Influence of Annealing at 1 100°C and 475°C on the Mechanical Properties at Room Temperature of an Iron Base ODS Alloy

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In the last few years the Fe-base oxide dispersion strengthened (ODS) PM 2000 alloy has been shown to be a biomaterial for its outstanding combination of mechanical properties and corrosion resistance. In this work, we are describing the effect of high temperature annealing at 1 100°C (pre-oxidation) and low temperature annealing at 475°C on the main mechanical properties at room temperature, with particular emphasis on tensile and fatigue properties, which are suitable for achieving the required biofunctionality of load bearing implants. It has been shown that annealing at 475°C is responsible for an increase in the YS and UTS with the subsequent decrease in ductility. However, despite of the loss of ductility, the material shows ductile behavior as is observed in the necked zone of tensile specimens, which contrasts with the so-called "475°C embrittlement" observed for another ferritic alloys. Moreover, aged material at 475°C exhibits a better fatigue limit than that non aged pre-oxidised material.

KEY WORDS: 475°C embrittlement; FeCrAl oxide dispersion strengthened alloy; fatigue; mechanical properties.
running water and then cleaned with alcohol.

Pre-oxidation treatment, aimed at generating the outer alumina layer, was performed at 1100°C for 120 h in air, followed by slow furnace cooling to room temperature. These experimental conditions were selected as the most suitable to obtain a dense and adherent α-Al2O3 scale.1) To investigate the influence of the scale on the mechanical properties, a set of specimens were machined from a bar which was heat treated under the conditions used for pre-oxidation. Therefore, these specimens have the same microstructure as the specimens with scale. Unless otherwise stated, the materials will be referred to as specimens with scale (heat treatment after the specimen preparation) and scale-free specimens (heat treatment before machining of the specimen). To assess the effect of ageing at 475°C, a set of specimens of both material conditions were annealed for several exposures at this temperature.

The mechanical properties were evaluated by tests of Vickers hardness, tensile, and rotating bending fatigue. Vickers hardness of polished samples was measured on a cross section perpendicular to the longitudinal bar direction. Indentations were made with 1-kgf load and 15-s dwell time. At least eight measurements were made on each sample. The tensile specimens had a gauge length of 45 mm and 8 mm in diameter. The samples were tested at room temperature using two strain rates, namely $5 \cdot 10^{-2} \text{s}^{-1}$ and $5 \cdot 10^{-5} \text{s}^{-1}$. At least two tests were conducted on any given material condition. The Young modulus, the 0.2% yield strength, the tensile strength, and the tensile elongation were evaluated from the stress/strain curves.

The fatigue strength at $10^6$ cycles was estimated from the data obtained by rotating bending tests ($R = -1$). Specimens were subjected to a constant amplitude loading at 300 Hz. Un-notched hourglass-shaped fatigue specimens with a 5.885 mm diameter waist and 80 mm in length were used. Once machined, these specimens were polished with successively finer silicon carbide and polished along the longitudinal direction with 1 μm diamond paste. In order to evaluate the notch effect and surface finish of machining on fatigue strength a U-notch of 1.75 mm in depth and a notch tip radius of 0.875 mm was ground using normal workshop practice on cylinders of 10 mm diameter and 80 mm in length. In this case no finishing operations were performed on the specimens. This notch geometry was chosen in order to provide oxide scale integrity at the notch tip. This notch resulted in a stress concentration factor of 1.86.12) Because of the small differences in the machining of the notch, the stress concentration factor ranged between 1.85 and 1.87.

Optical and scanning electron microscopy (SEM) was used for the microstructural analysis and examination of the fracture surfaces and in order to obtain a higher resolution a scanning electron microscope equipped with a field emission gun was used. Depending on the analysis, secondary (SEI) or backscattered electron images (BEI) were selected. From the SEI images obtained under 5000 times magnification of longitudinal sections of unbroken specimens the surface roughness of both pre-annealed and notched specimens was estimated.

3. Results

In the as-received condition, the material presents a weak (110) fibber texture and a very elongated and fibrous structure, as it can be seen in OM image of Fig. 1. At higher magnifications, Fig. 2, it can be seen from the backscattered image of the figure that the microstructure consists of grains of about 1 μm in diameter that are elongated in the longitudinal bar direction. Following the pre-oxidation treatment the texture does not vary significantly, the grain size grows slightly but still remain elongated. On the other hand, the pre-oxidation treatment generates a tightly adherent α-alumina scale between 3–4 μm thick, as it is shown in the SEM image of Fig. 3, which is consistent with the temperature and exposure times used for pre-oxidation.13)
addition, beneath the oxide scale a uniform layer of recrys-
tallised material with a thickness of about 10 microns was
found (as it is shown in the backscattered image of Fig. 4),
although occasionally surface patches of recrystallised ma-
terial of about 500 mm in depth could be observed. Grains
of this region were orientated towards the /H20855
/H20856
110
/H20855
111
/H20856
direction or
with the /H20855
/H20856
111
/H20855
110
direction parallel to the longitudinal axis of
the bar.

