Fundamental Issues in the Development of Austenitic and Nickel Based Alloys for Advanced Supercritical Steam and High Temperature Indirect Fired Gas Turbine Systems

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Abstract:

The long term creep strength of a variety of commercial austenitic and nickel based alloys is shown to be correlated with the austenite matrix diffusion rate, and the high temperature elastic modulus. Given the basic properties of the matrix, creep strength, at the desired operating temperature, is maximised in commercial alloys by a suitable choice of precipitate. The suitability, of a given precipitate, is governed by the rate at which it forms, and the rate at which it ages. The effects of these can be demonstrated by a plot of the Normalised Creep Strength of a given alloy, against temperature. The paper suggests an upper limit for the strength of high temperature steels and nickel based alloys. The implications of this for the use and development of materials in 700°C steam plant, and indirect fired gas turbine systems are discussed.

1. Introduction

It is a truism that the turbine inlet temperature determines the efficiency of a steam turbine plant. Although a basic fact of thermodynamics, this needs to be qualified by the recognition that as temperature increases, pressure too must keep in step. Without an adequate pressure drop, the temperature of the steam entering the condenser section will be unacceptably high, this obviously affecting output and efficiency. Figure 1 was plotted using data from steam plants of various vintages, since this is the most graphic way of showing the exponential relationship between steam pressure and temperature. This relationship has been a major barrier in the development of superheater materials, since as temperatures have increased, so have hoop stresses. Fifty years ago, typical generating plant steam temperatures were around 450°C. Pressures at the time were around 100 bar. Today operating temperatures are just 120°C higher, but pressures have gone up by a factor of two or more.

Within narrow limits, there is a trade off between these two functions. For example, if the steam temperature is fixed, it is usually worth increasing operating pressures somewhat in an effort to increase output and efficiency. Similarly if the steam pressure is limited it is usually worth increasing the temperature to get an efficiency gain. All organisations have their own view on what is the best option. This view will be determined by the perception of metallurgical difficulties in developing materials for boilers, superheater and reheater banks, steam turbine rotors and turbine blades. In recent years, the tendency in Europe has been to opt for high steam pressures and relatively low steam temperatures. In Japan, it seems to be the converse. The merit of the "European" approach is that it does postpone the need to move to high cost austenitic and nickel based alloys.

There is considerable opposition to the use of austenitic and nickel based alloys because of their cost, although concern about thermal stress is an important technical factor. Indeed these were the principal reasons behind the development of the 9 and 12 chrome martensitic steels. However, for a given physical size of plant, higher pressures and temperatures will increase output. This can help to counteract the cost of more exotic materials. A simple way of expressing this is to state the "specific output" of a power plant in terms of the number of kilowatts generated per kilogram second of steam flow. Unfortunately this figure is rarely provided in most papers on power plant development, but is as important as the thermal efficiency.

Current plants are limited to efficiencies of 43-47% when burning coal, with steam temperatures ranging between 540° and 580°C. Efficiencies of around 50% should be achievable within the next 10 years, but is it possible to advance to 55% using current steam plant technology? Is this practicable with off the shelf materials of construction? Alternatively, what are the prospects for the development of newer alloys to take these more advanced steam conditions? And if this is not possible, should we be focusing on materials for one of the currently favoured alternatives, the indirect fired gas turbine? This paper attempts to review the situation as realistically as possible.

2. Ultra High Efficiency Steam Plant: The Materials Requirements

The steam conditions, for a coal fired plant of 55% efficiency, seem to imply temperatures in the range 700°-740°C, and steam pressures in the range 350-400 bar. Although ball park estimates, these figures are broadly in line with extrapolations from presentations based on European plants that are currently operating, or at the conceptual design stage [1]. These estimates are, if anything, below those that might be based on Japanese data [2,3]. They are also well below those suggested in a recent paper by Birks and Smith [4]. These two authors, using the ASPEN program indicated that, even with a steam temperature of 815°C, an efficiency of 50% would not be attainable.

