Creep of heat resistant steel.

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CREEP OF HEAT RESISTANT STEEL

by

FANG WANG

A Thesis
Submitted to the Faculty of Graduate Studies and Research through the Department of Mechanical Engineering in Partial Fulfillment of the Requirements for the Degree of Master of Applied Science at the University of Windsor

Windsor, Ontario, Canada, 1991

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The thesis is dedicated to my loving parents.
ABSTRACT

The elevated temperature creep behavior of type 310 stainless steel and type HP-Nb heat resistant steel was determined for specific stress and temperature because of the scarcity data for these materials in these ranges.

The primary and steady-state creep behavior of 310 stainless steel has been investigated over the temperature range 500 °C to 700 °C (0.46-0.58T_m). The steady state stress exponent, n, increased slightly with increasing grain size, d, from n = 5.9 at d = 40 \(\mu\)m to n = 6.4 at d = 100 \(\mu\)m at creep test temperature T = 600 °C. Stress exponents in this range are in reasonable agreement with previously published values for other austenitic stainless steels. The activation energy for steady state creep determined at \(\sigma = 300\) MPa, \(d = 40\) \(\mu\)m, \(Q_c = 250\) KJ/mol, is approximately that for the volume self-diffusion of iron (280 KJ/mol). Also the activation energy determined for primary creep is almost the same as that for secondary creep. This means the controlling mechanism is almost the same for both primary and secondary creep. The grain diameter parameter, m, [ in equation \(\dot{\varepsilon}_c = A\sigma^n d^m \exp(-Q_c/RT)\) ] was determined to be -1.67 for \(\sigma = 300\) MPa and T = 600 °C. This value is slightly different from a previously published value of m = -2, which was obtained at a lower applied stress. The decrease in the absolute value of m with the increase of stress may be due to the subgrains developing during the primary creep.

For 310 stainless steel, using the data obtained in these tests, constitutive equations
have been developed to describe both the primary and secondary creep behavior. The creep strain, $\varepsilon_c$, is given by the polynomial expression:

$$\varepsilon_c = a_1 t^{1/3} + a_2 t^{2/3} + a_3 t$$

where $a_1$, $a_2$ and $a_3$ are all polynomial coefficients and $t$ is the time. This equation fits the measured creep curves to an accuracy (percent of residuals about the mean explained) of 95 to 100%.

The effect of second phase-carbides on the microstructure and high temperature mechanical properties was determined for experimental alloys of the HP-Nb type (Fe-35Ni-25Cr-1Nb) in both the as-cast condition and aged at 1100 °C condition. The creep rupture strength of the low (0.35%C) or high (0.62%C) carbon content alloys, that is low or high amount of carbides, was low; whereas carbon contents between 0.45% to 0.55%C produced the best creep rupture strength. These results are discussed in terms of the relative strengths of the matrix and grain boundaries, and the ductility of the matrix.
ACKNOWLEDGEMENTS

Primarily, I wish to express thanks to my advisor Dr. D. O. Northwood. Dr. Northwood’s advice, guidance, support and enthusiastic supervision was unending during this research project.

I am also indebted to John Robinson, Barbara Denomey, and to many other people who helped to make this thesis possible.

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CHAPTER I. INTRODUCTION

Most alloys used for industrial heat-resisting service are either of the Fe-Cr-Ni or Fe-Ni-Cr type. Depending chiefly on the chromium and nickel contents, the basic structures may be ferritic, martensitic or austenitic. Ferrite is soft, relatively weak and ductile at high temperatures. Martensite is unstable. Austenite is strong and relatively tough. Thus, the stronger industrial high-temperature alloys depend on an austenitic matrix. Table 1 [1] gives the designation and composition of selected heat resistant alloys.

Heat resistant alloy steels are finding wide usage as reformer tubes in chemical fertilizer and ethylene production plants in the petrochemical industry. The most commonly used alloy is probably HK-40 (Fe-25Cr-20Ni-0.4C), which has an as-cast structure of supersaturated austenite and eutectic carbides. On aging, dispersed secondary carbides are formed and the creep strength is increased. There is considerable interest in adding carbide forming elements such as Nb, Ti or Zr to the base HK40 composition to provide a more complex and stable eutectic and a larger volume fraction of finer, more evenly distributed secondary carbide, and thus obtain improved ductility and creep rupture strength [2].

Stainless steel can also be used for heat and corrosion resistance. The austenitic stainless steels are favored for structural uses in aircraft and transport equipment because of the high strength and corrosion resistance. The austenitic steels are normally hot-short, but small additions of the cerium may be used to improve hot-working. Varying the
Table 1. Designations and compositions of heat resistant alloys.

