Thermal Fatigue Behavior of Nitrocarburized and Low Pressure Nitrided JIS SKD61 Hot Work Mold Steel

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A novel method using induction heating equipment was employed to investigate the thermal fatigue behaviors of two hot-work steels, JIS SKD61 and modified JIS SKD61, vacuum hardened treated to 45 HRC. Selected specimens, austenitized at 1298 K for 25 min, gas quenched to room temperature and tempered at 873 K, were salt bath nitrocarburized at 843 K for 80 min and low pressure nitrided at 813 K for 6 h, respectively. Microstructure, microhardness, X-ray diffraction and thermal fatigue tests were conducted. The results show that the thermal fatigue properties of the 898 K tempered specimen were better than those of other treated specimens. The reason is that the hardened processes would give high tensile strength, which improved the tool material thermal fatigue resistance. The thermal fatigue properties of modified JIS SKD61 specimen, including mean crack length and crack distribution density, were better than those of JIS SKD61 specimen. Low pressure nitriding treatment with a homogeneous nitrided layer could better maintain thermal fatigue resistance than the nitrocarburized steel.

Keywords: hot work steel, nitrocarburizing, low pressure nitriding, thermal fatigue

1. Introduction

JIS SKD61 steel is used in applications where high temperatures are a crucial factor. This steel has good hardening ability, high toughness and excellent red hardness with less structural distortion.1-3 During the die filling process die casting mold steel is eroded by molten metals such as aluminum, magnesium or zinc at high velocity flow. Die casting is followed by cooling with water which causes mechanical stress on the hot work die. Such cyclic thermal stress will lead to plastic deformation, causing further heat crack initiation.4-8 Thermal fatigue cracking is the most common failure behavior in all hot work die damage mechanisms.8,9 Hence, a higher level of thermal fatigue resistance, thermal shock resistance and excellent high temperature strength are required in hot work die steel.

The last decade have seen growing importance placed on research in modified hot work die steel. The related works reported in the literature can be classified into two major categories, which include steel refining and chemical compositions modified. Refining process such as electro slag remelting (ESR) and vacuum arc remelting (VAR) can decrease carbide segregation in the steel matrix. However, the most studies and applications were focused on the change of chemical compositions. Decrease silicon content and increase molybdenum content can enhance the high temperature strength and thermal fatigue property, and several studies have suggested the benefit of it.7,10

JIS SKD61 hot work steel is usually treated with thermochemical surface treatments such as nitriding, PVD and HVOF processes in order to increase service lifetime.11-15 Among these processes, nitro-carburizing treatment is regarded an effective, low cost method with many advantages, such as low treatment temperature, short treatment time, high degree of shape and high surface hardness due to the ε-phase (Fe2.17N) and γ-phase (Fe3N) formed on the outmost surface.14,15 Low pressure nitriding (LPN—i.e., under a partial vacuum) treatment has also become preferred as a safe and more easily controlled treatment. In a typical system anhydrous ammonia gas is injected into the process chamber as the source of active nitrogen atoms, because ammonia to nitrogen and hydrogen thermal decomposition occurs at the hot work-piece surface. The nitrogen atoms immediately diffuse directly into the metal surface. The use of ammonia rather than pure nitrogen allows operating at a comparatively lower temperature.16-18

Increasing the mechanical properties and thermal fatigue resistance of hot mold steel using thermo-chemical surface treatments is more efficient for increasing tool lifetime. The thermal fatigue characteristics of JIS SKD61 die steel with various surface treatments were investigated by Ivanov et al.4 They concluded that the thermal fatigue resistance of hot work steel had an improvement ratio of 20% using shot peening and 33% using laser hardening or plasma spraying. This research also mentioned that the common feature of the longest crack was limited by the depth of the effective diffusion zone for a nitrided specimen. Bíró9 reported that the Cr content of the Stellite 6 alloy facilitated the formation of stable Cr-rich oxides which sustained the thermal stresses generated at the surface without spalling and thereby retarded crack initiation.