Much, however, depends on the selection of component efficiencies in such computer programs, and the degree of complexity of the plant in terms of reheating and feed heating. Here European manufacturers have made some remarkable improvements over the past thirty years [5]. Current European generating stations are offering thermal efficiencies of around 42%, with steam temperatures of 540°C, despite the burden of flue gas desulphurisation. This compares very well with Eddystone II, commissioned in 1958, which could at best offer a design efficiency of 42.5%. This was in conjuction with a design inlet temperature and pressure of 650°C and 345 bar to the HP turbine, and two stages of reheat. These improvements, which result from more sophisticated plant equipment, may account for the difference of opinion between the protagonists of conventional Rankine cycle plant in Europe and those elsewhere. It may also account for the current interest in the USA with coal fuelled indirect fired gas turbine cycles, which some consider offer high efficiencies in a technologically easier way [6].

Birks and Smith, in their evaluation of materials for advanced steam and indirect fired plant, used as a basis for calculation a heavy gauge tube with, approximately, a wall thickness to internal diameter ratio of 0.375. Design codes show that for this type of tube the hoop stresses can be taken as 1.89 times the internal pressure, keeping the same units [4]. This would suggest that for the lower pressure of 350 bar, 55% efficiency plant, the superheater hoop stress would be 66 MPa. For the higher pressure plant, with a steam chest pressure of 400 MPa, the hoop stress would rise to 75 MPa.

These values are for the design hoop stresses. For a life of 100000 hours the stress rupture properties of the tube material would need to be between 1.3 and 1.5 times greater. This suggests that, for a 55% efficiency plant, on the most optimistic basis, the minimum stress rupture values required would be around 90 MPa, and could be as high as 115 MPa.

This is with very high superheater metal temperatures, compared to units currently operating. Even with good design, wall temperatures are likely to be around 30°-40°C hotter than the steam, giving peak skin temperatures in the range 730°- 780°C.

3. Indirect Fired Gas Turbine Systems

The indirect fired gas turbine, would use air rather than steam as working fluid. A fired heater, fuelled by coal, replaces the combustion section of a conventional gas turbine. Turbine inlet temperatures, at 1100°C, are much higher than that of steam, but the peak operating pressures are much lower, somewhere in the range 15-30 bar. Tube metal temperatures would need to be around 50°-70°C higher than the turbine inlet temperature, so as to give an acceptable rate of heat transfer [7].

Using the approach of Birks and Smith this implies that the tube hoop pressure stresses would be in the range 3-6 MPa, an extremely low value by steam plant standards. This is the sort of stress level that is used in the preliminary design of ethylene plant. However, such units only operate in the 1100°C region for a relatively short fraction of their service life.

Tube materials are so weak at this kind of temperature that thermal stress and dead weight are vital factors in governing tube life. In the opinion of the authors an absolute minimum for sensible design would be a stress rupture value of 7 MPa.

4. Superheater and Indirect Fired Heater Materials Properties

Figure 2 shows the 100000 hour stress rupture properties of wrought austenitic, nickel based, and spun cast tubing as displayed in elementary textbooks on materials technology using a linear stress/ linear temperature plot. These stress rupture values were taken from manufacturer's data. All materials show a dramatic drop in stress rupture properties over the range 500° to 750°C. Figure 2 shows that only Alloy 617 and Haynes 230 meet the minimum criteria of 90 MPa @ 730°C. These are extremely expensive materials. There is little margin if it proves necessary to increase the skin temperature to 780°C and the design hoop stress to 115 MPa.

The situation for the heater tubing in indirect fired gas turbine systems is somewhat similar. The strongest of the off the shelf materials, the spun cast alloy, H46M, using the previously stated criterion of 7 MPa, falls short by about 100° C on what is really needed. It was this situation which obliged one of the authors to use an ODS alloy for an Indirect Fired Closed Cycle Gas Turbine Plant fired by natural gas [7].