<table>
<thead>
<tr>
<th>ACI</th>
<th>AISI(b)</th>
<th>Designations</th>
<th>ASTM(c)</th>
<th>C</th>
<th>Cr</th>
<th>N</th>
<th>Si</th>
</tr>
</thead>
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<tr>
<td>HA</td>
<td></td>
<td>A217, A199, A200</td>
<td></td>
<td>0.20 max</td>
<td>8 to 10</td>
<td></td>
<td>1.00</td>
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<tr>
<td>HB</td>
<td></td>
<td></td>
<td></td>
<td>0.30 max</td>
<td>18 to 22</td>
<td>2 max</td>
<td>2.00</td>
</tr>
<tr>
<td>HC</td>
<td>446</td>
<td>T0446 A297</td>
<td></td>
<td>0.50 max</td>
<td>26 to 30</td>
<td>4 max</td>
<td>2.00</td>
</tr>
<tr>
<td>HD</td>
<td>327</td>
<td>T0327</td>
<td></td>
<td>0.50 max</td>
<td>26 to 30</td>
<td>4 to 7</td>
<td>2.00</td>
</tr>
<tr>
<td>HE</td>
<td>312</td>
<td>T0312 A297</td>
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<td>0.20 to 0.50</td>
<td>26 to 30</td>
<td>8 to 11</td>
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<tr>
<td>HF</td>
<td>302B</td>
<td>T0308 A297</td>
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<td>309</td>
<td>T0309 A297, B190</td>
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<td>24 to 28</td>
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<tr>
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<td></td>
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<td>0.20 to 0.50</td>
<td>26 to 30</td>
<td>14 to 18</td>
<td>2.00</td>
</tr>
<tr>
<td>HK(d)</td>
<td>310</td>
<td>T0310 A297</td>
<td></td>
<td>0.20 to 0.60</td>
<td>24 to 28</td>
<td>18 to 23</td>
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<tr>
<td>HL</td>
<td></td>
<td>T0310A</td>
<td></td>
<td>0.20 to 0.60</td>
<td>28 to 32</td>
<td>18 to 32</td>
<td>2.00</td>
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<tr>
<td>HN</td>
<td></td>
<td></td>
<td></td>
<td>0.20 to 0.50</td>
<td>19 to 23</td>
<td>23 to 27</td>
<td>2.00</td>
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<tr>
<td>HT</td>
<td>330</td>
<td>T0330 A297, B207</td>
<td></td>
<td>0.35 to 0.75</td>
<td>13 to 17</td>
<td>33 to 37</td>
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<tr>
<td>HU</td>
<td></td>
<td>T0331 A297</td>
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<td>0.35 to 0.75</td>
<td>17 to 21</td>
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<tr>
<td>HW</td>
<td></td>
<td>T0334 A297</td>
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<td>0.35 to 0.75</td>
<td>10 to 14</td>
<td>58 to 62</td>
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<tr>
<td>HX</td>
<td></td>
<td>T0335 A297</td>
<td></td>
<td>0.35 to 0.75</td>
<td>15 to 19</td>
<td>64 to 68</td>
<td>2.50</td>
</tr>
</tbody>
</table>

(a) Manganese is 0.35 to 0.65% for HA, 1% for HC, 1.5% for HD and 2% for the other alloys. Phosphorus and sulfur are 0.04% max. Molybdenum is not intentionally added except in type HA, which has 0.50 to 1.20% Mo. Maximum for other alloys is set at 0.5% Mo. Type H11F also contains 0.2% max N. (b) Wrought alloy designation. All others are cast alloy designations. These are listed for identification only. Castings should be ordered under cast alloy designation. (c) ASTM specification numbers; alloy designations are the same as ACI. (d) AMS 5355.

ACI: Alloy Casting Institute.
AISI: American Iron and Steel Institute.
SAE: Society of Automotive Engineering.
alloying elements in these steels makes the number of possible types and grades almost unlimited. There are nearly 50 compositions that are recognized by the American Iron and Steel Institute (AISI) as standard stainless grades. The AISI type 300 steels are the chromium-nickel austenitic stainless steels in grades containing up to 30% chromium and up to 20% nickel. AISI type 304 is most used as it is generally available in all wrought forms and is easily welded. Where corrosive conditions exist, AISI type 316 is used. AISI 310 is often subjected to prolonged high temperatures (up to 1100°C) because of its good creep resistance. [It is claimed that AISI 310 can be used at higher temperatures than other austenitic stainless steels.] However, there is little data in the literature on the creep behavior of the AISI type 310, which is widely used in heat exchangers, petroleum refining, chemical processing equipment and gas turbines.

The steadily increasing amount of load-carrying and pressure-containing equipment that is being constructed to operate at temperatures in the 1600°F to 2000°F (870°C-1100°C) range is placing increasing demands on high-strength heat resistant materials. Important among such materials are the ACI Type HK-40 casting alloy and its counterpart, AISI 310 stainless steel. As knowledge of the elevated-temperature performance of these types of materials advances, they become used more widely, more effectively, and with increased confidence. It was in the interest of extending such knowledge that the present research work was conducted.

The present research work is focused on the creep behavior of both 310 stainless and HP-Nb heat resistant casting steel. The main difference between these two alloys is the carbon, with the carbon content of the heat resistant castings being significantly
higher than that of the stainless steel. Based on the different carbon content of these two alloys, the investigations have been separated into two parts. Primarily, due to Avery et al.'s pioneering work [3], which found the carbon content of HK alloy to be the most effective factor in the composition promoting creep-rupture strength, for HK-40 heat resisting steel, four alloys of different carbon content have been investigated and the effects of carbides (both eutectic carbide and secondary carbide) on creep properties have been studied.

Secondly, because of the low carbon content of 310 stainless steel (thus the very low volume fraction of carbides after aging), the research work is focused on the mechanical properties, such as the effects of stress, temperature, especially grain size on the creep behavior of this material in both the primary and secondary creep regimes. Finally, the constitutive equation for creep curve fitting has been determined.
CHAPTER II. LITERATURE REVIEW

When a material is loaded under constant stress at temperatures above one-half of the absolute melting temperature, the strain-time curve has several distinct regions. These are: (1) an initial elastic-plus-plastic extension accompanying the application of the load, (2) a primary creep region in which the creep rate is continuously decreasing, (3) a steady-state region during which the creep rate is constant, and (4) tertiary creep during which the strain rate increases continuously to fracture. Although the influence of many of the microstructural features will be discussed relative to steady-state creep rate, it should be noted that these features may also influence the initial plastic strain, the primary creep region and the tertiary creep region. This is quite important when the strain-time behavior must be estimated such that both the initial plastic strain and the primary creep strain are included.

An idealized creep curve is shown schematically in Fig.1.

It is now well established experimentally that there are at least two distinct types of creep behavior in metallic solid solutions. The first type is similar to the creep behavior of pure metals and has either been named Class M (metal type) by Langdon and his co-workers [4] or Class II alloy by Burke [5] and Karshima and his co-workers [6]. The major characteristics of this type of creep behavior are [7][8]: a stress exponent close to 5; an instantaneous strain on application of the load, a normal primary state of
Fig. 1. Idealized Creep Curve
creep; a steady state creep which depends on the stacking fault energy of the alloys; and the formation of subgrains. This type of behavior is generally considered to be due to some dislocation climb process being rate controlling [9].

The second type of behavior which is not found in pure metals has been termed as Class A (alloy type) [4] or Class I alloy [5][6]. The major characteristics are [7][8]: a stress exponent close to 3; little or no instantaneous strain on application of load; a brief period of normal or inverted primary creep; a uniform distribution of dislocations with no evidence of subgrains. The controlling mechanism for this type of behavior is generally considered to be viscous drag on the dislocation during glide [10].

