INFLUENCE OF AGING ON MICROSTRUCTURE AND TOUGHNESS OF DIE-CASTING DIE STEELS

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Abstract

This study investigates the modification of the carbide type, size, shape and the associated changes in the toughness properties after prolonged aging at temperatures close to that of maximum hardening during tempering treatment. The aging effects on the microstructure of both steels still consist of a tempered martensite matrix, with an increased amount of precipitates and more market prior austenitic grain boundaries. For H13 steel, the aging effects on fracture toughness show an appreciable increase in up to 50 hours’ treatment; raising the aging time to 250 hours causes considerable embrittlement. For H11 steel however, the fracture toughness decreases early, from the first stages of aging; this behaviour has been associated to an increase in the carbide size. At increasing aging time, also for H11 steel, the embrittlement of prior austenite grain boundaries prevails in controlling fracture initiation and in decreasing fracture toughness.

Keywords

Aging, toughness, die-casting die steels, carbides, embrittlement, microstructure, dissolution.

INTRODUCTION

In recent decades the die-casting industry has taken a closer look at the quality level of materials used to make its die cast tools. There is now a better understanding of the relationship between the material properties of the die steel and the ability to achieve an adequate die life. Many problems such as premature heat checking and gross cracking are associated with the toughness characteristics of the die steel. The material properties which have shown the greatest influence on toughness are the appearance of
primary carbides, the microcleanness level and the severity of chemical segregation (Breitler et al., 1996). Therefore a hot work tool steel intended for die-casting applications requires both sufficient strength and hardness properties and also a high level of ductility. Ductility may be defined as the ability of a material to accumulate plastic deformation prior to fracture. A high ductility level will help in extending tool life because it will deter the initiation and growth of thermal fatigue cracks (Norstrom et al., 1989).

Major process factors affecting the fatigue life of the die surface in high pressure die-casting applications are the initial bulk die temperature, and the temperature, heat of fusion and specific heat of the casting alloy, in addition to the high temperature physical and mechanical properties of the die material (Manson et al., 1966).

Today dies produced from chromium-molybdenum-vanadium steels with approximately 0.40% carbon, a minimum of inclusions and segregation and heat treated to a Rockwell C range of 45-50 have been shown to provide good thermal fatigue resistance. With an appropriate chemical composition, optimised austenitizing temperature and a fast cooling rate, experience shows that improved die life can be expected in most applications (Sjöström et al., 2004). In that study the thermal fatigue properties of a martensitic chromium hot-work tool steel alloy were evaluated with regard to the austenitizing treatment. It has been found that the thermal fatigue crack growth is strongly dependent on the different austenitizing temperatures, as well as the maximum test temperature. Thermal fatigue resistance has been assumed to rely on temper resistance at the high maximum cycle temperature and on toughness and ductility at the lower one. It has been found that the resistance to thermal fatigue could be increased by optimising the heat treatment.

However, for very complex dies and/or for some emerging technologies, under certain conditions and in specific locations these premium quality tool steels are still prone to early failure. In these cases the use of special inserts or cores successfully resulted in an improvement in service performance and in extending die life in severe conditions. With these premises higher bulk die temperatures can today be adopted in order to extend the fatigue life of the die surface. During service prolonged exposure to elevated temperatures unavoidably results in the modification of the microstructure and related properties (Kaszynski et al., 2002). In this review Kaszynski et al. reported that the die-casting process is probably the most demanding environment that any tooling material must withstand. During its service life the die steel has to resist softening and thermal shock and maintain a high degree of resistance to the onset of heat checking. With a specific grade of steel (i.e. H13 type) selected for most die cast tooling, it becomes important to define its quality level. With a basic description of the steelmaking process it can
be understood how techniques used during steel production will ultimately affect the mechanical properties of the die steel. In his work it has been demonstrated that specific steps in the steelmaking process could influence the quality of the die steel and die life.

In the present study the modification of the carbide type, size and shape after prolonged aging at temperatures close to that of maximum hardening during the tempering treatment have been investigated. The associated decrease in toughness properties have also been measured. García de Andrés et al. (García de Andrés et al., 1998) have investigated the effects of carbide-forming elements on the response to thermal treatment of X45Cr13 and X45CrMoV14 martensitic stainless steels. As a result, the concentration of carbon and alloying elements in the martensite were increased and, therefore, an increase in hardness up to a maximum value of 710 HV was found at austenitizing temperatures of 1120 and 1130°C for the X45Cr13 and X45CrMoV14 steels, respectively. The X-ray diffraction patterns of the steels in the as-supplied form showed only the presence of carbide M23C6.

