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# TOWARDS SELF-HEALING CREEP RESISTANT STEELS

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## ABSTRACT

We report the main findings of our work on the behaviour of binary Fe-Cu and Fe-Au model alloys designed to explore routes to create new creep resistant steels having an in-built ability to autonomously fill creep induced porosity at grain boundaries. The alloying elements were selected on the basis of their ability to be brought in supersaturation, their limited or even absent tendency to form immobile intermetallic compounds and their affinity to segregate to free surfaces. The model alloys were creep loaded to failure at various stress values at a fixed temperature of 550 $^0$C. As a result of creep loading, grain boundary cavities developed which were either fully or partially filled by the alloying element explored. The degree of pore filling was found to depend on the alloying element, the stress level and the orientation of the residing grain boundary with respect to the applied load. The clearest examples of full or partial pore filling were observed for the Fe-Au system. In addition to pore filling, extensive precipitate formation was observed in the Fe-Cu alloys.

**Keywords:** Creep damage, pore filling, self-healing, model alloys

## 1.0 INTRODUCTION

Due to a careful tailoring of composition and microstructure, modern creep steels have an outstanding ability to withstand high mechanical stresses at a high temperature for a long time. Nevertheless, even the best creep steels will show catastrophic failure for severe loading conditions outside their intended usage window. Various mechanisms may be responsible for the damage evolution but the most common failure initiation mode is that of the formation of pores at grain boundaries and their subsequent coalescence. Current strategies to create better creep resistant steels have invariably been based on the 'damage prevention' paradigm [1,2]. 'Natural' materials on the other hand seem to have a composition/structure which would follow from a 'damage prevention' paradigm: the occurrence of locally initially non-catastrophic damage is taken as inevitable and the material has an in-built ability to 'self-heal' the local damage to a level at which catastrophic failure does not occur. The concept of self-healing man-made engineering materials was pioneered in concrete by Dry et al [3], but gained wide visibility by the work by White et al [4] on hard thermoset polymers. Since then many new routes have been explored [5, 6, 7]. In all self-healing routes the healing of the damage involves the removal of 'empty' volume related to a damage site either by a zipping reaction starting at the crack tip (for example [8]) or by filling of the pore by a reactive fluid [3,4] or solid deposit [9,10]. Laha et al [11-16] are to be credited for the first demonstration of self-healing of creep damage in austenitic creep resistant steels. The enhanced creep resistance was suggested to be due to dynamic precipitation of Cu at the surface of the grain boundary cavities, reducing or preventing the further growth of the creep damage. The presence of B and N was shown to have a positive effect on the kinetics of the healing, but it is unclear whether the elements themselves directly contributed to the healing. In order to clarify the mechanism of healing of creep damage by solute depletion in the grain boundary cavity, we have studied the healing behaviour of creep damage in a number of high purity binary Fe-X alloys. Binary substitutional alloys were used to make sure that the healing reactions were not masked by competing metallurgical reactions. Our first set of alloys were based on the Fe-Cu system, given the composition of the first self-healing stainless creep steel [12]. The second set of alloys was based on the Fe-Au system. The choice for Au as the active solute is based on the fact that: i) the solute Au atoms are appreciably larger than the matrix Fe atoms resulting in a higher nucleation barrier for precipitation within the matrix, ii) the Au atoms will not form intermetallics and iii) the Au atoms having a strong tendency to segregate to a free surface. The individual results for all Fe-X systems have been presented in more detail elsewhere [17-28], but are brought together here to present similarities and differences between the two systems. Work on healing of creep damage of other Fe-X model alloys is in progress and will be reported at the conference.