Since the pioneering research of Andrade [11], it has been established that creep under constant stress can exhibit a significant amount of transient deformation before setting down to a steady state. Indeed, during creep of most metals and alloys, at temperatures of around 0.4 \( T_a \) and above, after the initial strain on loading, the creep rate decreases gradually during the "primary" stage until an apparently constant or steady state rate is reached during the "secondary" stage, as illustrated in Fig.1.

Changes in the stress state can evoke new transients, while some complex engineering alloys often show only small amounts of such transient creep. Pure f.c.c and b.c.c metals show important amounts of primary creep. In spite of this, in many alloy systems, the vast majority of all creep studied have been devoted in the past to secondary, or so-called steady state creep.

The mechanisms for both primary and secondary creep will now be discussed, followed by a description of some of the factors influencing creep.
Somewhat enlightening approaches on the nature of primary creep were made by
Dorn et al.,[12]. They have demonstrated that at a given constant stress, the strain rate
during primary creep is governed by a combined time-temperature parameter \( \theta = t \exp(-Q/RT) \), where \( Q \) is the activation energy for self-diffusion that affects the steady-state
creep rate. Indeed, at the same constant stress level, all primary creep curves were shown
to collapse on one another, when plotted as a function of \( \theta \). This indicates that the
kinetics of primary creep is governed by the same processes that govern the steady state
creep, which at elevated temperature is diffusion controlled static recovery. In a later
study, Amin [13] has likened primary creep to the rate of approach to equilibrium in an
unimolecular reaction in which time is measured by steady-state creep rate. He
demonstrated the validity of this approach in a large number of pure metals and simple
solid solution alloys. This demonstrates that during primary creep, both the temperature
and the stress dependence are the same as that in steady state creep.

The strain rate \( \dot{\varepsilon} \) in high temperature creep of pure metals is determined by the
balance between strain-hardening and softening and can be expressed by the Orowan type
equation:

\[
\dot{\varepsilon} = \frac{r}{h} \tag{2.1}
\]

where \( r = d\sigma/dt \) is the true recovery rate and \( h = d\sigma/d\varepsilon \) is the true strain-hardening rate
( \( \sigma \) is the external stress ). Here, the word "true" means that the influence of strain
hardening, which occurs unavoidably during a measurement of recovery rate, or the
influence of recovery, which occurs unavoidably during a measurement of strain-hardening rate, is eliminated from the measured value. Creep curves of pure metals under ordinary test conditions show a primary stage, in which the strain rate decreases continuously with time, or strain, down to the steady state value. The change of creep rate during the primary stage depends on relative changes in $r$ and $h$. No quantitative data have been reported on the strain dependence of $h$ and $r$ during primary creep of pure metals, though some results were reported on alloys. Evans and Wilshire investigated $h$ and $r$ during creep of Cu-30% Zn [14] and Cu-15% Al alloys [15]. In these concentrated alloys, however, dislocations glide viscously [16] and the measured value of $h$ and $r$ in such alloys are only apparent ones [17].

The experimental results of the strain hardening rate as a function of strain during the primary stage of polycrystalline aluminum are reported to show the strain dependence of $h$ during the normal primary creep of pure metals, in which dislocations glide in free glide motion. The strain hardening rate was determined from the measurement of instantaneous plastic strain on a sudden stress increase.

During the primary stage, only a limited number of stress change tests can be made, this is because the structure of a specimen depends greatly on strain in the primary stage and the influence of the stress change on the evolution of the structure is expected to be larger in the primary stage than in the steady state stage. The strain interval between the stress change tests must be taken large enough to obtain meaningful data during the primary stage. Because of this experimental difficulty, M. Nakata et al.,[18] used the following method to define the strain hardening rate of primary creep: the true strain -
hardening rate $h$ can be estimated as:

$$h = \lim_{\Delta \sigma \to 0} \left( \frac{\Delta \sigma}{\Delta \varepsilon} \right)$$  \hspace{1cm} (2.2)

where $\Delta \varepsilon$ is the plastic strain caused by the stress increase $\Delta \sigma$. For primary stage, only the value of $H_{\Delta \sigma}$ for $\Delta \sigma = 0.4$ MPa was measured in this investigation as a function of strain to get enough strain interval, the results are shown in Fig.2, in which it is clearly seen that the value of $H_{\Delta \sigma}$ increases with strain at the very beginning of the creep, it reaches asymptotically the value for the steady state stage.

It becomes evident that the strain hardening rate reaches a constant value during most of the creep period. It increases with strain at the beginning of the primary stage, i.e., for less than 20% of the primary stage strain, or less than 10% percent of the duration of the primary creep. The results of M. Nakata are in accord with those obtained recently by Nakashima and Yoshinaga [19], who investigated the initial strain hardening rate $h_i$ of annealed pure aluminum over the temperature from 623 K to 823 K, and stresses ranging from 0.8 MPa to 6.7 MPa. They reported that $h_i$ is about one-tenth of $h$ at steady state.

Creep at high temperatures is usually considered in relation to detailed dislocation models. The ideas developed by Weertman [20] regard dislocation climb as the rate controlling recovery process and the general features of the analyses are illustrated in Fig.3. The deforming material is assumed to contain $N$ identical dislocation sources per unit volume. During creep, these sources emit dislocations which are confined to their
Fig. 2. The strain hardening rate $H_{0.4}$ obtained for $\Delta \sigma = 0.4$ MPa as a function of strain of polycrystalline aluminum. [Ref. 18]
Fig. 3. Model for climb controlled creep process. [Ref. 20]
glide planes. The leading dislocations are eventually held up at obstacles and, after a sufficient number of dislocation loops have been emitted, the elastic back stress prevents further source operation. The leading dislocation will however climb out of its slip plane by vacancy emission. After climbing a distance, $P$, the dislocation may either be annihilated by a dislocation of opposite sign or may be free to glide in a new slip plane. In either case, a new dislocation can be emitted from the source and creep continues. The climb process represents the recovery event. The area swept out by the old dislocation on its new glide plane plus that swept out by the dislocations on the old glide plane is $A$, so that the overall creep rate is:

$$\frac{de}{dt} = AbN\bar{X}/P$$  

(2.3)

where $X$ is the rate of climb of the leading dislocation, and $b$ is Burger Vector.