The ageing treatment at 475°C for 100 h produces a
hardening effect. According with previously reported re-
sults ins MA956,5,6) and bearing in mind the similar chemi-
cal composition between PM2000 and MA956, this phe-
nomenon could be explained by a nanometric scale decom-
position of the supersaturated solid solution into Fe-rich
a
and Cr-rich a
11032
phases, as it would be theoretically demon-
strated in the next paragraphs.

In the following sections, the influence of ageing at
475°C on specimens with and without scale on their me-
chanical properties at room temperature is described. The
whole set of data is summarised in Table 1.

3.1. Hardness

Hardness measurements show a relative hardness de-
crease after the pre-oxidation treatment from 300 to
287 HV, which is associated with the moderated grain
growth and annihilation of microstructural defects. After
ageing at 475°C, the as-received and pre-oxidised speci-
ments experience a significant hardening from the shortest
period of testing, Fig. 5. No significant differences in the
hardness increase for a given ageing time was observed be-
tween both material conditions.

### Table 1. Tensile and fatigue properties of investigated condi-
tions for PM 2000.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>As-received</th>
<th>Aged (475°C/100h)</th>
<th>Aged (475°C/100h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain rate ($\varepsilon^*$)</td>
<td>5.10^-5</td>
<td>5.10^-4</td>
<td>770</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>916</td>
<td>913</td>
<td>1067</td>
</tr>
<tr>
<td>Fatigue Strength at 10^8 cycles (MPa)</td>
<td>925</td>
<td>921</td>
<td>1130</td>
</tr>
<tr>
<td>Elongation (L/Cd) %</td>
<td>19</td>
<td>23.5</td>
<td>19</td>
</tr>
<tr>
<td>Area Reduction (%)</td>
<td>66.4</td>
<td>70</td>
<td>62</td>
</tr>
<tr>
<td>Yield Strength (MPa)</td>
<td>5.10^-6</td>
<td>16</td>
<td>21</td>
</tr>
<tr>
<td>Fatigue Strength/ Tensile strength</td>
<td>63.2</td>
<td>69.2</td>
<td>60</td>
</tr>
<tr>
<td>Time (h)</td>
<td>100</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Hardness increase (HV)</td>
<td>40</td>
<td>50</td>
<td>60</td>
</tr>
</tbody>
</table>

Fig. 5. Hardness increase as a function of ageing time at 475°C.

3.2. Tensile Tests

The Youngis modulus of the material disregarding the
material state was 170±10 GPa. With regards to the tensile
properties in the as-received condition, pre-annealing of
PM 2000 at the oxidation temperature causes a slight de-
crease in the yield (about 6%) and tensile (about 1%) strengths, and an increase (50%) in the ductility, Table 1.
The moderate decrease in the tensile properties provides ev-
edence of the high stability of the microstructure during
pre-oxidation. The tensile properties of pre-oxidised speci-
ments (with scale) are similar to those obtained for the alloy.
pre-annealed at the oxidation temperature (scale free). These results, therefore, indicate that neither the oxide scale nor the under layer of recrystallised material affect the tensile behaviour significantly. Thus, the ageing effect was only considered for the pre-oxidised specimens, i.e. samples with scale.

Ageing of the pre-oxidised specimens at 475°C for 100 h causes a significant increase in both yield and tensile strengths, with the concomitant decrease in elongation. An increase in the strain rate for pre-oxidised and pre-oxidised plus aged tensile specimens produces an increase in the yield and tensile strengths without significant changes in the elongation.

The macroscopic appearance of the fracture surface, Fig. 6, indicates a strong area reduction and a typical “cup-cone” fracture, which agree with the large elongation values. In the case of the specimens tested at the highest strain rate, the shape of the necking is rather asymmetric. It is interesting to note that the fracture surface of specimens tested at the lowest strain rate shows splitting that does not greatly affect either the elongation or the area reduction values. FEG/SEM micrographs of the surface of delaminations, Fig. 7, indicate that the material separation runs along the fibres by almost an intergranular mode with some tear ridges. From the macroscopic aspect of the fracture surface of the aged material, Fig. 8, it can be seen that delamination radiates from the ductile tear at the specimen centre. Two relevant conclusions arise from these observations. Firstly, splitting could be a diffusion-controlled process, presumably due to hydrogen embrittlement, since it was found to be sensitive to the strain rate. Secondly, the longitudinal embrittlement does not affect the tensile properties. These aspects should be treated in a further work.