In the present work a high level of aging temperatures has been selected in order to investigate the possibility of cumulative damage building up during die service and resulting in the temper embrittlement of the die steel. Temper embrittlement is in fact inherent in many steels and is characterized by reduced toughness. The state of temper embrittlement has practically no effect on other mechanical properties at room temperature. Many alloy steels have two temperature intervals of temper embrittlement. For instance, irreversible temper brittleness may appear within the range of 250-400°C and does not reappear when the steel is tempered at higher temperatures, while reversible temper brittleness affects the steel whenever it is maintained within 450-650°C. The most important feature of embrittlement on high-temperature tempering is that the process is reversible. If a steel embrittled through tempering at a temperature above 600°C with subsequent slow cooling or through tempering at 450-600°C (with any rate of cooling) is again heated above 600°C and cooled quickly, its toughness will return to the initial level.

Steels in the state of reversible temper embrittlement have a bright intercrystalline fracture at boundaries of former austenitic grains. A fundamental fact is that alloy steels of very high purity are utterly unsusceptible to temper embrittlement which is caused by the presence of various impurities, principally phosphorus, tin, antimony and arsenic. Zaoli et al. (Zaoli et al., 2001) have proposed a new interpretation of temper embrittlement dynamics, based on the diffusion of phosphor atoms to grain boundaries by the complex of phosphor atom-vacancy. The dynamics of temper embrittlement in a medium-carbon Cr steel during 538 °C tempering
were carefully examined. The results have shown that the dependence of 50% fracture appearance transition temperature (FATT) on tempering time had a maximum, which could be satisfactorily elucidated by diffusion of the complex of phosphor atom-vacancy. The dependence of hardness on tempering duration decreased all the time.

Nikolaeva et al. (Nikolaeva et al., 2001) have shown that the grain-boundary segregation of impurity elements, such as phosphorus, arsenic, antimony, and others, decreased the grain-boundary cohesion, which could substantially increase the temperature of the ductile-brittle transition in low-alloy structural steel. Since the mechanisms of embrittlement during development of reversible temper brittleness and radiation-stimulated grain-boundary segregation of phosphorus were the same, the main characteristics of the influence by the latter on the mechanical properties of steel could be determined by investigating steel treated in the range 400–600°C.

Finally, McMahon (McMahon, 2003) investigated the effect of molybdenum on the segregation of phosphorus and pointed out that in a steel quenched to form martensite the vacancy content of the parent austenite was of little relevance.

Temper embrittlement is today explained by an increased concentration of impurities in boundary layers. This was first proved by an increased etchability of grain boundaries in embrittled steel by picric acid and was subsequently proved by Auger spectroscopy that made it possible to detect segregations of phosphorus and other impurity elements at the fracture surface in embrittled steel and measure their concentrations (as also the concentrations of alloying elements) at the fracture surface. It was also shown that the development of temper embrittlement is directly linked with the rise of impurity concentration near the prior austenite boundaries.

The rate and degree of development of temper embrittlement depend on the temperature and time of holding steel within the dangerous temperature range (450-600°C) and on the mechanisms that control the diffusion of impurity elements towards the prior austenite grain boundary. Each steel is also characterized by a certain temperature of tempering within this range for which the initial stages of embrittlement appear appreciably sooner than at a higher or a lower temperature. As the temperature increases, the diffusion process of grain boundary segregation is accelerated, with the absolute value of equilibrium segregation simultaneously decreasing owing to thermal motion. At temperatures above 600-650°C, the segregation of impurities either disappears fully (Sb) or drops to a very low level (P). On subsequent cooling of the steel in water, the segregates have no time to restore and toughness undergoes no more negative effects.
EXPERIMENTAL
In the present study H11 and H13 die-casting die steels have been investigated and their chemical composition is shown in Table 1.

Table 1: Chemical composition of the studied steels (in weight percentage)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>P</th>
<th>Sn</th>
<th>Al</th>
<th>Ca</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>H11</td>
<td>0.41</td>
<td>1.06</td>
<td>0.36</td>
<td>4.93</td>
<td>1.21</td>
<td>0.34</td>
<td>0.015</td>
<td>0.006</td>
<td>0.017</td>
<td>0.021</td>
<td>0.008</td>
</tr>
<tr>
<td>H13</td>
<td>0.41</td>
<td>1.06</td>
<td>0.4</td>
<td>5.11</td>
<td>1.28</td>
<td>0.89</td>
<td>0.023</td>
<td>0.005</td>
<td>0.013</td>
<td>0.001</td>
<td>0.009</td>
</tr>
</tbody>
</table>

The samples used in the experiments have been machined from 71 mm diameter commercial bars in AISI H11 and AISI H13 steel. Prismatic samples measuring 11x11x55 mm, with a 3.5 mm deep V-notch have been machined and then heat treated in industrial vacuum furnaces, according to the following procedure.