5. Development of High Temperature Tube Materials: The Underlying Factors

A difficulty with the usual way of exhibiting stress rupture properties of sets of alloys is that, at higher temperatures, the curves for the various materials converge and overlap. For this reason at least two alloy producers have begun to produce stress rupture graphs plotted in a less conventional way [8,9]. Here the stress axis is given in terms of log rupture stress. The temperature axis remains in a linear form.

Figure 3 shows such a graph for advanced superheater alloys. Note that the stress rupture values for all the alloys fall within a fairly tight band. Indeed it is possible to take an "average" of the stress rupture values and plot a straight line which runs through the centre of the band. Note that the log stress/temperature gradient for most alloys is remarkably similar to the average line. For much of their length, individual lines are parallel to the average line, suggesting that there is a deeper underlying relationship.

This deeper relationship results from the fact that creep in high temperature tube materials is principally due to the climb of dislocations over precipitates. At a constant stress, the rate of dislocation climb is governed by the diffusion rate and by the shear modulus of the alloy matrix. Diffusion rate and modulus are of course temperature controlled, the former very strongly, the latter much less so.

Precipitates are then, barriers to the movement of dislocations, and as such, crucial to creep resistance. Without such precipitates, all the commercial alloys would fall in strength, so that the "average curve" would be displaced downwards to a significant extent.

Conversely, if we could somehow grow a precipitate of optimum size and coherency, and it was absolutely stable and did not decompose as the temperature increased, we would again have the same stress versus temperature gradient as in Fig. 3. In this case, the average gradient curve would be displaced upwards, roughly following, but somewhat above the respective curves for Inco 617 and H46 M. This would represent a "wonder material" indeed.

However, even with a wonder material, the fall off in creep properties with temperature is inexorable. Using the conventional approach to high temperature materials development, the best that can be done to counteract the effects of temperature is to slow up the diffusion rate, and increase the elastic modulus of the alloy matrix. There are limits to what can be done. These improvements are achieved by increasing the proportion of nickel in the alloy, and adding high melting point elements, such as tungsten and molybdenum.

For the more conventional materials, each of the precipitates that we can use is only viable over a relatively small temperature range. All of these precipitates are intermetallic compounds and, like all such compounds, can only form when conditions are favorable. Below the optimum temperature, diffusion is too slow to permit the necessary aggregation of elements that make up that particular intermetallic. Growth of the precipitate is then sluggish; hence the alloy is relatively weak. Above the optimum temperature, the intermetallic loses coherency or becomes unstable, the constituent elements redissolving in the matrix. Again there is a loss of strength.

Each of the commercial alloys makes use of one or more of these strengthening precipitates, in conjuction with a judicious mix of elements in the alloy matrix. This mix of elements should have just the right impact on diffusion rates. At the service temperatures for which the alloy is intended, the diffusion should be fast enough to permit the precipitate to form, but not so fast that the precipitate overages within the design lifetime. Accordingly every alloy will have a temperature range over which the alloy will perform at its best. Above or below this range, the creep resistance, relative to its best performance, tends to fall away.

Even when the increase in mechanical properties appears to be due to a "solid solution" hardening effect, as with additions of nitrogen and carbon over certain temperature ranges, the strengthening process probably involves the interaction of a number of different types of atom with a dislocation line [10]. This being a complex, diffusion dominated process, it too will only be really effective at one temperature.

Figure 4 shows schematically the useable temperature ranges for a variety of common strengthening "precipitates" in the alloys being discussed. For the reasons given above, as the temperature increases, the creep rupture strength falls. Note, however, that this is no reflection upon the capabilities of the individual strengthening mechanisms. The fall off is governed by the fundamental properties of the alloy, which leads to the increasing ability of dislocations to climb over, or free themselves from the various obstacles as the temperature rises.

