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Thermomechanical fatigue of cast aluminium alloys for cylinder head applications – experimental characterization and life prediction

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Abstract

TMF loading in diesel cylinder heads made of cast aluminium alloys is expected to steadily become more severe in the future. This increasing loading condition will lead to an early crack initialization and eventually determine component life. Against this background several cast aluminium alloys have been studied with respect to their thermal and mechanical properties. In addition to standardized specimens, near component-shaped samples were tested under thermomechanical fatigue conditions in a testing device which represents near-service conditions, in order to characterize life until a long crack is formed. The sample geometry tries to represent the valve bridge of a diesel cylinder head, which is known to be the most thermomechanically loaded and hence critical part in this component. The results of the TMF tests with this new type of sample were compared with the results obtained on standardized specimens.

The experimental results formed a sound basis to improve the thermomechanical life prediction methodology for cast aluminium alloys. Two different life prediction models were used to assess the TMF life of the near-component samples. Furthermore, an aging model for cast aluminium alloys was derived from the experimental results including the pronounced change of the mechanical properties which result from the combined effects of aging and cyclic plastic deformation. The comparison of the experimental and predicted results clearly shows that the new model leads to an improvement of the TMF life prediction. © 2010 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: Cast aluminium alloys; thermomechanical loading; near-component-shaped specimen; numerical life time predition; aging model

1. Introduction

In many high temperature applications, the lack of thermomechanical fatigue resistance of materials limits the lifetime of engineering components. This holds also true for the thermally high-loaded diesel engine cylinder head. The cylinder head experiences a multi-axial loading, and different from isothermal fatigue, this multiaxial fatigue is more complex due to the complex stress states in combination with temperature gradients and transients. Therefore, the crack initiation at the highest thermomechanically loaded section of the diesel cylinder head, the valve

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crosspiece, has been examined in this study using a near-component-shaped specimen called *valve bridge sample*, which will be presented in chapter 2.

Another major obstacle when using aluminium alloys for high temperature applications is the decrease of strength when aluminium alloy is exposed to high temperature. It is known that hardenable aluminium alloys starts to diminish mechanical strength markedly already at 150 to 200°C and that the mechanical properties of cast aluminium alloys are strongly influenced by the metallurgical and microstructural properties. A cylinder head locally experiences temperature cycles ranging from 20 to 300°C. If the drop of the material strength with time cannot be predicted accurately, the resulting consequences can become severe.

In the study presented, the thermal and mechanical properties of the hardenable cast aluminium alloys AlSi7Mg-T6, AlSi5Cu1-T6, AlSi5Cu3-T7, AlMg3Si1-T6, AlMg3Si1(Cu)-T6 and AlMg3Si1(Sc,Zr)-T5 have been examined on the one hand with standardized samples on the other hand with the near-component specimens with respect to their thermomechanical fatigue resistance. The experimental results are shown in chapter 3. The AlSi7Mg-T6 (A356 alloy) is the most commonly used cast aluminium alloy for diesel cylinder heads and serves as reference. The other cast aluminium alloys considered are also commonly used cast aluminium alloys and have been examined in order to judge their applicability as cylinder head material.

The development in numerical simulation in the last years has led to strongly increased performance of numerical life time prediction, and many methods for estimating the fatigue life of aluminium alloys have been proposed in order to save development time and cost. However, in order to improve material description and to reproduce the change of the material strength during the thermal exposure of the TMF loading, a numerical model for the aging of the material must by incorporated, which represents the decrease of the material strength during the TMF loading. The approach developed in the framework of this investigation will be illustrated in chapter 4.

2. The near-component-shaped specimen "valve bridge sample"

Commonly the mechanical properties of materials are determined with standardized tests and specimens. These specimens are mostly loaded uniaxially and represent only an approximation of the real stress condition within a component such as a multi-axially loaded cylinder head. The most thermomechanically loaded section in a cylinder head is the valve crosspiece. Against this background the near-component-similar specimen (shown in Fig. 1) has been designed and was used in this study for the determination of the crack initiation under thermomechanical loading conditions. The valve bridge sample has been developed within a research project (BMBF project "Development of aluminium design for high loaded engines with a new TMF/HCF method"; [1]) and similar types of near-component specimens have been used also in other investigations ([2] and [3]).