The idea that dislocation creep of pure metals is controlled by recovery rather than glide process has also received experimental support from studies which report that following small stress reductions during creep, an incubation period of zero creep rate is recorded before creep commences under the reduced stress [21][22]. The strain-time behavior observed immediately after small stress decreases during creep of aluminum can be seen from Fig.4. In this case, even after a very small stress reduction, a positive creep rate was not found immediately after the instantaneous specimen contraction. Instead, for stress reductions in the range 0.06 to 0.5, an incubation period was noted before the creep rate gradually accelerated at the reduced stress.
Fig. 4. The strain/time behavior observed following stress reductions of different magnitude made during creep in polycrystalline aluminum (grain diameter 0.2 mm) in tests carried out at 10.3 MNm$^2$ and 573 K. [Ref.22]
The occurrence of an incubation period or dwell time of zero creep rate has been interpreted on the basis that, after a small stress reduction, the flow stress of the material must decrease by recovery before creep can begin again at the lower stress. This type of stress-change experiment has been widely adopted since the original studies of Mclean and co-workers [23], which lead to the network-growth models of creep. Essentially, these investigations were concerned largely with examination of the Bailey-Orowan relationship, namely, that the creep rate can be predicted from Eq. 2.1 using measured values of the rate of recovery, \( r \), and the coefficient of strain hardening, \( h \). Experimentally, \( r \) (\( = -\partial \sigma / \partial t \)) was determined from the duration of the incubation period obtained for a given small stress reduction, \( \Delta \sigma \), as

\[
r = \lim_{\Delta \sigma \to 0} \left( \frac{\Delta \sigma}{\Delta t} \right)
\]

(2.4)

The relevant value of \( h \) (\( = \partial \sigma / \partial \varepsilon \)) was then estimated either as the strain-hardening rate at the creep stress determined as the gradient of the stress-strain curve recorded at room temperature for specimens cooled under load after a known creep strain, or more usually, as determined in Eq. 2.2. Using these techniques, the data of Mclean and co-workers [23] supported the view that the creep rate appears to be closely approximated by the ratio \( r/h \).

The relative changes in \( h^{-1} \) is obviously different from the change in \( \dot{\varepsilon} \) during the primary stage. For example, the change in \( h^{-1} \) appears only up to about 0.05 strain, whereas the change in \( \dot{\varepsilon} \) lasts to about 0.25 strain [18]. The difference between these two
quantities is caused by the relative change in the true recovery rate, \( r \), that is, the change in \( \dot{e} \) during the primary stage results mainly from the change in \( r \), except in the initial part of the primary stage. In the very beginning of deformation, not only \( r \), but also \( h \) affects \( \dot{e} \).

The creep behavior of materials has been described by many researchers using phenomenological equations. For example, Odqvist [24] described some phenomenological aspects of creep and creep rupture. The relations often have the form:

\[
\dot{e} = A \sigma^n d^m f(T)
\]  

(2.5)

where \( \dot{e} \) is the steady state creep rate, \( \sigma \) is the applied stress, \( d \) is the grain diameter, and \( f(T) \) can be written as \( \exp(-Q_e/RT) \), where \( R \) is the gas constant, \( T \) is the absolute temperature, and \( A, Q_e, m \) and \( n \) are parameters describing the creep properties. For creep of a given material at temperatures above one-half of the melting temperature, which will be discussed in this paper, \( A, Q_e, m \) and \( n \) are usually constant over certain ranges of stress and temperature (sometimes relatively narrow ranges) of these parameters. \( Q_e \), the activation energy for creep, is the best defined, since it is usually in good agreement with the activation energy for self-diffusion, \( Q_{\text{diff}} \), in the material over a wide range of temperature [4][5].

The parameters \( A, m \) and \( n \) are quite sensitive to the microstructural features of the materials, e.g., dislocations, grain boundaries and composition. This is to be expected
since creep strain is produced by the movement of the various types of defects or elements of structure in the material. Any atomistic models describing the creep behavior should predict these parameters quantitatively in terms of the particular defects believed to be controlling the creep rate.

Although the details of physical mechanisms which control creep are still not known in most instances, there is a growing understanding of how changes in A, m and n are affected by changes in microstructure, stress and temperature. Much of this understanding is still in the form of empirical formulations relating the phenomenological creep equations to the material properties and to observations of the microstructure. Many creep models have been suggested which relate the creep properties to various microstructural features and which are consistent with the observed stress and temperature dependence of the steady state creep rate. They serve to emphasize the dependence of creep behavior on the microstructure.

2.1. Effect of Temperature

Experimental evidence showing that creep involves thermally activated processes has been available for sometime [27]. These processes show a rate dependence on temperature through the factor \( \exp\left(-\frac{\Delta H_i}{RT}\right) \), where \( \Delta H_i \) is the activation energy for the process which is controlling; \( R \) is the gas constant, and \( T \) is the absolute temperature. Such rate dependence indicates that the processes that control the creep rate involve micromechanisms on the atomic scale. It will not be possible to understand creep,
therefore, until the micromechanisms that control the creep are well established. The first step in this direction is the determination of the activation energy for the controlling mechanisms.

Creep, however, is a very complex phenomenon, and under certain conditions several mechanisms may be operating at any one time. The activation energy determined under these conditions would not be a meaningful quantity unless the importance of one mechanism overrode that of all others. If the different mechanisms operating depend on each other, the one that is slowest and requiring the largest activation energy will control. If the mechanisms are independent of each other, the one that is fastest and requiring the lowest activation energy will control. Under these conditions the determination of a meaningful value of the activation energy even for such a complex phenomenon as creep seems feasible. However, it is difficult to determine $\Delta H_i$ experimentally because the exact function giving the dependence of creep rate on temperature, stress and structure has not been defined for sufficiently wide ranges in each of these variables. Thus it may not be possible to determine $\Delta H_i$ explicitly, but it may be possible to determine an apparent activation energy, $\Delta H_c$. In recent years, a large amount of experimental work has been devoted to the determination of $\Delta H_c$ for many materials at various temperatures, stress and creep strains.