Also note, that the rate of diffusion in the alloy matrix, and competition from other precipitates that utilise some of the same alloying elements, will influence the temperature range over which a given precipitate comes into play. For example in the Type 321 stainless steel, TiC, as a strengthening precipitate, is effective in the range 600°-750°C. In the case of Incoloy 800 HT the range over which TiC is active is much higher, between 700° and 900°C. Obviously, because of diffusion rate and climb considerations, TiC in Incoloy 800HT at 900°C, will not give the same strengthening effect as does TiC in stainless steel at 700°C.

6. Evidence for Climb Controlled Creep in Superheater Materials

The well known Monkman-Grant relationship shows that the time to failure is inversely proportional to creep rate. That is:

$$1/t \propto d\varepsilon/dt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Where t = time to failure and ε is the amount of creep

Since most tube materials are designed to give final creep ductilities in the 10–20% range, and the stress rupture life of the materials under consideration is 100000 hours, dε/dt can be taken as being fixed. A recent paper by Bina and Hakl gives additional support to this hypothesis [11]. They showed that for a wide variety of austenitic stainless steels there was a good correlation between strain rate and stress rupture resistance.

We can therefore use equation (1) in combination with a modified form of the Weertman equation for dislocation climb in creep, as outlined in the paper by Lagneborg [12]. This is:

$$d\varepsilon/dt = (2b^2 LD\theta /kT)\ (B\sigma/G)^n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots...(2)$$

Where:

b= Burgess Vector
L = Mean Free Path of Dislocations
θ = Dislocation Line Tension
D= Matrix Diffusion Coefficient
k = Boltzmanns Constant
T = Absolute Temperature
σ = Stress
α = Factor Related to Dislocation Interaction Stresses
G= Shear Modulus

Making the assumption that the Burgess vector, mean free paths of dislocations etc, are constant, this equation can be simplified as follows:

$$d\varepsilon/dt = A(D/T)\ (\sigma/G)^n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3)$$

Where A is a constant

Furthermore, taking the original assumption that the creep rate is constant for the range of materials under review, and using Youngs Modulus rather than the Shear Modulus, since the two are interrelated, we can write the variation in stress with temperature as follows:

$$\sigma = E\ (T/AD)^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Where E = Youngs Modulus

Temperature appears directly in the equation, but is also at work indirectly through its influence on the elastic modulus and on the matrix diffusion coefficient. It is the latter term that dominates, since the diffusion rate increases by more than six orders of magnitude between 600° and 1100°C.

A spreadsheet was used to introduce the results of eq (5) into Figure 3 as an equation for "Climb Controlled Creep". So as to normalise the results, and eliminate the effect of the constant "A" in eq (5), the high temperature end of the climb controlled creep line was "anchored", so as to give a stress rupture value of 1.75 MPa at 1200°C. It was then possible to investigate the effects of changing the stress exponent.

The resulting line for the climb controlled creep has a curved form which, at the low temperature end of the graph, is steeper than the straight line "average" curve, but somewhat less steep at the high temperature end. Operation of the spreadsheet power functions showed that the "n" value or stress coefficient that gave the closest fit to the average gradient was 4. Stress coefficients lower than this gave gradients that were significantly more steep than the average, with the converse being the case. The stress exponent of four matches well with that usually given with the Weertman equation, given the wide range of materials covered.

It seems reasonable that gradient of the climb controlled creep line should become less steep as the temperature increases, rather than steepen even more, as is the usual case for real materials. The climb equation represents, in some respects, the wonder material referred to above. This material, it will be remembered, is supposed to be strengthened by a precipitate whose size and distribution remains constant, no matter how high the temperature. The stability of a precipitate in real materials is temperature dependent, and at some point, the precipitate will begin to overage. Above this temperature, the chief obstacles to dislocation climb disappear, so that there is a dramatic drop in stress rupture properties.

Most high temperature alloys show this fall off in properties, since they are designed for the intermediate temperature range. One exception appears to be Alloy 602CA. With this material the stress rupture gradient gets less with temperature, although of course the alloy still gets weaker as the temperature rises. 602CA is a nickel based alloy which relies on a fine dispersion of titanium and zirconium carbides which are said to be very stable in the region of 1100°C [13]. Chromium carbides are also present which pin grain boundaries. It is noteworthy that in his review of high temperature heat treatments Klarstrom states that both titanium and zirconium carbides are destabilised by the presence of refractory metals and this alloy is free from these [14]. Hence it would seem that, in accordance with the climb equation, given the right sort of precipitate, alloy strength does not have to suffer the usual drop.