Fig. 1. Near-component-shaped specimen "valve bridge sample", dimensions in mm

The near-component-shaped "valve bridge sample" was made of cast aluminium alloys and contains two holes, which represent the inlet and outlet valve of the cylinder head. In between is the valve crosspiece, which is thermally loaded on one side of the specimen surface, which represents the heating of the cylinder head through the combustion. Cold water permanently flows through drill-holes above and below the two holes (see Fig. 1). Thereof an inhomogeneous temperature field results on the surface of the valve bridge sample with high temperatures in the centre of the valve bridge and rather cool outer parts of the specimen. The near-component-shaped specimen is a simplified geometry, which can easily be implemented in a numerical simulation. Due to symmetry only a quarter of the specimen must be considered and therefore simulations can be performed quickly.

The thermal expansion of the heated valve bridge is constrained by the cooled outer part of the valve bridge sample. A compression stress will result at high temperatures due to this constraint, which eventually will lead to a plastic deformation under compression. After plastic deformation has appeared and the valve bridge sample has cooled down, tensile stresses result in the centre of the bar. This thermal loading in the valve bridge sample gives rise to an out-of-phase thermomechanical loading (OP-TMF). This OP-TMF loading of the valve bridge is superimposed by a decrease of the mechanical properties of aluminium alloys due to over aging at high temperatures in combination with plastic deformation.

The near-component-shaped specimen has been tested in a specially developed test rig. The heating of the valve bridge was performed locally by induction heating. In order to obtain an early crack initialization the mid bar of the near-component-shaped specimen was heated and cooled down with the highest possible temperature transients of the test rig. After a predefined number of cycles the test was interrupted and the valve bridge sample was examined by eddy current tests whether a crack has formed. The automated crack initiation measurement was used to terminate the TMF test as soon as a predefined value at the eddy current signal (corresponding to a predefined crack length) had been reached.

3. Experimental results obtained on hardenable cast aluminium alloys

The experimental results on the hardenable cast aluminium alloys refer to their thermal and mechanical properties and thermomechanical fatigue resistance. The aluminium alloys AlSi7Mg-T6, AlSi5Cu1-T6, AlSi5Cu3-T6, AlMg3Si1-T7, AlMg3Si1(Cu)-T6 and AlMg3Si1(Sc,Zr)-T5 have been selected for this study.

The linear thermal expansion coefficient and the thermal conductivity were measured to characterize the thermal properties. Monotonic tensile tests with standardized specimen were performed to examine the influence of the decrease of the material strength on aluminium alloys. For this purpose, the samples were exposed to specified temperatures for a defined time, and the material properties were subsequently determined at room temperature. The crack initiation stage under TMF loading was studied with the near-component-shaped specimens (valve bridge samples). After the TMF tests the degree of aging, which corresponds to the decrease of the material strength of the aluminium alloys, was examined by means of hardness measurements and transmission electron microscopy.

3.1. Experimental results obtained on standardized specimens

3.1.1. Thermal properties

The linear thermal expansion coefficient for the various aluminium alloys under investigation was determined at different temperatures ranging from 50 °C up to 400 °C (see Fig. 2) according to DIN 51005. All aluminium alloys show that the linear thermal expansion coefficient rises with the temperature due to the fact that the possibility for the oscillating movement of the atoms in the crystal lattice increases at higher temperatures. The AlSi7Mg has the lowest thermal expansion of the cast aluminium alloys studied because of its high silicon content in the microstructure. On the contrary, it can be seen that AlMg3Si1 possesses the highest thermal expansion coefficient as compared to the other alloys. This is probably a consequence of the lack of free silicon phase in the AlMg3Si1.



Fig. 2. Linear thermal expansion coefficient as a function of temperature

The thermal conductivity has been determined as a function of temperature ranging from 50°C up to 400°C. All specimens had been stabilized in advance at 200°C for 500h. The thermal conductivity measurements were performed using the Laserflash method at TU Freiberg and FH Jülich. The results are shown in Fig. 3. AlSi7Mg has the highest thermal conductivity of the cast aluminium alloys investigated, whereas AlMg3Si alloys exhibit the lowest thermal conductivity. In general, the thermal conductivity increase with increasing temperature for all cast aluminium alloys examined.