For H11 steel: i) austenitizing at 1000 °C for 2 hours (with a heating rate of 2.7 °C/min) and quenching under nitrogen pressure to room temperature (with a cooling rate of 50 °C/min); ii) the first tempering at 585 °C for 8 hours, the second one at 560 °C for 3 hours (with a heating rate of 4.5 °C/min and a cooling rate of 6 °C/min for both temperings).

For H13 steel: i) austenitizing at 1030 °C for 2 hours (with a heating rate of 2.7°C/min) and quenching under nitrogen pressure to room temperature (with a cooling rate of 50 °C/min); ii) the first tempering at 590 °C for 8 hours, the second one at 560 °C for 3 hours (with a heating rate of 4.5 °C/min and a cooling rate of 6 °C/min for both temperings).

The hardness of the quenched and tempered steels is 44-45 HRC for the H11 steel and 45-46 HRC for the H13 steel.

After quenching and tempering, aging treatments at 525 °C for 10, 50 and 250 hours, followed by a rapid cooling, have been executed. Final precracking of the specimens has been carried out after tempering or aging.

Fracture mechanics experiments have been carried out in accordance with the ASTM E399-90 Standard and after preliminary tests, three different test temperatures, namely 0°C, 25°C and 40°C, were selected.

The microstructure has been investigated on samples etched with Nital etch by means of an optic microscope.

Fractographic observations have been carried out by means of a scanning electron microscope (LEO EVO 40) coupled with the EDXS microprobe (Link Pentafet Oxford mod 7060).

The modification of the carbide type, size, and shape after the prolonged aging at temperatures close to that of maximum hardening during the tempering treatment have been investigated and related to the fracture behaviour of the steels. For a better characterization of morphology, size
and chemical composition, carbides have been extracted from the steel matrix by acid dissolution. A steel sample of about 3 grams has been ground with 1200-grit SiC paper to remove surface oxides and has been then dissolved into 200 ml aqueous solution of hydrochloric acid (1:1) under heating (80-100°C). After a few hours all the iron was dissolved and 250 ml of hot de-ionised water has been added. The hot iron solution has been then filtered over a cellulose nitrate membrane with pores of 0.2 µm. The residue has finally been washed alternately with hot hydrochloric acid (1:25) and hot de-ionised water, 5 times with each, in order to ensure the removal of all iron salts.

This non-conventional procedure has the drawback of losing the spatial distribution of the carbides in the steel matrix, yet has the great advantage of concentrating them on the filter, enabling the structural analysis of the precipitates by X-ray diffraction (XRD).

The diffraction measurements have been performed by an X-Pert Philips diffractometer set to a current and voltage of 40 mA and 40 kV respectively.

**RESULTS AND DISCUSSION**

As shown in Fig. 1, the resulting microstructure for both steels in the as-quenched and tempered condition is a tempered martensite matrix with various randomly dispersed carbide and carbonitride precipitates; no microsegregations or carbide banding are observed. With a more detailed examination, by comparison of X-ray diffraction and SEM analysis of extracted carbides, in H11 steel the largest carbides are represented by some primary vanadium carbides and by coarsened chromium carbides, both with a globular shape and about 300 nm in diameter, while in H13 steel the largest carbides are essentially provided by primary vanadium carbides, globular and with a 400 nm diameter. Data about size distribution of carbides are reported in Fig. 2. In both steels further molybdenum carbides and also mixed carbides and carbonitrides have been identified, all of smaller diameter compared with previously reported carbides.
Figure 1: Microstructure of H11 and H13 steels in the as-quenched and tempered condition. Etchant: Nital’s reagent

Figure 2: Size distribution of carbides in H11 and H13 steels in the as-quenched and tempered condition
After aging at 525 °C for 250 hours the microstructure of both steels still consist of a tempered martensite matrix, with an increased amount of precipitates and more marked prior austenitic grain boundaries (Fig. 3).

**Figure 3:** Microstructure of H11 and H13 steels after aging at 525 °C for 250 hours. Etchant: Nital’s reagent

As regards the largest carbides in H13 steel, further coalescence causes primary vanadium carbides to grow roughly from 400 to 500 nm and to change into mixed vanadium and chromium carbides. Clear evidence of a new precipitate is also observed at a prior austenite grain boundary, while X-ray and EDS examinations allow this new precipitate to be identified as chromium nitride.

After aging at 525 °C for 250 hours in H11 steel the largest carbides are represented by roughly 500 nm diameter chromium carbides with some molybdenum and vanadium; only weak precipitation at the austenite grain boundary could be observed but not identified as chromium nitride as for the H13 steel. Coalescence is also observed for mixed carbides and carbonitrides of a smaller diameter.