3.3. Rotating Bending Fatigue Tests

The estimated surface roughness (Ra) of the annealed (polished) and notched (ground) specimens were about

0.5 μm and 1.3 μm, respectively. Figures 9–11 show plots of the stress amplitude versus cycles number of cycles to failure for the conditions under investigation. From the analysis of these figures, the role of the annealing, oxide scale, notch and ageing can be envisaged. The fatigue limit
estimated from these plots is also tabulated in Table 1. As can be seen, Fig. 9, the annealing treatment produces a decrease of about 40 MPa in the fatigue limit with regards to the as-received material (fine grained). As regards the annealed material, no effect of the oxide scale on the fatigue limit is observed. Fig. 10 shows that the ageing treatment increases the fatigue limit of pre-annealed and pre-oxidised material, the increase being lower in the latter case. The combination of notch and machining factors produces a decreasing in the fatigue limit of the as-received material, Fig. 11. However, the magnitude of this decrease is lower than the ratio of the fatigue limit of un-notched specimens upon the stress concentration factor. The aging treatment does not produce an appreciable improvement in the fatigue limit.

4. Discussion

A theoretical study of the $\alpha$ and $\alpha'$ distribution has been carried out in PM2000. The thermodynamic calculations involved here have been performed using the commercial software package, MTDATA$^{[14]}$. Calculations revealed that Al-content affects the presence or absence of $\sigma$-phase in the microstructure. Since this precipitation could also cause a hardening, the evolution of the $\alpha'$ and $\sigma$ phase for different Al-contents has been analysed. Figure 12 shows the evolution of the $\alpha$ and $\sigma$-phase in the Fe–Cr–Al system for
Al content ranging from 0 to 6 wt%. It is clear from this figure that the \(\sigma\)-phase is not predicted for the studied alloy. Hence, the hardening effect could be caused by spinodal decomposition. Finally, Fig. 13 shows the Cr distribution in \(\alpha'\)-phase with temperature. It is worth noting that an Al content increase leads to an increase in the amount of Cr which is located in the \(\alpha'\)-phase. With regards to the precise strengthening mechanism, a simultaneous effect of the misfit in the coherent internal stresses and the spatial variation of the Young modulus is likely to occur.19

Somewhat surprising is the fact that hardening increase for the as-received and pre-annealed specimens, Fig. 5, is rather similar, which contrasts with previous results for MA 956 alloy where hardness increase was much higher for the pre-annealed condition.9,10 Microstructural comparison between both alloys reveals that recrystallisation of MA 956 during annealing at 1 100°C produces a severe grain growth, of up about 150 \(\mu\)m, and a change in the fibber texture from \(\langle 110\rangle\) to \(\langle 100\rangle\).16 The relation of these microstructural differences with the different hardening behaviour is uncertain since microstructural factors should not influence spinodal decomposition. With regards to the tensile behaviour, the increase in hardness after ageing is accompanied by an increase in the yield and tensile strength and by a decrease in the ductility, which is consistent with previous results for MA 956.5 Despite the loss of ductility, the material exhibits ductile behaviour as is shown in the necked zone of tensile specimens. This ductile behaviour contrast with the so-called “475°C embrittlement” observed for other aged ferritic alloys.17 As a matter of fact, MA956 exhibits brittle behaviour when testing under similar conditions that can be explained by the recrystallisation of the material. Effectively, as it is well known the ferritic alloys experience a ductile-brittle transition (DBT) at a temperature that depends on the grain size, strain rate, and stress triaxiality.18 Therefore, the effect of ageing at 475°C is to produce an increase in the yield strength that facilitates the achievement of the cleavage stress characteristic yielding to a brittle behaviour. Such an effect is similar to the effects on the DBT of a temperature decrease and the increase in both, the strain rate and stress triaxiality. The ductile behaviour observed for PM 2000, with regards to that of MA956 could be therefore attributed to its smaller grain size (2 \(\mu\)m versus 150 \(\mu\)m, respectively). Moreover, considering the effect of the texture on the DBT temperature for MA956 alloy,19 the \(\langle 110\rangle\) fibber texture determined for the PM 2000 investigated in the present work would be less favourable for embrittlement than that of the \(\langle 100\rangle\) fibber texture reported for the recrystallised MA956 alloy.17