Fig. 3. Thermal conductivity as a function of temperature

3.1.2. Mechanical properties

The monotonic tensile tests of the aluminium cast alloys were carried out at room temperature and after the standardized specimens had been preaged at defined temperatures for 500 hours in order to determine the effect of aging on the tensile strength properties of the aluminium alloys examined. 500 hours were used to establish a

completely over-aged material condition at least at the highest temperatures applied. The presented values of the ultimate tensile strength in Fig. 4 are the mean value from five performed tensile tests.

Between the temperatures of 150° C and 250° C the material strength decreases rapidly for almost all of the cast aluminium alloys as expected. Only in the case of AlMg3Si1(Sc,Zr)-T5 the annealing is very much delayed even at the highest temperature of 350 °C.

AlSi7Mg-T7 shows the highest reduction of the tensile strength with temperature. After 500 hours at an aging temperature of 200°C or higher the tensile strength has reached a minimum and therewith a stable condition. At temperatures of 150°C and higher more and more incoherent Mg₂Si particles are formed from coarsening, explaining the strength decreases of the AlSiMg alloys. At 200°C and higher incoherent Al₂Cu appears and reduces the tensile strength in the case of AlSiCu. Al₃Sc is responsible for precipitation-strengthening in AlMg3Si(Sc,Zr)-T5 and is stable up to 300°C. Hence, strength reduction due to aging is slow for this alloy.



Fig. 4. Ultimate tensile strength of aluminium castings at room temperature as a function of preaging temperature after 500h aging

3.2. TMF results of near-component-shaped specimens

3.2.1. Crack initiation

Cyclic thermal loading was performed in the centre on the surface of the bridge of the near-component-shaped specimen until crack initiation. The temperature was cycled between 50° C - 250° C within a time range of 10 seconds. The maximum, minimum and mean value of the cycle numbers until crack initiation is presented in table 1.

Table 1. Number of thermal load cycles until crack initiation

Aluminium alloy	Thermal load cycles (mean value)	Maximum	Minimum
	(-)	(-)	(-)
AlSi7Mg-T6	9 853	11 230	8 540
AlSi5Cu3-T7	17 615	20 500	15 540
AlSi5Cu1-T6	17 553	18 670	16 780
AlMg3Si1-T6	11 128	12 065	10 789
AlMg3Si1(Sc,Zr)-T5	14 987	15 563	14 010
AlMg3Si1(Cu)-T6	19 987	22 540	16 300

The AlSiCu alloys could withstand the thermomechanical loading almost twice as long compared to AlSi7Mg-T6 as expected from the higher tensile strength. The AlMg3Si1(Cu)-T6 has the highest number of TMF load cycles until crack initiation of the aluminium castings and shows also a high tensile strength after exposure to high temperatures in a range between 200°C and 250°C (see Fig. 4).

High resistance against crack initiation under TMF loading conditions is also shown by AlMg3Si1(Sc,Zr)-T5 compared to AlSi7Mg-T6, although AlMg3Si1(Sc,Zr)-T5 has a higher the linear thermal expansion coefficient and a lower thermal conductivity in comparison to the other aluminium alloys. However, the tensile strength of specimens aged in the temperature range at and above 250°C showed that after 500h AlMg3Si1(Sc,Zr)-T5 possesses the highest tensile strength of all alloys investigated and therefore may explain the high strength against crack initiation during TMF loading.

All results obtained indicate that the decrease of strength due to the exposure to high temperatures in combination with cyclic plastic deformation during TMF loading is responsible for an early crack initiation. Therefore, further investigations of the valve bridge samples before and after TMF loading were performed to explain the influence of TMF loading on the material properties on a microstructural basis. The most significant results are shown in the following chapters.

3.2.2. Hardness measurements on the surface

Hardness measurements were carried out on the surface of the valve bridge samples before and after the TMF tests in order to identify the decrease of the hardness and therewith the material strength due to the TMF loading. The hardness on the surface before testing was approximately independent of the location and therefore a mean value was determined as reference. The surface hardness was recorded with a BAQ hardness scanner according the UCI method using a specified raster on the near-component-shaped specimen.