The creep of metals and alloys is usually separated into low and high temperature behavior. At low temperature, creep is believed to be governed by non-diffusion-controlled mechanisms. On the basis of theoretical considerations and experimental observations, three thermally activated mechanisms have been suggested as possibly
controlling low-temperature-true creep in metals and alloys. These are: (1). cross-slip; (2). intersection of dislocations; and (3). lattice friction arising from what is usually called "Peierls Force". Low temperature creep will not be discussed in more detail since in actual service, most creep behavior occurs in high temperature regime above 0.5 \( T_m \), and, it is also this high temperature that is the subject of the present research work.

At high temperatures, creep is believed to be governed by diffusion-controlled mechanisms. It has been established for many metals that at high temperatures the diffusion-controlled mechanism governing creep involves self-diffusion. It is generally accepted that self-diffusion in metals is controlled predominantly by a vacancy mechanism which involves the movement of atom through the lattice by interchanging position with vacancies. The coefficient for self-diffusion, \( D_v \), is given by:

\[
D_v = D_0 \exp(-\frac{\Delta H_v}{RT})
\]  

(2.6)

where \( \Delta H_v \) is the activation energy for self-diffusion and \( T \) is the absolute temperature.

It has been found empirically [25] that:
\[ \Delta H_d = 38T_m \]  

(2.7)

where \( T_m \) is again the absolute melting temperature. This relation is an approximation [28], which does not always apply. It is possible from Eq.2.6 and Eq.2.7 to determine approximately the ratio \( T / T_m \) below which self-diffusion is too slow to play an important role in creep. Assuming \( D_o = 1 \) and combining Eq.2.6 and Eq.2.7 leads to:

\[ \frac{T}{T_m} = \frac{38}{R \ln(1/D_e)} \]  

(2.8)

For \( D_e \leq 10^{-18} \), self-diffusion becomes slow and very likely will not have a controlling influence on creep. Substituting \( D_e = 10^{-18} \) in Eq.2.8 gives:

\[ \frac{T}{T_m} = 0.46 \]  

(2.9)

Thus below about 0.5 \( T_m \) creep in pure metals is likely to be governed by mechanisms that do not depend on self-diffusion.

Because creep depends on thermally activated processes and the creep rate depends on the factor \( \exp \left( -\Delta H_c / RT \right) \), the range of \( \Delta H_c \) which may satisfy the measurable
range of creep rates at any one temperature is obviously limited. If $\Delta H_c$ is too high, the creep rate will be too small to measure. If $\Delta H_c$ is too small, the creep rate will be too fast. At high temperatures this means that if the activation energy is not strongly stress-dependent, as seems to be the case, creep mechanisms requiring high activation energies will control. At low temperature, the reverse will be true [29]. The dependence of $\Delta H_c$ on temperature is shown in Fig.5 [29] and Fig.6 shows the dependence of creep rate on temperature [30].

2.2. Effect of Stress

Compared with the consistency of the evidence reported on the temperature dependence of the creep rates, representation of the stress dependence of the initial and secondary creep behavior is less straight forward. The stress dependence of the primary creep rate for stainless steel at 704 °C [31] shows a gradual rise at low stresses. But as higher stress levels are reached, a much more rapid rise is found. Somewhat similar results were obtained for polycrystalline tin at 250°C [32]. On the other hand, aluminum-magnesium alloys tested at low stresses and temperatures of 258 to 580 °C [33] show a stress dependence of the form:

$$\dot{\varepsilon} = A_0 \sigma^n$$  \hspace{1cm} (2.10)
Fig. 5. Variation of the apparent activation energy for creep in aluminum with temperature. [Ref. 29]
Fig. 6. Dependence of log secondary creep rate on inverse temperature for an 20Ni-25Cr austenite stainless steel. [Ref. 30]
where \( A \) and \( n \) are independent of stress. A set of results obtained on an Al-3.1\% Mg alloy satisfy Eq.2.10 as shown in Fig.7 [25]. In this plot, the experimental points fall on a single straight line as predicted by Eq.2.10 when setting \( A = B_1 \exp(-\Delta H_c / RT) \), where \( B_1 \) is a constant, \( \Delta H_c \) is the apparent activation energy for creep, \( R \) is the gas constant, and \( T \) is the absolute temperature.

2.3. Effect of Dispersed Second Phase

Addition of a finely dispersed second phase is often used to increase the creep strength. The dispersion may originate by precipitation from solid solution or it may be introduced during fabrication of the material as hard, nondeforming, stable particles. If the dispersion is obtained by precipitating from solid solution, the precipitate is usually not stable at elevated temperatures. This may enhance the creep strength by causing precipitation during creep, thus pinning the dislocaitons and inhibiting them from gliding and recovery by climb as shown by Raffo [34], or, the creep strength may be decreased if overaging and coarsening of the precipitate occur during creep.

Carbides can significantly affect the properties of heat resistant steel by precipitating at grain boundaries and changing the strength of such regions [35]. The strengthening effect of \( M_{23}C_6 \) carbides also depends on their precipitation morphology. When \( M_{23}C_6 \) carbides are precipitated as dispersed particles within grains and at grain boundaries, the alloy properties are excellent. If the carbide precipitates as a continuous film, properties can be severely degraded. The presence of a continuous film provides an
Fig. 7. Stress dependence of temperature compensated initial creep rate at low stresses for Al-3.1at%Mg alloy, where $\dot{\varepsilon} = A \sigma^a$, $[A = B e^{-\Delta H/R T}]$, so $\dot{\varepsilon} = B e^{-\Delta H/R T} \sigma^a$, and then $\dot{\varepsilon} e^{-\Delta H/R T} = B \sigma^a$. [Ref.25].
easy fracture path. Also, grain boundary sliding would be restricted, leading to excessive stress build-up. On the other hand, the absence of carbides at grain boundaries can lead to premature failure. Because the carbides in grain boundary can interact directly with dislocations, making it more difficult for them to glide or to climb. Therefore for a given matrix strength, optimum alloy properties are achieved by a specific distribution of carbides at the grain-boundaries. The carbide distribution required is one such that stresses can be relieved by a restricted degree of sliding, but where a continuous path is avoided. The condition where the carbides are relatively uniform and small seems to lead to the best combination of properties [36].