Although the reasons for the surface treatment improvements from thermal fatigue resistance treatment are known, several researches4,7 reported that the thermal fatigue cracking of hot work tool steels is negatively influenced by surface engineering such as gas nitriding. Hence, the aim of this study is to clarify the nitrocarburizing (NC) and low pressure nitriding (LPN) effects on the mechanical and thermal fatigue properties of JIS SKD61 hot work steel using induction heating and water cooling procedures.

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2. Experimental Procedures

2.1 Materials and characterization

The materials selected in this study were two hot work steels, JIS SKD61 and modified JIS SKD61 (i.e., chemical compositions content modified). The specimens were sectioned from a round steel bar and machined to \( \frac{2}{5} \times 25 \) mm \( \times \) t50 mm dimensions. Table 1 lists the chemical composition of the specimens. The specimens were heated to 1298 K austenitizing temperature for 20 min, followed by 0.2 MPa \( \text{N}_2 \) gas quenching and tempering at 898 K. Before the nitrocarburizing and low pressure nitriding treatment, specimens were ground using 1200-grit abrasive paper with a surface roughness \( (Ra) \) of 0.21 ± 0.03 \( \mu \)m, obtained using a Mitutoyo Surftest SV-400 surface profiler.

The cross-sectional microstructure and thermal fatigue pattern of the specimens were revealed using a 95 ml alcohol + 5 ml \( \text{HNO}_3 \) chemical solution and observed using an optical microscope (Nikon OPTIPHOT-100) and scanning electron microscope (JEOL JSM-5600). The prior austenite grain size given by austenitizing treatment was about ASTM 10 for both steels. The phases precipitated in the case layer of the nitrided specimen were characterized with an X-ray diffractometer using Cu-K\( \alpha \) radiation source over the 2\( \theta \) range from 30 to 90°. The dominant peaks of the vacuum heat treated specimen in the XRD pattern were those of the tempered martensite phase. Substrate hardness was measured using a Vickers micro-hardness tester with an applied load of 0.98 N. The case depth diffusion layer profiles of specimens treated by nitrocarburizing and low pressure nitriding was measured using Vickers indentation on a polished cross-section with an applied load of 0.98 N. The effective case depth of the nitrided specimen was determined at the depth case hardness value becoming 50 HV higher than the substrate hardness.\(^{19}\)

2.2 Nitriding procedure

Prior to submerging into a salt bath for the nitrocarburizing treatment, the tempered specimens were degreased and ultrasonically cleaned in acetone for 20 min. The nitrocarburizing treatment was conducted in a 843 K salt bath for 80 min, followed by washing in 343 K warm water. Some of the quenched and tempered specimens underwent a low pressure nitriding process: evacuating the chamber pressure to 1 Pa and then convection heat to treatment temperature with \( \text{N}_2 \) gas in \( 8 \times 10^4 \) Pa pressure and then vacuum the chamber to 1 Pa. To remove the passive oxide layer a cleaning cycle was carried out with \( \text{N}_2\text{O} \) gas at a pressure of \( 3 \times 10^4 \) Pa. The chamber was then purged to 10 Pa. Low pressure nitriding was performed at 813 K for 6 h. The chamber atmosphere was filled with \( \text{NH}_3 \) gas to \( 3 \times 10^4 \) Pa and inert \( \text{N}_2 \) gas to dilute the nitriding power of the treatment gas. Cooling was accomplished in the chamber using \( \text{N}_2 \) gas convection to room temperature. The specimen and treatment notations are in Table 2.