Fig. 5. Results from hardness measurements on the surfaces of the valve bridge sample after TMF test leading to crack initiation

The temperature concentration in the bridge of the specimen led to a decrease of the hardness as clearly shown in Fig. 5. The hardness profiles clearly reflect the inhomogeneous temperature field applied during TMF testing. Severe over aging is observed within the bridge area, while no hardness reduction occurs within the well cooled areas on the outer side of the specimens.

The highest decrease of hardness was shown by AlSi7Mg-T6 as compared to the other aluminium alloys. As the tensile tests already had indicated for AlSi7Mg-T6, the material strength decreases significantly already at temperatures of 150°C and higher. Also the high thermal conductivity of AlSi7Mg-T6 contributes to high temperatures spread along the whole bridge. The hardness decrease for the AlSiCu alloys is lower as compared to AlSi7Mg-T6 and more concentrated on the centre of the valve bridge. This result can be compared also to the

experimental results with the standardized specimen. Although the AlSiCu alloys possess a high thermal conductivity and hence temperature is expected to broadly distribute over the mid bar, the hardness decrease was found to be not so high as compared with AlSi7Mg-T6. The tensile strength tests showed that the decrease of the strength for the AlSiCu alloys mainly occurs at temperatures between 200°C and 250°C.

The lowest hardness decrease was found for the AlMgSi alloys. Especially the hardness for AlMg3Si1(Sc,Zr)-T5 was nearly the same before and after the TMF test. The influence of thermomechanical loading during the TMF test does obviously not lead to a significant decrease of strength of the AlMgSi alloys. Therefore despite the low tensile strength and thermal conductivity of the AlMg3Si1 alloys compared to the AlSi7Mg and the AlSiCu alloys, the number of TMF load cycles until crack initiation is higher than for AlSi7Mg-T6

These results of the TMF tests and these post TMF test hardness measurements on the surface of the nearcomponent-shaped specimens lead to the assumption that the tensile strength after the aging of the material and the strength distribution resulting from the inhomogeneous temperature field strongly influence the crack initiation period during TMF loading. A function, which correlates the thermal loading during TMF testing with the material strength properties, would lead to a much better life time prediction under TMF conditions.

3.2.3. TEM results

TEM examinations have been performed in order to show that the increase of incoherent Mg_2Si and Al_2Cu concentrations in the aluminium alloy crystal lattice lead to a strength decrease and develop during the thermal loading of the TMF test. Therefore for AlSi7Mg-T6 and AlSi5Cu3-T7 TEM examinations have been performed before and after the TMF test at the highest loaded section of the valve bridge sample as shown in Fig. 6.



AlSi7Mg-T6 before TMF test



AlSi7Mg-T6 after TMF test (8500 load cycles)



AlSi5Cu3-T7 before TMF test



AlSi5Cu3-T7 after TMF test (16 000 load cycles)

Fig. 6. TEM micrographs of AlSi7Mg-T6 (left) and AlSi5Cu3-T7 (right) before (upper) and after (lower) TMF loading; TEM samples were taken from the valve bridge of the component-shaped specimens

As expected, the TEM examinations of AlSi7Mg-T6 and AlSi5Cu3-T7 show that during the TMF loading incoherent Mg_2Si and Al_2Cu precipitates form as a consequence of coarsening of coherent metastable transient phases which existed before TMF testing. Therefore, the particle coarsening leads to an over-aged condition and is responsible for the decrease of the material strength.

4. Improvement of TMF life time prediction

4.1. Life time prediction models

Thermal and mechanical simulations of the valve bridge sample were performed with ABAQUS in order to numerically predict the thermomechanical life time. In a first step the thermal distribution on the valve bridge sample surface was measured and than numerically simulated. A mechanical simulation including the boundary conditions of the TMF test rig and the thermal results was then performed. The resulting stresses and strains were used to determine the cycles until failure with two different life time prediction models. The damage prediction model of IWM Fraunhofer Institute Freiburg [4] and a simplified Chaboche model ([5] and [6]) were implemented in the mechanical simulation.