The spreadsheet programme used in this work allows an even easier method to show relative changes in alloy properties. Here the stress rupture strength for an alloy, at a given temperature, is divided by the average strength of materials at that temperature. This value can be read off the straight-line average curve in Figure 3. The result is the **Normalised or Relative Creep Strength** which is defined as:

$$\frac{\textbf{Creep Strength of Material at Temperature T°}}{\textbf{Averaged Creep Strength of HT Materials at Temperature T°}}$$

For a material with only one strengthening precipitate, the Normalised Creep Strength would be expected to be low at low temperatures. It would then peak at an intermediate temperature before falling away. At low temperatures, very little precipitate will have formed, due to the slow rate of diffusion, hence the strength would be low under these conditions. At high temperatures the relative strength would again fall away, this time due to overageing effects. Only at intermediate temperature would the alloy perform well in comparison to the average. The average value, by definition, is unity, at all temperatures.

In practice, a variety of precipitation processes will take place in a modern high temperature alloy. As one type of precipitate begins to overage, another begins to form. In this way the

Normalised Creep Strength can be held reasonably constant across a wide temperature range. Figure 5 shows how this parameter behaves for a number of alloys. The hatched line in Figure 5 represents the average value of unity. As might be expected, higher alloyed materials, such as Inconel 617, are grouped above the average line.

7. Discussion

Log stress/linear temperature graphs for a wide variety of high temperature tube materials confirm that the stress rupture properties are dominated by the climb of dislocations over precipitates. Climb being basically a diffusion governed and temperature limited process, there seems to be no easy way of getting increased strength into materials.

In principle eq. (2) should enable one to forecast what are the likely upper limits. For example, if the diffusion rate was reduced by a factor of ten, the creep strength would increase by a factor of three. Similar calculations could be made about the effects of precipitate density. At the present time it would appear that it is going to be difficult to improve significantly on materials like Alloy 617 and Haynes 230. Furthermore, although the Japanese have shown a very high degree of initiative in the development of materials such as St3Cu (Tempaloy A-1) and Tempaloy A-3, it can be shown that these alloys have properties which are very close to the average line [15].

The principle disadvantage with the wrought alloys currently in use or under development is that since the strengthening precipitate appears during service, there is a strong possibility that after long term use the precipitate will begin to overage. An acceleration in the rate of creep will then result.

A different approach might be to use an alloy which, in principle, was intended for service at somewhat higher temperatures, but would be first given a pre-ageing treatment. The alloy could then be used at the lower temperature, with the confidence that the precipitate formed would be extremely stable. This treatment might be combined with a very mild degree of warm working so as to produce a suitable dislocation network for inducing an optimum dispersion.

In welding terms, pre-aged materials such as this would have two disadvantages. Sections of the HAZ would lose the benefit of the ageing effect. Conversely in comparison to conventional materials, unaged parts of the HAZ would be quite stiff and would be unable to stress relax to any great extent. Hence any deformation within the weldment, during start up, or during long term plant operation, would tend to be taken up by the weaker material. Obviously this would need to be considered at an early stage in an alloy development. Here the insights developed within HIDA and related programmes would be of considerable value [16].

8. Summary

It appears that the prospects for getting 55% efficiency from a Rankine cycle type plant could be difficult. Before embarking on costly alloy development programmes, we need to review the fundamental properties of austenitic and nickel based alloys to see just what are the practical limits. In this respect this paper has shown that is possible to use a mix of simple corelations and fundamental thinking to assess the prospects for improvement in creep properties. The paper has also suggested that a more cost effective route to alloy development could be in the formualtion of an effective heat treatment and working procedures, using existing alloys.