2.3 Thermal fatigue testing

A novel method using induction heating and water cooling procedures was employed in this study. The thermal fatigue testing equipment was based on cyclic induction heating, using 0.4 MHz high frequency and 30 kW power to induce fast heating on the specimen surface. A schematic of the experimental set-up used in the thermal fatigue test is shown in Fig. 1. In order to simulate the die casting temperature condition rapidly, a circular coil made by copper tube was designed to furnish the heating and cooling stage simultaneously in one rotation cycle, by drilling several holes in 30° range of coiler for water jet and the remaining 330° range for heating only. The specimen was heated gradually in heating region to the maximum surface temperature of about 973 K. Water injection from hole of coil brought the specimen to a minimum temperature of about 473 K in cooling region. For a point on the specimen which was heated to the maximum

<table>
<thead>
<tr>
<th>Notation</th>
<th>Treatment</th>
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<tbody>
<tr>
<td>Ferritic substrate</td>
<td>As received hot work steel</td>
</tr>
<tr>
<td>(FS-A), (FS-B)</td>
<td>(A: Standard JIS SKD61, B: Modified JIS SKD61)</td>
</tr>
<tr>
<td>Tempered martensite</td>
<td>Quenched and tempered at 898 K</td>
</tr>
<tr>
<td>substrate (TMS-A), (TMS-B)</td>
<td></td>
</tr>
<tr>
<td>Nitrocarburizing</td>
<td>Nitrocarburized at 843 K for 80 min</td>
</tr>
<tr>
<td>(NC-A), (NC-B)</td>
<td></td>
</tr>
<tr>
<td>Lower pressure nitriding</td>
<td>Lower pressure nitrided at 813 K for 6 h</td>
</tr>
<tr>
<td>(LPN-A), (LPN-B)</td>
<td></td>
</tr>
</tbody>
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Table 1 Chemical compositions of JIS SKD61 (A) and modified JIS SKD61 (B) (mass%).

<table>
<thead>
<tr>
<th>mass%</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Fe</th>
</tr>
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<tr>
<td>JIS SKD61</td>
<td>0.398</td>
<td>0.968</td>
<td>0.406</td>
<td>0.018</td>
<td>0.008</td>
<td>5.145</td>
<td>1.252</td>
<td>0.920</td>
<td>Bal.</td>
</tr>
<tr>
<td>Modified JIS SKD61</td>
<td>0.371</td>
<td>0.390</td>
<td>0.613</td>
<td>0.006</td>
<td>0.005</td>
<td>4.767</td>
<td>2.569</td>
<td>0.679</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Fig. 1 Schematic of thermal fatigue equipment.
temperature and subsequent cooled by water jet. The above thermal fatigue testing procedure was defined as one cycle. The each cycling time was 0.3 s while rotating at 200 rpm. The temperature was measured using an infrared meter by using a stopper to decrease the influence of water spraying.

Three specimens were used to observe of crack initiation and propagation for each data point. The thermal fatigue testing was conducted with 500, 1000, 2000 and 3000 cycles, respectively. The specimens were free from any externally applied load and taken out to observe the cracks on the surface every 500 cycles. After testing, the surface thermal crack morphology and the crack propagation behavior beneath the surface was investigated using an optical microscope (OM). The thermal fatigue properties including the mean crack length and crack density (number of cracks per unit length) were revealed from a polished longitudinal cross-section investigated using an optical microscope.

Micro-hardness profiles after thermal cycling for all tested specimens were measured using Vickers indentation on the polished cross-section with an applied load of 0.98 N.

3. Results

3.1 Characteristics of nitrided layer

Typical tempered martensite was observed in the specimen austenitized at 1298 K for 20 min and then gas quenched to room temperature and tempered at 898 K for 1 h twice. Figure 2 shows cross-sectional micrographs of nitrided JIS SKD61 and modified JIS SKD61 specimens. A slightly etched outer white compound layer of approximately 1~2 and 4 µm can be observed in the NC-A and NC-B specimen, soundly bonded with the nitrogen diffusion layer underneath. Non-homogeneous compound layers such as voids and porosities were observed in both the NC specimens, as shown in Figs. 2(a) and 2(c). The thickness of the outer white compound layer was about 3 and 4 µm for LPN-A and LPN-B specimens, respectively. There is no evidence of voids and porosities across the nitrided layer, even as the nitriding duration reached to 6 h, as shown in Figs. 2(b) and 2(d). It is thus concluded that the low pressure nitriding process employed in this work produced sound metallurgical bonds between the homogeneous nitrided layer and the steel substrate.