The intragranular precipitation of $M_2C_6$ carbides on dislocations is a prominent feature of both 304 and 316 type stainless steels when creep tested at temperatures below 700 °C. It has been argued by several authors [37][38] that carbide precipitation would reduce dislocation mobility and thereby prevent the formation of subgrains. The same argument has also been used to associate the presence of intragranular carbides with a precipitation strengthening effect, since a lower dislocation mobility will obviously lead to a smaller secondary creep rate.

Another argument [39] put forward in support of the effect of carbide precipitation is based upon the observation that creep resistance increases with carbon content. In fact, Beckitt et al [39] related the higher creep strength observed for a 304 type stainless steel to the extensive carbide precipitation on dislocation which accompanied creep below 700 °C. No carbides were found in 304L type samples and, as expected, these samples showed a low creep resistance. The precipitation strengthening effect has also been used by
Morris and Harries in order to explain higher-than-usual stress exponents found at low
temperatures [40].

2.4. Effect of Grain Size

One of the microstructural factors known to affect primary and secondary creep
is grain size. This effect is usually not large when compared to the effects of stress or
temperature, at least within the normal ranges of grain sizes obtainable in polycrystalline
metals and alloys. An example of the effect of grain size on the creep curve is shown in
Fig.8 [41] for an Fe-Cr-Ni-Mn alloy tested under a constant tensile stress of 65.8 Mpa at
704 °C (0.55 $T_m$). For this alloy an increase in the grain diameter from 9 to 82 μm
decreased both primary and secondary creep rate.

In many situations coarse-grain material has lower creep rates and higher stress-
rupture strengths than a fine grain size material. Parker [42] has suggested that the effect
of grain size on creep rate is due primarily to the change in grain boundary structure with
different grain-coarsening treatments. Since high temperature creep depends on dislocation
climb, the rate at which vacancies can diffuse to edge dislocations is the controlling
factor. Vacancy diffusion is more rapid along high energy grain boundaries than through
the bulk lattice. In a fine grain size material with many high angle grain boundaries,
vacancy diffusion is rapid and the creep rate is high. When the same material is heated
to high temperature to coarsen the grain size, most of the high energy grain boundaries
disappear due to grain growth. The boundaries which remain are fewer in number and are
Fig. 8. Effect of grain size on the creep curve of an iron-base austenitic alloy (Fe-Cr-Ni-Mn) tested at 704 °C under a constant stress of 65.8 Mpa. [Ref. 41]
mostly lower energy grain boundaries for which vacancy diffusion is relatively slow. Therefore dislocation climb will be slower in the coarse grain material and the creep rate will be lower.

As with the uncertainties surrounding grain boundary sliding, the experimental observations concerning the effects of grain size on secondary creep behavior in the power-law range are varied and sometimes conflicting [26]. Several early studies indicated that, at the same stress and temperature, a decrease in average grain diameter decreased creep resistance [43][44]. Other investigations have suggested that the creep rate decreases with decreasing grain size at large grain diameters but then increases with further reductions in grain size [45][46][47]. Also several reports maintain that the creep rate is insensitive to grain size except with very fine grain diameters [48][49]. In general, with pure metals, the effects of variations in grain diameter are not large. For aluminum tested within the power-law range, virtually identical creep curves were found for single crystals and for polycrystalline samples of different grain size [48]. Similarly, the creep rate for copper is grain size insensitive, Fig.9, except with very fine grain diameters for which the increase in creep rate was attributed to an increase in the contribution of grain boundary sliding to the overall strain rate [49].

Unlike the weak dependence of creep rate on grain diameter in the power law range when creep occurs by the generation and movement of dislocations, the creep rate would be expected to increase rapidly with decreasing grain size at low stresses when deformation is considered to take place by stress-directed vacancy flow without dislocation movement. Thus, in the low-stress or diffusional creep regime, the variation
Fig. 9. The grain size dependence of the secondary creep rate of polycrystalline copper at 20.68 MNm$^{-2}$ and 796 K. [Ref.49]
of the steady state creep rate with stress, temperature and grain diameter is described as:

\[ \dot{\varepsilon} = A\sigma^n(1/d)^m \exp(-Q/RT) \]  

(2.11)

This equation is almost the same as Eq.2.5 when we put \( f(T) = \exp(-Q/RT) \). A decrease in \( n \) value from greater than four at high stresses to almost unity at low stresses is shown for polycrystalline copper in Fig.10 [50].

It should be noted that for very fine grain size material, the activation energy for creep is equal to the activation energy for grain boundary self-diffusion; for coarse grain size material, the activation energy for creep is almost equal to the activation energy for volume self-diffusion.

2.5. Effect of Prestrain

It is generally believed that creep, except near the melting point, is governed by the rate of work hardening and recovery which have opposite effects. It is thus reasonable to expect that mechanical and thermal treatments, short of complete recrystallization, performed before testing should modify creep behavior considerably. It has been found that in general creep resistance is enhanced by prestrain. Primary creep is minimized and secondary creep rate is reduced. This type of behavior is shown in Fig.11 [51].
Fig. 10. The variation of the grain size compensated creep rate with stress for polycrystalline copper tested at 1093K, where $\dot{\epsilon} = A \sigma^m \exp \left(-\frac{Q}{RT}\right)$, so $\dot{\epsilon} d^m = A \sigma^m \exp \left(-\frac{Q}{RT}\right)$, $m = -2$, and $Q$ is the activation energy. [Ref. 50]
Fig. 11. Effect of prestrain at 23 °C and recovery for one hour at 800 °C on creep curves for nickel. [Ref. 51]
If creep is recovery or climb controlled, then the normal primary curve can be interpreted in terms of a gradual decrease in dislocation mobility as the dislocation density is increased with increasing creep strain [52]. A steady state condition would then be reached when the rate of rearrangement and annihilation of dislocations matches the rate of generation, leading to an ostensibly constant dislocation structure. On this basis, a high dislocation density introduced by prestraining before starting the creep test should reduce the initial creep rate, i.e. progressively lower initial creep rates would be anticipated with increasing prestrain levels. Furthermore, as creep of the prestrained samples continues, recovery processes should reduce the initially high dislocation density towards the equilibrium values for the applied stress, permitting the creep rate to increase gradually with time. This type of behavior is shown for aluminum in Fig.12 [52].