The aluminium alloys AlSi7Mg-T6 and AlSi5Cu3-T7 were selected to determine the necessary parameters for the TMF life time prediction. The overall purpose of this numerical investigation was to take into account the influence of the material strength decrease under TMF loading into account and to improve the thermomechanical fatigue life time prediction accordingly.

4.2. Numerical aging model for the life time prediction

The material strength decreased at high temperature and during the TMF tests as shown in the tensile tests on the standardized specimens and by means of the TEM results. This observation has been used to improve the thermomechanical life time prediction. Hardness measurements at different temperatures and aging times have shown that the mechanical properties decrease almost exponential to a minimum value. Therefore, a simplified aging model, given in equations (1) and (2), was implemented into the mechanical simulation, which describes the decrease of the mechanical properties x as a function of temperature and exposure time (see Fig. 7). The aging parameters A, C, X₁ and X₂ were determined by hardness measurements on the aluminium alloys AlSi7Mg and AlSi5Cu3 carried out after aging at different aging temperatures and times.

$$x(T,t) = \begin{cases} X_{0} & \text{for } t = 0h \\ X_{0} \cdot e^{(A \cdot B(T,t)^{C})} \cdot X_{1} \cdot \overline{T}^{X_{2}} & \text{for } 0 < t < 250h \\ X_{0} \cdot e^{(A \cdot B(T,t)^{C})} \cdot X_{1} \cdot \overline{T}^{X_{2}} & \text{for } t \ge 250h \end{cases}$$
(1)

$$B(T,t) = \int_{0}^{t_{cycles}} f(t) \cdot n_{cycles} \cdot dt$$
⁽²⁾

100 90 80 70 value x (%) 60 50 40 30 T2 20 T1 < T210 0 0 10 20 30 40 50 time (h)

Fig. 7. Schematic representation showing the change of the value x with time according to the aging model

All strength parameters used in the IWM model and the Chaboche damage prediction model, which have been determined by isothermal LCF tests, were continuously recalculated according to the aging model (1) during the thermal and mechanical numerical simulation of the TMF test. Only the Young's modulus E was considered to be solely temperature-dependent.

4.3. Comparison of the numerical TMF life time predictions

Several simulations with different boundary conditions for the material parameters have been performed to identify the influence of the aging model on the thermomechanical life time prediction. For this purpose the material properties for three extreme cases, namely (i) at the beginning of the TMF tests, (ii) with the minimum strength values in the over-aged condition after 500h, and (iii) with the values continuously calculated with the aging model were used to determine the thermomechanical fatigue life of the valve bridge sample for both life time prediction models implemented. In Fig. 8 all results are compared on the basis of the predicted cycles until crack initiation for the TMF tests of the aluminium alloys AlSi7Mg-T6 and AlSi5Cu3-T7.



Fig. 8. Numerical life time predictions until crack initiation for AlSi7Mg-T6 and AlSi5Cu3-T7 for different material properties and including the simplified aging model

The results of the numerical life time prediction show that the number of cycles until crack initiation calculated on the basis of the aging model lies between the numbers predicted with the start material properties and those assuming the over-aged condition. However, in case of the AlSi5Cu3-T7 all numerical results predict a longer life time than observed experimentally. The differences in the simulation results for AlSi7Mg-T6 are very high as compared to those of AlSi5Cu3-T7. The main reason is that in the temperature range of the TMF tests and therefore also in the numerical simulations AlSi7Mg-T6 is more susceptible to aging than AlSi5Cu3-T7 as already shown with the tensile tests on the standardized specimens after exposure to high temperatures.

Figure 8 also indicates that the aging model leads to better life time predictions for the AlSi7Mg-T6 as well as for the AlSi5Cu3-T7 in combination with both the IWM- and the Chaboche life time prediction model. The simulations

with the start values lead to a longer predicted life and the simulations with the over-aged values to a shorter predicted life for the IWM model as expected. In the Chaboche model it is the other way around, since the over-aged values lead to an earlier plastic deformation and therewith to a smaller stress range, while the start values give rise to a later plastic deformation and therewith to a higher stress range. In this model mainly the stress range seem to mainly determine the damage evolution.