Figure 3 displays the XRD patterns for JIS SKD61 and modified JIS SKD61 specimens treated with salt-bath nitrocarburizing and low pressure nitriding, respectively. As can be seen in the Figure, the dominant peaks of the received and vacuum heat treated specimen in the XRD pattern were ferrite phase and tempered martensite phase, respectively. From the diffraction patterns, two different phases can be identified in the nitrided layer: ε-phase (Fe23N) and the γ'-phase (Fe4N). The highest surface microhardness values to about 1100 HV0.1 was obtained for the modified JIS SKD61 specimens treated by salt-bath nitrocarburizing and low pressure nitriding. The cross-sectional hardness profiles of nitrided specimens in given conditions are shown in Fig. 4. The effective case depth of the nitrided specimen was determined by the depth of hardness value becoming 50 HV over the substrate hardness, and the effective case depth of the NC-A and LPN-A specimen are about 60 and 80 µm, respectively. The effective case depth of the NC-B and LPN-B specimen are the same of about 75 µm (see Fig. 4).

3.2 Surface cracking

The response of hardened JIS SKD61 (TMS-A) specimens to thermal cycling is shown with a series of micrographs in Fig. 5. The hardened JIS SKD61 specimen kept its integrity for 500 thermal cycles with no evidence of heat cracks on
the surface. The thermal cracks were easily and obviously observed at the surface after 1000 thermal cycles. Because the heat cycled specimens were investigated thoroughly with an optical microscope every 500 cycles, the cracks might have initiated several hundred cycles earlier. Several slight cracks stretched and cross-linked gradually as the thermal cycles increased to 2000 cycles. After 3000 cycles thermal fatigue testing, the cracks propagated continuously and then cross-linked together with a dendritic structure observed, see Fig. 5(d). Compared with the TMS-A specimen, thermal fatigue tested as-received JIS SKD61 (FS-A) specimen shows a severe crack distribution at the surface as shown in Fig. 5(e). A net-like structure could be clearly observed. This shows that the hot-work steel is positively influenced by hardening treatment. On the other hand, the thermal cracks were clearly observed at the surface after 3000 thermal cycles for TMS-B specimen. For comparison with TMS-A specimen, the surface cracks of TMS-B specimen shown in Fig. 5(f) demonstrates the thinner and fewer cracks after 3000 cycles thermal fatigue testing.
3.3 Crack length and density

Thermo-chemical treatments to prolong hot work steel lifetime are well developed and research is ongoing. The reasons for the improvement in thermal fatigue resistance surface treatments are known. However, reports on thermal fatigue cracking in hot work tool steels negatively influenced by surface engineering such as gas nitriding remain.\(^7\)

Clarifying and comparing the effects of other nitriding processes on the mechanical and thermal fatigue properties of JIS SKD61 hot work steel is crucial in this study. The typical pit-like thermal cracks can be observed clearly, as shown in Fig. 6. Persson\(^7\) mentioned that the crack path was distinguished by different testing temperatures, relatively straight cracks dominated after heat cycling to 973 K, both straight and branched cracks were observed after thermal cycling at 1123 K. OM micrographs suggest that crack propagation is not interdendritic. Nevertheless, crack growth involved interdendritic carbide fracture when cracks traversed the dendrite boundaries in hot work steels.\(^8\) Iron oxide was also observed around the crack. Since the thermal cracks were developed at the surface after 1000 thermal cycles or earlier, the cracks were still exposed in the air at 973 K temperature during thermal fatigue testing and until 3000 cycles. The cracks in the TMS-A specimen were evidently created earlier compared with TMS-B specimen due to the broad iron oxide around the cracks in TMS-A specimens and tapered shaped cracks in the TMS-B specimens. This positively reflected the delay in crack initiation, as shown in Fig. 6.