In the preceding discussion, we have drawn attention to a number of cases where it is apparent that creep behavior of crystalline solids is sensitive to the microstructure. The application of phenomenological creep equations to relate the creep rate to applied stress and temperatures is standard practice. The usefulness of these formulations can be extended when the influence of various microstructural features is included in them. The effect of these features, such as grain size, is already known empirically in some materials. Others, such as the influence of specific dislocation substructures and dispersions of a second phase will be more fully characterized in the future. It will then be possible to predict, in some cases, absolute or relative changes in the creep rate when the condition of the material is changed from that for which a set of creep properties was measured.
Fig. 12. Creep curves recorded at 6.9 Mpa and 523 K for aluminum samples which had been prestrained by 0, 6.1 and 8.6% at room temperature prior to testing.[Ref.52]
Atomistic theories of creep include microstructural parameters in their formulations since the creep strain is provided by the relative motion of the microstructural defects. These theories indicate the form of the phenomenological equation corresponding to a certain type of creep and also the relative magnitude of the creep rate. However, validation of these theories is often difficult because appropriate examination of microstructure is omitted by investigators, who instead rely on the mechanical behavior alone to deduce the creep mechanisms. It is clear that both the mechanical behavior and microstructural observations must be considered in order to assess the physical validity of proposed creep models.

2.6. Creep Curves

In this section, the general nature of the creep curves will be examined.

Generally, two classes of alloy can be defined depending on whether or not Class I creep characteristics are displayed under certain test conditions. If a material is classified as a Class II alloy, it will display a normal primary creep curve; if it is defined as the Class I alloy, it will display an inverted primary creep curve. However, many single phase alloys seem to behave in an intermediate manner, e.g. with 70-30, α-brass [53] a transient from normal, through sigmoidal, to inverted primary creep behavior has been recorded with decreasing stress at 597 K: see Fig. 13.

The principal features of a normal creep curve, including the now standard terminology of primary, secondary and tertiary creep, originate in the classical work of
Fig. 13. Constant stress creep curves recorded at 597 K for polycrystalline samples of a copper-33wt% zinc alloy showing the change from a normal to an inverse primary curve as the applied stress is reduced. [Ref. 53]
Andrade. Eq.2.12 is widely used to describe the rate of strain accumulation during the early stages of a creep test.

\[
e = a_1 t^{1/2} + a_2 t^{2/3} + a_3 \cdot t
\]  \hspace{1cm} (2.12)

where \( e \) is the creep strain.

\( t \) is time.

\( a_1, a_2 \) and \( a_3 \) are constants.

It should be emphasized that the normal creep curve presented in Fig.1 is idealized and, in practice, the extent of the three stages can vary markedly with respect to both strain and time for different materials and for different stress / temperature conditions. Thus, the actual creep curves recorded for metals and alloys may be dominated by either the primary or the tertiary stages. Furthermore, the shapes of the primary curves can vary such that the creep rate may be almost constant or may even increase with time giving an "inverse" primary stage rather than the "normal" form depicted in Fig.1.

2.7. Creep of Heat Resistant and Stainless Steel

The above is a general review of some important factors influencing creep behavior. As for the creep of heat resistant and stainless steel, much work is still required to examine the relationship between microstructure and properties. For example, for heat
resistant steel, most work is focused on the resistance to corrosion at high temperatures; the resistance to carburization, creep crack growth, etc. The higher temperature mechanical properties of the cast HK alloy have been the subject of several previous investigations. However, in the bulk of these earlier studies, creep-rupture properties were investigated over lower temperatures than used in the work reported here. E. A. Schoefer presented a comprehensive report on heat-resistant cast alloys including short-time tensile and creep rupture date on the HK alloy at 1400, 1600 and 1800 F [54]. In addition, Mangone and Hall published a summary of their work on the HK alloy which was the forerunner of the research that forms the basis of the current work [55]. This work comprised principally an investigation of the influence of composition variables on the microstructure and mechanical properties of the HK alloy.

For the stainless steel, the high temperature mechanical properties of Type 304 and 316 have been the subject of numerous investigations. Also some research is focused on the grain size effect on the high temperature properties of stainless steel [56][57]. Seemingly inconsistent experimental findings have led to a certain amount of confusion concerning the effect of grain size on creep behavior. The confusion is attributed to a lack of test results obtained over sufficiently wide ranges in grain size, stress and temperature. In order to define and understand the effect of grain size on creep, it is necessary to determine the variation in the temperature and stress dependence of creep parameters as a function of grain size. Experimental results presented in this paper and results available in the literatures [58][59] show a consistent behavior and lead to a unified concept for the dependence of secondary or steady-state creep rate on grain size.
The creep behavior of 310 stainless steel will be discussed first followed by that of HP-Nb heat resistant steel.
CHAPTER III. EXPERIMENTAL DETAILS

3.1. 310 Stainless Steel

3.1.1. Materials

The 310 stainless steel was received in the form of hot-rolled rod. Table 2 shows the chemical composition of this material.

There are two kinds of 310 stainless steel. One is called 310 stainless and the other is named 310S stainless steel. For the "regular" 310 stainless steel, the carbon content is usually around 0.2 wt%, while for the 310S steel, the carbon content is usually below 0.08 wt%. With a carbon content of 0.065wt%, the material investigated is more correctly referred to as 310S stainless steel. Because of the high nickel content, this material is an austenitic stainless steel.

3.1.2. Sample Preparation

3.1.2.1. Heat Treatment

In order to obtain differing grain sizes, a two-step heat treatment process was
Table 2. Chemical Composition of 310 Stainless Steel Used in Present Creep Test and Compositions of AISI Type 310 and 310 S.