Similar remarks can be made about the difficulties in developing tube materials for indirect fired gas turbine systems. Here, however, the option of using an ageing heat treatment to improve tube performance does not exist. Peak tube temperatures, at 1170°C are already very high already. This was one reason why ODS alloys are attracting such interest in this area. The ODS alloys do have significant drawbacks, unfortunately. Cost, high directionality, and poor weldability are just a few of its problems. Some of the characteristics of this and other high temperature materials have been covered in a recent IOM publication [17].

All in all there seems no easy way through to better materials, although there is no reason for an abrupt stop in alloy development. Perhaps we need to adopt a more radical approach to the thermodynamics of converting the chemical energy in coal and gas to electric power. All of these innovative systems will require heat exchange and turbine development in one form or another. We in Europe need to be more purposeful in investigating these newer options, some of which are already in the public arena.

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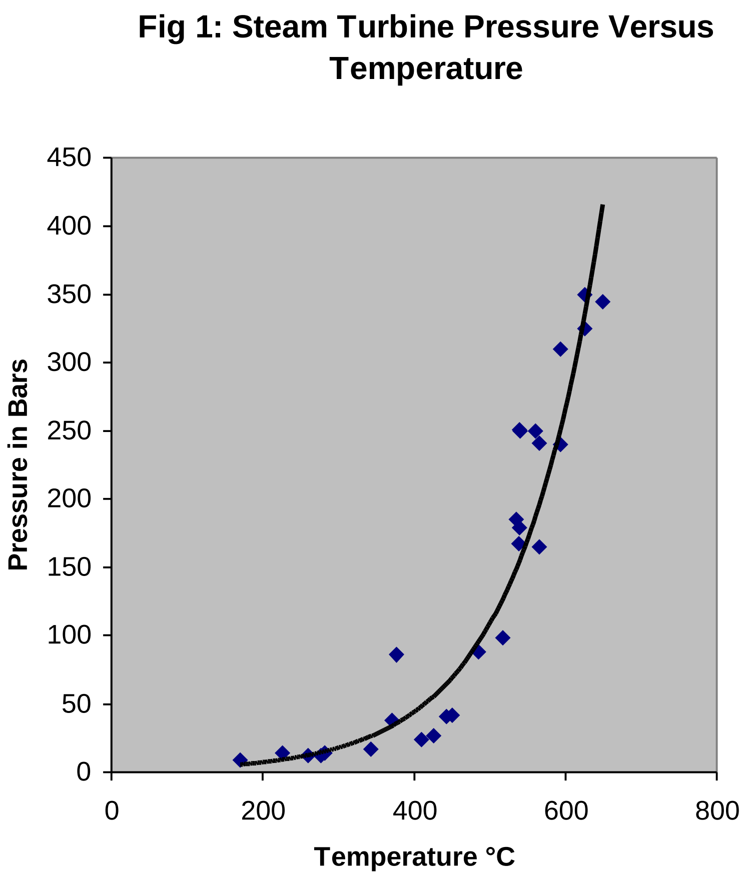


Fig 1: Steam Turbine Pressure Versus Temperature
450
400
350
300
250
200
150
100
50
0
Pressure in Bars
0
200
400
600
800
Temperature °C