The fatigue behaviour of structural components is strongly affected by the presence of notches or section changes and by the surface state, i.e. the surface finish and the material properties in the near-surface zone. Nucleation of fatigue cracks is usually preceded by the formation of persistent slip bands that emerge to the free surface and act as notches. Therefore, any change in the surface state during fabrication or service modifies the fatigue behaviour. Regarding the pre-annealed (without scale) material, the oxidised alloy presents the following features that could modify the fatigue behaviour. Firstly, the initial surface state is removed upon heating to 1 100°C. Secondly, \(\text{Al}_2\text{O}_3\) scale of about 5 \(\mu\)m thickness is generated at the above temperature during 100h. Moreover, during oxidation the region of the substrate below the scale is plasticly deformed because of the growth stresses. Additionally, a recrystallisation of a thin region of the substrate below scale takes place which produces an increase in the grain size and a texture change from a weak \(\langle 110\rangle\) fibre texture of the substrate to that of grains with the \(\langle 111\rangle\) direction or the \(\langle 110\rangle\) direction in the longitudinal sense of the bar.19 Upon cooling to room temperature the oxide scale and presumably the recrystallised/deformed region of the substrate become highly compressed and the remaining substrate slightly tensioned because of the mismatch of the thermal expansion coefficients. The magnitude of the stresses in the scale is about 4 GPa.16 The oxide scale is well adhered to the substrate and presents some isolated pores without signs of spallation. Because of these features of the scale, it could be expected that during fatigue test, the scale locks the egress of mobile dislocations, delaying the nucleation of the fatigue cracks. Once the scale cracking takes place, the stress relaxation in the scale would produce first a delamination and then a spallation of the scale.20 Therefore, the scale cracking would lose the protective capacity but would not enhance the crack propagation through the substrate. Regarding the annealed material, fatigue behaviour of the oxidised material, in which scale spallation has occurred, should be expected to be different enough because of the very different surface state. The first difference concerns a sample size effect, associated with the lower surface area susceptible to localised deformation. The annealed material shows a smooth surface, while a rough surface was generated during oxidation of the material. The magnitude of the surface residual stress should also be different. While in the oxidised material, a thin region of the substrate (the plastically deformed region during oxidation) could be highly compressive, in the polished samples of the pre-annealed material, negligible surface compression stresses should be expected. On the other hand, grain size of the material below the oxide scale is higher than that of the annealed material or equivalently than that of the oxidised samples below the recrystallised zone. Therefore, as the resistance to initiation of a slip band decreases with increasing grain size, the resistance to fatigue nucleation should be lower in the oxidised cracked material. However, the effect of grain
size on cyclic plastic deformation is lower than that of monotonic plastic deformation.\(^1\) Furthermore, it is also necessary to take into account the variation of the crystalline orientation of the grains in the surface of the oxidised material, with regards to those corresponding to the annealed material. The microstructure of the recrystallised region, Fig. 4, consists of a string of grains, ones with the \((111)\) direction parallel to the longitudinal direction of the bar and ones with the \((110)\) direction parallel to the longitudinal direction. This feature could produce an additional size effect because, in regard to the applied stress, the \((111)\) orientation of grains are less favourable to yielding than those of the texture components of the annealed material. In spite of the above considered scale-related effects and the surface and subsurface state of the annealed and oxidised materials, great differences in their fatigue behaviour are not appreciable, Fig. 9. Two possible reasons could be the cause of this behaviour. Firstly, that the oxide scale was cracked. Secondly, the negative effects of a higher grain size and of the surface roughness of oxidised specimens could be offset by a higher magnitude of the surface residual stresses and the sampling effects above mentioned.

Now, we will consider the effect of aging on the fatigue behaviour, Fig. 10. The results of Fig. 10(a) shows that aging produces a notable increase in the endurance limit respect to that un-aged of pre-annealed material. The fatigue ratio (ratio of fatigue strength to tensile strength for \(10^7\) cycles) ranges from 0.4 for high strength steels to 0.6 for low and medium strength steels.\(^2\) It could be considered this parameter as a qualitative measure of the propensity to plastic strain localization and/or of the plastic strain magnitude needed to crack nucleation. In the last row of Table 1 the fatigue ratio values for each condition of the material here considered are given. It can be noted a sensible decrease from 0.545 of the annealed material to that of 0.519 of annealed and aged material. Therefore, the aging treatment produces not only an increase in the endurance limit but also a higher propensity to the elastic strain localization to crack nucleation. Because of the uniformity of the phenomenon occurring during aging, it should be expected a decrease of the plastic strain magnitude to crack nucleation instead of the observed enhanced propensity to plastic strain localization. It is also important to note that in the case of the material in the oxidised state the effect of aging is still more pronounced.

4. Conclusions

(1) Aging treatment at 475°C for 100 h produces an increase in the YS and UTS with the subsequent decrease in ductility. However, despite the loss of ductility, the material exhibits ductile behaviour as is observed in the necked zone of tensile specimens, which contrast with the so-called “475°C embrittlement” observed for other ferritic alloys.

(2) Surprisingly, similar fatigue results between annealed and oxidised samples are obtained in spite of the a priori very different scale related effects, the sub-surface state, grain size near the surface, and the surface roughness.

(3) In absolute terms, the aged material exhibits a better endurance limit that that unaged material. However, the lower value of fatigue ratio of aged material indicates a higher sensitivity to fatigue damage.

REFERENCES