Data about size distribution of carbides are reported in Fig. 4.
Figure 4: Size distribution of carbides in H11 and H13 steels after aging at 525 °C for 250 hours

Fig. 5 gives the results of the fracture mechanics experiments, expressed in terms of $K_Q$ and $K_{IC}$, for steel H11 and steel H13 respectively, as a function of the aging time at 525 °C. The effect of the test temperature is negligible and the scatter of toughness results, which affects some test conditions, in particular specimens aged for 50 h, is most likely to be related to the statistical distribution associated with the fracture mechanism. In fact as-quenched and tempered specimens show a quasi cleavage fracture mechanism for both H11 and H13 steels (Fig. 6). The difference in the fracture toughness level (~ 55 MPa√m versus ~ 108 MPa√m for H13 and H11 steels respectively) is to be associated with the different carbide size and volume fraction: in H13 steel larger primary vanadium carbides have been observed and nearly a double volume fraction can be calculated for equilibrium conditions starting from the V content of the steel. Fracture surface examination shows that cleavage is not controlled by a weakest link
mechanism, but should instead be associated with multiple cracking of brittle particles uniformly distributed ahead of the crack front. These brittle particles can be identified with the largest primary carbides and under these assumptions H13 steel fracture, compared with H11 steel, is then anticipated by the occurrence of large carbides fractures evenly distributed at a high number of sites ahead of the crack tip.

On aging at 525°C fracture toughness shows an appreciable increase for H13 steel up to 50 hours of treatment and raising the aging time to 250 hours causes appreciable embrittlement. The largest carbides in the microstructure (essentially primary vanadium carbides) remain unchanged while intermediate size carbides (mixed chromium and molybdenum carbides) undergo coalescence; their influence in strengthening the steel matrix becomes less effective, as proved by a decrease in the steel hardness (from 46 HRC down to 42 HRC). A decrease in yield strength is therefore also expected and this causes the spread of the plastic zone ahead of the crack tip over a larger volume; also the level of the stresses acting over the carbides within the plastic zone is therefore diminished and the onset of cracking is delayed at higher loads, i.e. at a higher fracture toughness level.

For specimens aged for 50 hours the fracture surface shows some intergranular facets at prior austenite grain boundaries (Fig. 7) while after 250 hours of aging the fracture becomes totally intergranular (Fig. 8). The most likely mechanism of embrittlement of prior austenite grain boundaries on aging at 525 °C is the segregation of impurity elements, in particular of P, but further experiments are needed to prove this assumption in full.

For H11 steel a somewhat different behaviour has been observed. In fact fracture toughness apparently decreases as from the early stages of aging. In this case the largest carbides that have been observed are chromium carbides coalesced during the tempering treatment; these carbides undergo a more pronounced increase in size (from 300 nm to 500 nm) and this makes them more prone to initiate the fracture of the specimens.

As the aging time as increased, the embrittlement of prior austenite grain boundaries prevails in controlling fracture initiation and in decreasing the fracture toughness of the steel.
Figure 5: Results of the fracture mechanics experiments for H11 and H13 steels. $\circ = 0^\circ C$, $\square = 25^\circ C$, $\triangle = 40^\circ C$.

Figure 6: Fracture surfaces of the as quenched and tempered condition H11 and H13 steels, tested at 25 °C

Figure 7: Fracture surfaces of 50 h-aged H11 and H13 steels, tested at 25°C and 0°C respectively
CONCLUSIONS
The modification of the carbide type, size and shape after prolonged aging at temperatures close to that of maximum hardening during tempering treatment have been investigated. The associated decrease in toughness properties have also been measured.
After aging at 525 °C for 250 hours the microstructure of both steels still consists of a tempered martensite matrix, with an increased amount of precipitates and more marked prior austenitic grain boundaries.
On aging at 525°C the fracture toughness shows an appreciable increase for H13 steel with up to 50 hours treatment and raising the aging time to 250 hours causes appreciable embrittlement.
For specimens aged for 50 hours the fracture surface shows some intergranular facets at prior austenite grain boundaries while after 250 hours of aging the fracture becomes totally intergranular. The most likely mechanism of embrittlement of prior austenite grain boundaries on aging at 525 °C is the segregation of impurity elements, in particular of P, but further experiments are needed to prove this assumption in full.
For H11 steel a somewhat different behaviour has been observed. In fact fracture toughness apparently decreases as from the early stages of aging.
The early decrease in fracture toughness has been associated with an increase in the carbide size which makes them more prone to initiate the fracture of the specimens.
At increasing aging time, also for the H11 steel, the embrittlement of prior austenite grain boundaries prevails in controlling fracture initiation and in decreasing the fracture toughness.

Figure 8: Fracture surfaces of 250 h-aged H11 and H13 steels, tested at 40°C
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REFERENCES