Based on the investigated transverse crack morphology, the polished cross-section micrograph also analyzed crack features such as the mean crack length and crack density. Two crack features in the specimen surface altered with the series of thermal cycles for the two kinds of hot-work steels, as shown in Fig. 7. When the first thermal cracks were detected after 1000 thermal cycles, the mean crack lengths in TMS-A and TMS-B specimens were 20 and 5 µm, respectively. As the thermal cycles were increased to 3000, the mean crack length in TMS-A rose rapidly 6 times to 120 µm and the tested TMS-B specimen showed obvious growth 7 times to 35 µm, see Fig. 7(a). This proves that crack length has a clear dependence on the number of cycles. However, the crack density was not strongly dependent on the number of cycles for both steels, just slightly increasing or remaining constant with increasing thermal cycles, see Fig. 7(b). This reveals that the crack density saturates at a relatively low number of cycles and some cracks propagate into the material due to the stress concentration.

Figure 8 shows the mean crack length and crack density of nitrided specimens after 3000 thermal cycles for JIS SKD61 and modified JIS SKD61 specimens. One can see that regardless of the crack length or density, all of these thermal properties show negative influence after nitrocarburizing treatment compared with the TMS specimens. The thermal fatigue property of mean crack length for the LPN specimens is still worse than that for the TMS specimen, but better than NC specimen. The crack density for LPN specimens is even better than that of the TMS specimen. It can be concluded
that LPN treatment can provide excellent mechanical properties and produce good thermal fatigue resistance. In addition, both thermal fatigue properties of mean crack length and crack density for nitrided modified JIS SKD61 specimens are better than those of JIS SKD61 specimens.

3.4 Hardness after thermal fatigue

Figure 9 shows the microhardness profiles of hardened and nitrided specimens for both hot-work steels after 3000 cycles of thermal fatigue testing. One can see that thermal cycling to 973 K causes softening in the surface area for all hardened and nitrided specimens. After 3000 cycles at 973 K, the initial surface hardness for the TMS-A and TMS-B specimens was reduced approximately in the 45–55% range. The hardness increased with increasing depth from the surface down to the substrate. The TMS-B specimen presented a higher hardness value than the TMS-A specimen from the surface to center region (see Fig. 9(a)). In general, molybdenum forms alloy carbides at the temperature between 773–823 K. As a consequence, the hardness increased with the secondary hardened phenomenon generates at this temperature range. Medvedeva\(^{(19)}\) also mentioned that higher molybdenum content shows a higher thermal stability with superior resistance to softening among the tested grades at all temperatures. This indicated that a higher thermal stability for modified JIS SKD61 material, which also supports the excellent thermal fatigue properties results (crack length and density) for modified JIS SKD61 material.

Because the treatment time duration of 6 h for the low pressure nitriding was longer than nitrocarburizing treatment time duration of 80 min, the hardness of the matrix for both LPN treated specimens was lower than those of NC treated

Fig. 8 Mean crack length (a) and crack density (b) of nitrided specimens after 3000 thermal cycles of JIS SKD61 and modified JIS SKD61 hot-work steels.

Fig. 9 Microhardness profiles of (a) hardened and (b), (c) nitrided specimens for both hot work steels after 3000 cycles thermal fatigue testing.
specimens. After 3000 cycles the initial hardness of the substrate surface area for LPN-A, NC-A, LPN-B and NC-B specimens were reduced by 35, 45, 36 and 50%, respectively (see Figs. 9(b) and 9(c)). The LPN treated showed less surface hardness reduction than the NC treated specimen. This phenomenon is resulted by the deeper cracks in NC treated specimen, which facilitate stress relief in the surface layer.9) This indicated that the LPN process has a dominant positive effect on inhibiting crack initiation compared with the NC process.