An improvement of the thermomechanical life time prediction has been reached by the implementation of the simplified aging model. The adaptation of the mechanical properties on the thermal distribution and the resulting microstructural changes leads to a more accurate and physically more meaningful life time prediction. The results of the numerical simulation for AlSi5Cu3-T7 at higher temperatures would show an even stronger influence on the predicted life time, since AlSi5Cu3-T7 ages more pronounced at higher temperatures as compared to AlSi7Mg-T6.

5. Conclusion

Various hardenable cast aluminium alloys (AlSi7Mg-T6, AlSi5Cu3-T7, AlSi5Cu1-T7, AlMg3Si1-T6, AlMg3Si1(Cu)-T6 and AlMg3Si1(Sc,Zr)-T5) have been studied and compared regarding their applicability as diesel engine cylinder heads. The focus with put on the resistance against thermomechanical fatigue (TMF) loading, which is typical of the cylinder head application, and the development of an accurate TMF life prediction model, which takes the change of the mechanical properties during TMF into account. A near-component-shaped specimen, the so called "valve bridge sample" was developed and TMF tested in a special testing system which closely matches the real component loading situation. Furthermore the thermal and mechanical properties of the alloys were determined as a function of time, temperature and number of TMF loading cycles.

The mechanical properties obtained in tensile tests on standardized specimens after 500 hours of annealing at various aging temperatures indicate that the influence of the aging temperature is high for AlSi7Mg-T6 and low for AlMg3Si1(Sc,Zr)-T5 compared to the other aluminium alloys studied. Furthermore, the TMF tests on the valve bridge samples showed that the AlSiCu alloys possess a higher resistance against TMF crack initiation in terms of the number of TMF cycles necessary to form a detectable fatigue crack as compared to AlMgSi and the AlSiMg alloys. The aging of the microstructure due to the combined thermal exposure and cyclic plastic deformation occurring in the TMF tests was proven macroscopically by 2-dimensional hardness measurements on the surface that is heated in the TMF loading system, and microstructurally by TEM examinations of samples taken from the critical location of the valve bridge samples.

It could be shown that a simplified aging model, which reproduces the decrease of the mechanical strength during TMF loading, can improve the thermomechanical fatigue life time prediction. For this purpose, two life time prediction models (IWM Freiburg and a simplified Chaboche model) were used to assess the TMF life time until crack initiation of the valve bridge samples. Several numerical simulations with different assumptions for the mechanical properties, i.e. constant values related to the starting condition, constant values from the final condition and changing values according to the aging model, were run for TMF loading of near-component-shaped specimens made of the aluminium alloys AlSi7Mg and AlSi5Cu3. The resulting life times were compared with the experimental results of the TMF tests. The comparison showed that the incorporation of the aging model improves the predictive capability and accuracy of both damage evolution models. This hold true in particular for AlSi7Mg, since the mechanical properties of this alloy change rapidly within the temperature range of the TMF loading.

References

[1] Schmid M., Gese H., Plege B., Claus J., Langer S., 2004. Ein neuer Prüfkörper für das experimentelle Ranking von Al-Zylinderkopflegierungen bei thermomechanischer Beanspruchung, *Werkstoffwoche* 2004.

[2] Cano V., 1996. Instabilites et ruptures dans les solides elastoviscoplastiques. ISBN 2-11-089-940-9.

[3] Nechtelberger E., 1976. Temperaturwechselrissverhalten der Gusseisenwerkstoffe. Leoben Werkstoffprüftagung 25/26 November 1976; Gefüge und Bruch; *Materialkundlich-Technische Reihe*, Bd. 3.

[4] Mohrmann R., Hauss R., Seifert T., 2003. Workshop Hochtemperaturverhalten.

[5] Lemaitre J., Chaboche J. L.1974. A non-linear model of creep-fatigue Damage Cumulation and Interaction; IUTAM Symposium.

[6] Lemaitre J., 1985. A Continous Damage Mechanics Model for Ductile Fracture. *Journal for Engineering Materials and Technology* 107, 83-99