## 2.0 MAIN FINDINGS

### 2.1 The Fe-Cu System [17-21]

The creep curves for the solutionised and solution-depleted (i.e. pre-aged) Fe-1 wt % Cu alloy for a constant load at a temperature of 550 °C are shown in Figure 1. For the solutionised sample, the sample was quenched from the homogenization temperature and the excess solute Cu atoms remain mobile in the Fe matrix. In the solution-depleted samples the solute atoms have been largely removed from the matrix by an additional annealing step leading to the formation of (immobile) Cu-rich precipitates prior to the creep test. For both alloys a conventional creep curve was observed with a rapid initial strain development (stage I), followed by a regime with a nearly constant strain rate (stage II) until a strain acceleration sets in near failure (stage III). It is found that samples containing mobile solute Cu atoms have a significantly extended life time, notwithstanding an initially lower yield stress. The microstructure of a solutionised Fe-Cu-B-N sample loaded to failure at a stress of 83 MPa and a temperature of 550 °C is shown in Figure 2. A limited number of submicron-sized Cu precipitates were observed at the grain boundaries, but from the shape of the macro-precipitates it is impossible to deduce whether these precipitates just formed at the grain boundary or whether their formation was preceded by the formation of the creep induced pores. Notwithstanding the fact that the presence of super-saturated Cu has a positive effect on the creep behaviour, the healing potential of Cu is to be rated relatively low as too large a percentage of the Cu atoms precipitated on the dislocation structure formed during creep loading as shown by SANS and TEM [19]. Hence, a large proportion of the Cu atoms brought into supersaturated state in order to be 'available' to fill creep damage was 'lost' in the formation of Cu precipitates in the grain interior.

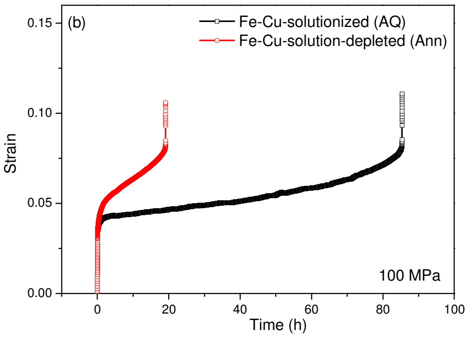

Figure 1: creep curves Fe-Cu alloy at 550 $^0$C and 100 MPa (from [27])

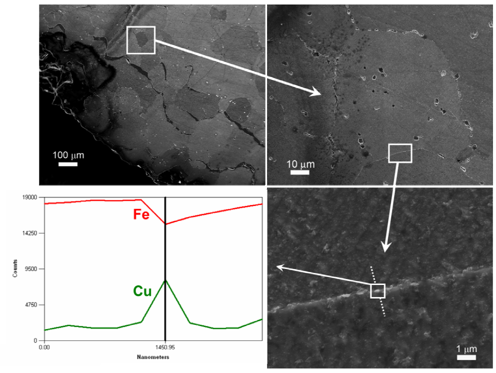

Figure 2: SEM micrograph of creep failed solutionised Fe-Cu sample showing Cu-rich precipitates at grain boundaries (from [27]

## 2.2 The Fe-Au System [22-26,28]

In order to retain the driving force for segregation at the creep cavity surfaces, but to suppress premature precipitation within the matrix, we replaced the Cu by Au as healing agent as Au atoms have a strong tendency to segregate to open surfaces and a high energy barrier to form precipitates because of their larger atomic size. This makes Au a very interesting site-selective healing agent within a ferrous matrix. For a solutionised Fe-Au alloy the Au solute remains dissolved until an open-volume defect has formed. This then triggers solute diffusion towards the defect site and subsequent pore filling by precipitation.

Creep tests were performed on high purity Fe-1at% Au alloys in vacuum at a constant temperature of 550 $^o$C and at applied stresses ranging from 60 to 133 MPa. In the binary Fe-Au alloy the equilibrium solubility of Au in the Fe-rich phase is negligible at 550 $^o$C. Hence a solute concentration of about 1 at.% Au provides a strong chemical driving force for segregation and precipitation. In Figure 3 the creep curve for the solutionised Fe-Au alloy is compared with the ones for the solutionised and solution-depleted Fe-Cu alloy to demonstrate the effect of solute Au and Cu atoms on the creep properties. The creep failure resistance of the Fe-Au alloy clearly exceeds that of the Fe-Cu alloys. The stress dependence of the creep data could be fitted to the Sherby-Dorn equation and from the fit it was determined that in the Fe-Au system the deformation proceeds by a combination of volume diffusion and grain boundary sliding, while the Fe-Cu alloy deforms via a dislocation climb and glide mechanism