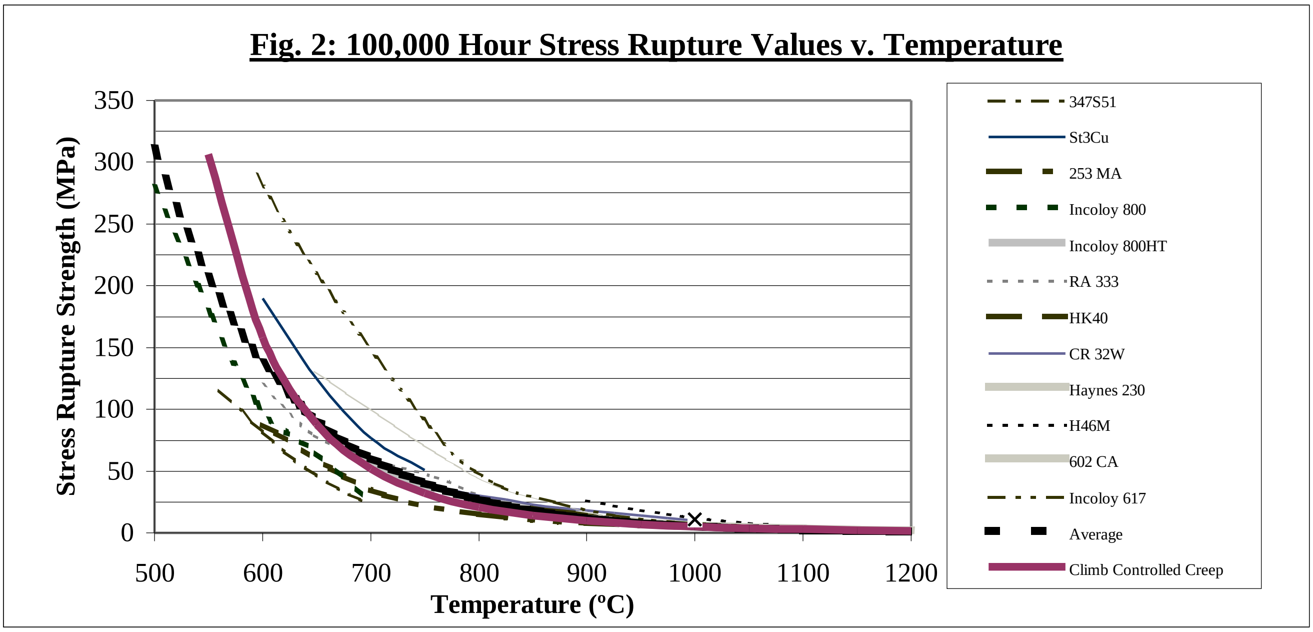


Fig. 2: 100,000 Hour Stress Rupture Values v. Temperature
350
300
250
200
150
100
50
0
Stress Rupture Strength (MPa)
500
600
700
800
900
1000
1100
1200
Temperature (°C)
347S51
St3Cu
253 MA
Incoloy 800
Incoloy 800HT
RA 333
HK40
CR 32W
Haynes 230
H46M
602 CA
Incoloy 617
Average
Climb Controlled Creep

