Figs. 4(a) and 4(c)). The carbides were coarsened when the tempering temperature was increased to 600°C (see Figs. 4(b) and 3(a)).

The microstructure of super bainite is generated by isothermal transformation at temperatures in the range 200–300°C for long time (1–9 days), which containing carbon supersaturation bainitic ferrite and carbon-enriched retained austenite. Despite the high Si content (0.91 wt%) is typically used to suppress cementite formation during the isothermal bainitic transformation,14 some fine Fe–C clusters and carbides were found.15 The M₇C carbides (Fig. 5) were also observed by selected area electron diffraction (SAED) in high temperature and long time tempering (700°C for 8 hrs).

**Fig. 1.** TEM micrographs of bainitic-ferrite (BF) and retained austenite (RA) isothermally formed at 200°C, (a) Co & Al contained Alloy 2 in 78 hrs and (b) parent Alloy 1 in 192 hrs.
Fig. 2. TEM micrographs in the tempered Alloy 2 (a) 400°C for 2 hrs, (b) 400°C for 8 hrs, (c) 500°C for 2 hrs and (d) 500°C for 8 hrs.

Fig. 3. TEM micrographs in the tempered Alloy 2 (a) 600°C for 2 hrs, (b) 600°C for 8 hrs, (c) 700°C for 2 hrs and (d) 700°C for 8 hrs.
Kozeschnik and Bhadeshia\textsuperscript{15} revealed that silicon is ineffective in retarding the precipitation of cementite if the parent phase is highly supersaturated with carbon.

3.3. Hardness

The effect of tempering temperature and time on the hardness of both bainitic samples is shown in Fig. 6. In the case of Alloy 2, there is a sharp increase in the hardness ($\sim 40$ HV1) when tempering at $400^\circ$C for 8 hrs. The hardness of Alloy 2 remained between 558 to 576 HV1 after tempering at $500^\circ$C for 2 and 8 hrs. Softening was commenced when the tempering temperature exceeds $400^\circ$C for parent Alloy 1 and $500^\circ$C for Co & Al contained Alloy 2. This clearly demonstrates the benefit of adding Co and Al for high temperature applications. In the early stages of tempering, formation of carbides led to some precipitation strengthening in Alloy 2, indicating its tempering resistance. In contrast, the hardness of Alloy 1 was gradually decreased as the tempering temperature increased. Substantial reduction in hardness occurred in both steels when the tempering temperature reached $700^\circ$C.

3.4. Volume Fraction and Carbon Content of Retained Austenite

The volume fraction and carbon content of retained austenite after tempering was determined by XRD (Fig. 7). It is seen that the retained austenite fraction of both Alloy 1 and Alloy 2 was decreased after increasing tempering temperature (Fig. 7(a)). It is also seen that the decrease was slower for Alloy 2 than Alloy 1 under the identical tempering condition. The volume fraction of retained austenite in
Alloy 2 was decreased by 5.2 vol% (from 16.2 to 11.0 vol%) when tempering reached 700°C for 2 hrs, whereas Alloy 1 was decreased by 10.4 vol% (from 26.8 to 16.4 vol%).

The maximum carbon content in the retained austenite was 1.39 and 1.48 wt% for Alloy 1 and Alloy 2, respectively, prior to the tempering (Fig. 7(b)). The carbon concentration in the austenite decreases in both steels due to partitioning when the tempering temperature increased. Nevertheless, the carbon content was much higher in the Alloy 2 which is another sign of its superior tempering resistance. The peak carbon content in the retained austenite in the Alloy 1 was higher than the bulk carbon concentration when the tempering temperature was below 500°C (e.g. 1.12 wt% as to the bulk concentration of 0.78 wt%). Unlike Alloy 1, the carbon concentration in the retained austenite in Alloy 2 remained above bulk carbon concentration even when tempering temperature reached 600°C (e.g. 0.83 wt%).

4. Discussion

When the retained austenite and bainitic-ferrite were tempered, the secondary hardening effect occurs due to the precipitation of very fine carbides, which restricts the dislocation mobility. In the present work, the hardness remained unchanged or even increased about 40 HV1 (from 580 to 620 HV1) in Alloy 2, when specimens were tempered at 400–500°C for a longer time (8 hrs). Simultaneously, the hardness of Alloy 1 decreased about 80 HV1 (from 540 to 460 HV1) in the same condition (tempered at 500°C for 8 hrs). Therefore, it was concluded that the tempering resistance of the super-bainitic steel containing Co & Al was superior (Fig. 6). When the tempering temperature and/or time were increased, the mean cementite radius as well as the spacing between them were increased, resulting in much coarser cementite particles as can be seen in Figs. 3(c), 3(d) and 8. This observation is consistent with previous reports.16–18)

The driving force for precipitate growth stems from the interfacial energy, and the growth rate is controlled by the volume diffusion. Krishtal19) already showed that the Co and Al increase the diffusion rate of carbon in steels, but the retardation of coarsening of carbide is mainly attributed to the suppression of iron (or substitutional atoms). In Alloy 2, the Co retards the diffusion of substitutional atoms20,21) and Al reduces the diffusion coefficient of iron atoms22) in steels. The coarsening of cementite is also influenced by carbon diffusion. At high temperature, carbon diffusion is very fast. The coarsening of cementite is dominated by the diffusion of substitutional atoms. In the meantime, the partitioning of Co and Al between bainitic ferrite and cementite occurs and this should be much larger effects on coarsening kinetics because long-range diffusion of those elements is necessary.

![Fig. 7. Effect of tempering temperature on (a) the volume fraction and (b) carbon content in retained austenite (horizontal line represents bulk carbon content).](image1)

![Fig. 8. Effect of tempering temperature and time on mean radius of carbides in modified Alloy 2 containing Co & Al.](image2)
in this process. Therefore, the addition of Co and Al in the steel retarded the coarsening of carbide during tempering. Hald and Straub have found that various carbide precipitation behaviors are retarded by Co. In the meantime, the coarsening rate of carbides decreased with increasing concentration of Co. The Al has also a strong effect to retard the formation and coarsening of alloy carbides. Yi and Wang found that the spheroidal carbides could maintain a smaller size even at a higher spheroidization temperature in high-carbon steels containing high Al (1.5–2.0 wt%). Shi have also reported that the aggregation of Al in grain boundaries substantially suppresses the nucleation and growth of carbide in the boundaries. Therefore, the addition of Co & Al can concurrently delay the carbide precipitation from carbon-enriched retained austenite and supersaturated bainitic-ferrite, hence, resulting in an enhanced stability at high temperatures.

5. Conclusions

The effect of tempering temperature on the microstructure and hardness of a super-bainitic steel with and without Co & Al was investigated. The hardness of the steel with added Al & Co was increased after a low temperature tempering cycle (400–500°C) and only plummeted as the tempering temperature was increased to 600°C. In contrast, the parent alloy without Co & Al showed gradual reduction in the hardness as the tempering temperature increased. The softening was due to coarsening of the bainitic-ferrite plates and carbides. The improved tempering resistance of the modified steel was attributed to the slower carbide precipitation from carbon-enriched retained austenite and supersaturated bainitic-ferrite in the presence of Co & Al.

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