Fractography on creep failed samples showed a high density of Au precipitates on the inter-granular fracture surface (figure 4a). The filling of the creep cavities on the grain boundaries became more clear in cross sections parallel to the loading direction (Figure 4b). At grain-boundary triple junctions two different types of behaviour are observed: one grain-boundary triple junction shows an unfilled wedge crack, while another one is filled by Au precipitation, as indicated by the arrows. Two grain-boundary regions are studied in higher magnification in Figure 4c-d: (1) a damage region partially filled with Au precipitates and (2) a damage-free region with irregular-shaped Au precipitates. For region (1), the shape of the Au precipitates formed along the grain boundaries cavities is irregular and matches the geometry of the creep cavity. Clearly creep defects form first and are subsequently filled by Au precipitation, which results in partial healing. In region (2) the isolated Au ribbon has fully filled the creep damage. Once again the irregular shape of the formed precipitates reflects the morphology of the creep damage. Detailed metallographic examination of samples loaded to failure gave clear evidence of partial and complete filling of the grain boundaries depending on the grain boundary and grain orientation with regards to the applied stress. Atom probe measurements on needle-shaped samples taken from creep failed macro samples confirmed the assumed transport of Au atoms along the grain boundary towards the filled cavities [27]. BSE-SEM images showed gold-depleted regions along grain boundaries containing a large number of Au deposits.

In general the Au deposits form preferentially in cavities at grain boundaries oriented perpendicular to the stress and at triple-point junctions. As these are also the grain boundaries that are most likely to induce final fracture, a clear correlation between creep damage and site-selective precipitation is observed. The degree of pore filling depends on the ratio of the pore growth and the pore filling rate and at a fixed temperature decreases with the stress level. The model predictions fitted very well to the observations and indicated that for the model alloy at a stress level of 145 MPa the rate of Au deposition cannot keep up with the rate of pore growth and Au has no beneficial effect on creep life any longer [28].

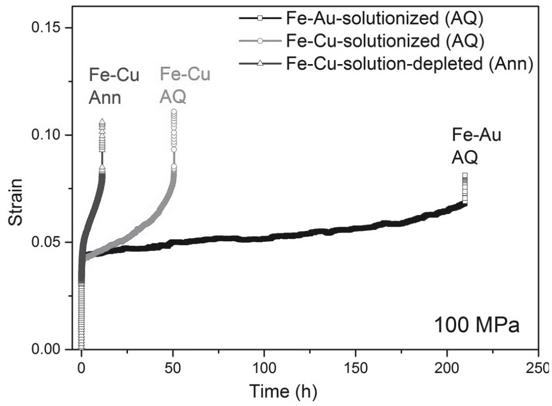

Figure 3: Fe-Au and Fe-Cu creep curves (from [28])

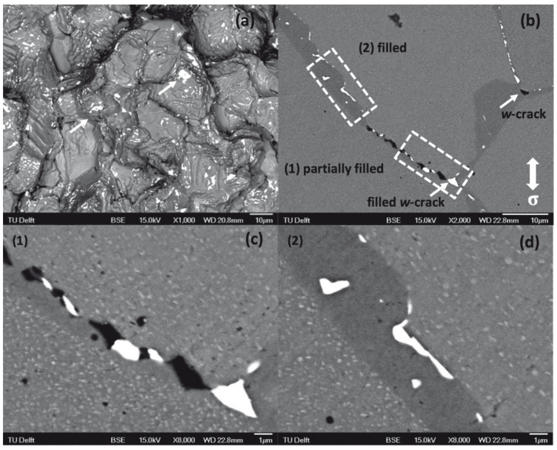

Figure 4: a) SEM micrograph of fracture surface. b-d) cross sections showing Au deposits at grain boundary cavities (from [28]

## 3.0 CONCLUSIONS

Creep experiments on high purity binary Fe-Cu and Fe-Au alloys brought to a supersaturated state (1% supersaturation) show a significantly improved creep behaviour and extended creep life time. The improved behaviour could be attributed to the precipitation of mobile solute atoms at local damage sites. In the case of Fe-Cu most of the solutes are deposited at creep deformation induced dislocations. In the case of the Fe-Au system the solutes are deposited primarily at cavities formed at grain boundaries and triple junctions. The observations are of key importance for the design of self healing multi-component creep resistant steels.

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