4. Discussion

This study clearly demonstrates that non-homogeneous compound layer of salt bath nitrocarburized hot work tool steels showed a tendency to reduce the resistance against thermal fatigue cracking. However, the positive effect observed in this study is that low pressure nitriding treatment reduces the crack density. According to the JIS G 0562 standard,19) the effective case depth of the nitrided specimen was determined by the depth of hardness value becoming 50 HV over the substrate hardness. Based on Fig. 4(a), the effective case depth of the NC and LPN specimen were about 60 and 80 μm, respectively. LPN specimens showed better thermal resistance compared with NC specimens, obtained from thermal fatigue test results. It was found that the thicker effective case depth with higher compressive stress and thereby retarded crack initiation and propagation.

The shorter crack length and fewer cracks in the tested modified JIS SKD61 specimen can be observed in Figs. 5 and 6. Considering the alloy elements were different in the two kinds hot work steels employed in this study, such as silicon, manganese, chromium, molybdenum and vanadium, Medvedeva20) concluded that higher molybdenum content shows superior resistance to softening among the tested grades at all temperatures. Delagnes10) further pointed out that silicon inhibits the coarsening of the cementite and promotes its dissolution, carbon is available to form alloy carbides at lower tempering temperatures for the high silicon grade. As a consequence, the secondary hardening peak of the low silicon grade is shifted towards higher temperatures. In this study, the higher molybdenum and lower silicon content in the modified JIS SKD61 specimens played a key role in maintaining the mechanical properties and high temperature strength during thermal fatigue testing, although the other alloy elements are different compared with JIS SKD61 steel.

In Ivanov’s thermal fatigue study4) the carbonitrides in the surface perform better than nitrides for thermo-cycling conditions, but still worse than conventional heat treated specimens. The thermal stress was estimated at 500 MPa while the temperature difference reached 473 K.9) The cyclic induction temperature difference was larger than 473 K in this study. The thermal stress was estimated at above 500 MPa. Comparing the features of both nitriding processes, similar dominant peaks for the ε-phase (Fe2N3) and γ’-phase (Fe2N) with 1000–1100 HV0.1 appeared. Yatsuhashi31) mentioned that the nitrided layer such as ε-phase (Fe2N3) was decomposed gradually with increasing thermal cycles. Hence, the thicker and dense compound layers of LPN treated specimens showed the better thermal fatigue properties was proved. In addition, crack propagation is retarded when the cracks encounter a material with sufficiently high toughness,22,23) a thicker compound layer will make the surface more hard and brittle.24) Non-homogeneous areas such as porous areas or cracks in the compound layer are pathways connected between the test environment and substrate through the nitrocarburized layer.20,22) The stress might be concentrated rapidly during cyclic induction heating and cause cracks to form and propagate more easily. Generally, the induction heating method and water cooling procedures employed in this study could simulate the mold working condition in a die casting machine and evaluate the thermal fatigue properties of tool steels more rapidly and effectively.

5. Conclusions

This study investigated the thermal properties of two kinds of hot-work steels; JIS SKD61 and modify JIS SKD61, in vacuum hardening treatment and nitriding. Processed steels were experimentally evaluated for thermal fatigue response. The following conclusions can be made.

A novel method using induction heating and water cooling procedures can effectively study the thermal fatigue behavior of hot work steels. The crack lengths were strongly dependent on the number of thermal cycles, but the crack density saturated at a relatively low number of cycles. The modified JIS SKD61 specimens with higher molybdenum content could maintain mechanical properties and high temperature strength during thermal fatigue testing; exhibiting effectively improved thermal fatigue resistance. Low pressure nitriding with a homogeneous nitrided layer can increase the thermal fatigue resistance of hot work steels. The crack density for LPN specimens was even better than that of the TMS specimen. Hence, if the hot-work steel has to be nitrided to increase its’ mechanical properties and thermal fatigue resistance, the low pressure nitriding treatment is a good method that offers high thermal fatigue performance with respect to crack density.

Acknowledgement

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