Fig. 3: 100,000 Hour Log Stress Rupture Values v. Temperature

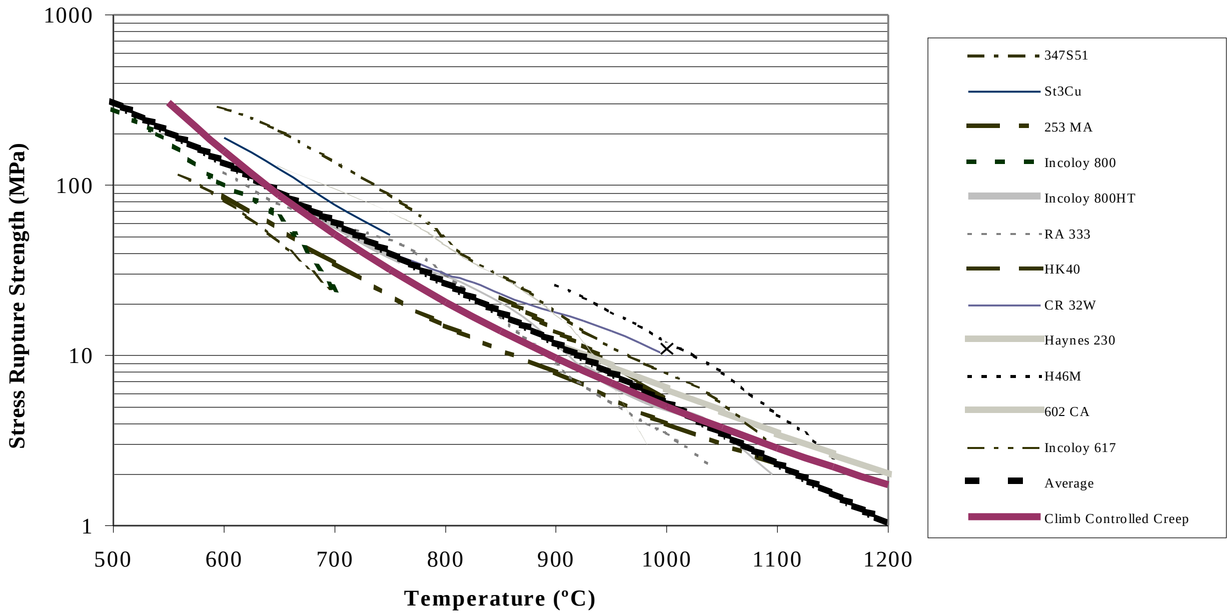
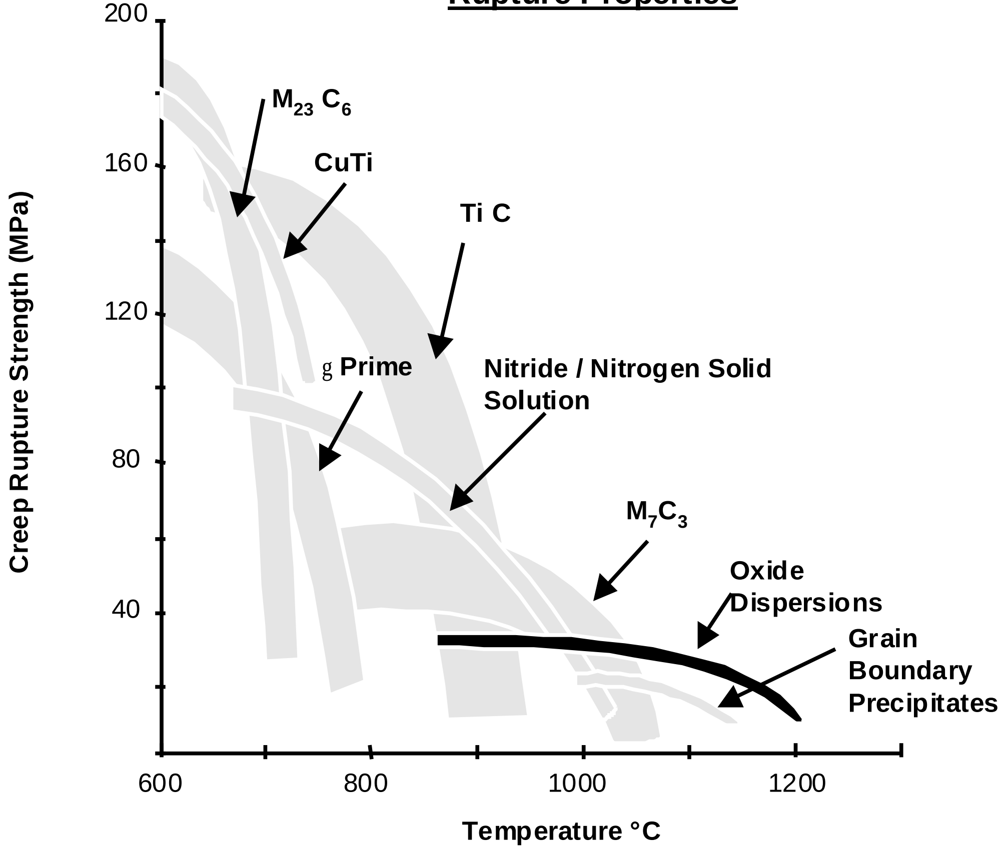


Fig 4: Contribution of Phases to Stress Rupture Properties



<u>**Fig 5: Normalised Stress Rupture Value v.s Temperature**</u>