<table>
<thead>
<tr>
<th>310 Stainless Steel Used in Present Creep Study</th>
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<tbody>
<tr>
<td>El.</td>
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<td>wt%</td>
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<th>310 (AISI Classification)</th>
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<td>El.</td>
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<th>310 S (AISI Classification)</th>
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<tr>
<td>El.</td>
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<td>wt%</td>
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carried out. See Table 3 for a summary of the heat treatment procedures and the grain sizes obtained. In the first step, the steel was heated for 5h at 1000 °C, 1100 °C or 1200 °C and then water-quenched. This treatment gave the different grain sizes. Subsequently, quenched specimens were heated 700 °C (creep test temperature) for 15 hours. This 700 °C pretreatment gives thermally stable microstructures for the subsequent creep tests. The mean grain diameters, d, of the heat-treated samples, were measured by the grain intercept method [60] and the results are given in Table 3.

3.1.2.2. Creep Samples

Fig. 14 shows the type of sample used for the creep tests. The specimens, with a gauge length of 35 mm and a diameter of 6.25 mm, were machined from the hot-rolled rod.

3.1.2.3. Metallography

Optical metallography was performed on both the as-received and heat-treated samples. Specimens for optical microscopy were prepared in the conventional way. The specimens were ground first on silicon papers, then cleaned with water to remove any residue; and final polished with Al₂O₃ powder (0.05μm) to obtain a scratch-free surface. Finally, the specimens were placed into the etching solution for around 10 seconds and then removed. The etching solutions used to reveal the microstructure are:
Table 3. Heat Treatment and Grain Sizes for 310 Stainless Steel Specimens

<table>
<thead>
<tr>
<th>Primary Heat Treatment</th>
<th>Secondary Heat Treatment</th>
<th>Mean Grain Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Received</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>1000 °C, 5h</td>
<td>700 °C, 15h</td>
<td>60</td>
</tr>
<tr>
<td>1100 °C, 5h.</td>
<td>700 °C, 15h</td>
<td>80</td>
</tr>
<tr>
<td>1200 °C, 5h.</td>
<td>700 °C, 15h</td>
<td>100</td>
</tr>
</tbody>
</table>
G -- Gauge length : 35.0 ± 0.10 (mm)
D -- Diameter : 6.25 ± 0.12 (mm)
R -- Radius of fillet : 6.00 (mm)
A -- Length of reduced section : 45 (mm)

Fig.14. Creep test sample of 310 stainless steel.
a. 5% Bromine in Methanol Solution

(As received Samples)

b. FeCl₃ . 6H₂O  5g
HCl  50 ml
H₂O  100 ml

(Heat Treated Samples)

Using these etching solutions, we can clearly see the grain boundaries in the sample as well as any remaining twin boundaries.

Specimens for the scanning electron microscope (SEM, Nanolab 7) with Energy Dispersive X-ray (EDX, Kevex) analysis were prepared in the same manner as the optical microscopy specimens.

3.1.3. Phase Identification

X-ray analysis of the bulk alloy samples showed no signs of second and/or third phases because the precipitate particles were too small and too few. Thus, for diffraction analysis, separation of the precipitate particles was required. This involves using the rod sample for the anode, a 10% HCl in methanol for the electrolyte, and a potential of 20.0 volts. For this experiment, 48 hours was needed for the processing to get enough X-ray diffraction spectra. The resulting residue was treated with alcohol to dissolve all non-metallic precipitate. The metallic precipitate was collected using a centrifuge, washed with
distilled water and dried.

3.1.4. Creep Testing

The creep test machine is the Instron Model 8560 Dynamic Testing System, which is an all-digital system designed specifically for testing the strength and measuring the physical properties of materials and components. The system consists of several major components: a load frame for the test forces to push or pull against, a force-producing device (the electric actuator), a load measuring device (the load cell), a source of servoelectric power (the electric power back) and a means to control the whole system (the electronic controls).

The Model 8560 Control System consists of a console "tower", a front panel with the displays and pushbuttons, and a load frame interface box. These units are interconnected. These connections should be checked for correct routing and tightness periodically. And then turn on the power and calibrate the system.

Specimens of the test material are attached to gripping devices on the system's load frame after the calibration. Then the specimen is heated up in a furnace attached with the main body of the machine. At each test temperature, the specimen is heated for 1.5 hours to stabilize the structures. An electrically operated actuator moves to apply tensile force to the specimen, and the resulting elongation are displayed in the front panel to an accuracy of 10^(-7) mm. The temperature was controlled by the self-adaptive temperature controller and the temperature scattering was within ± 0.5 K during the period of each
test and the gradient along the specimen was controlled within 1 K.

The test temperatures and the creep stresses ranged from 773 K to 973 K and 200 MPa to 400 MPa, respectively.

3.1.5. Creep Curve Fitting

Best fit methods, including linear, power and polynomial, are used for the data analysis and creep curves polynomial fitting statics.

3.2. HP-Nb Heat Resistant Cast Steel

3.2.1. Materials

The materials were received in the form of centrifugally cast tubes. The chemical composition of the four alloys are given in Table.4. The main point to be noted is that the Cr content remains at about 25 wt%, the nickel content about 35 wt% and the niobium content about 1 wt%. The carbon content varies from 0.35 wt% to 0.62 wt%.

3.2.2. Sample Preparation

Standard sectioning and polishing techniques were used for the preparation of the metallographic specimens. The electrolytic etching solution used to reveal the
Table 4. Chemical Compositions of HP-Nb Heat Resistant Steels Used in Present Study

<table>
<thead>
<tr>
<th>No.</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.35</td>
<td>0.84</td>
<td>0.79</td>
<td>0.013</td>
<td>0.008</td>
<td>25.05</td>
<td>35.70</td>
<td>0.89</td>
<td>0.08</td>
</tr>
<tr>
<td>7</td>
<td>0.44</td>
<td>0.76</td>
<td>0.60</td>
<td>0.019</td>
<td>0.009</td>
<td>24.31</td>
<td>24.28</td>
<td>0.93</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>0.56</td>
<td>0.88</td>
<td>1.02</td>
<td>0.013</td>
<td>0.003</td>
<td>24.83</td>
<td>25.43</td>
<td>1.05</td>
<td>0.08</td>
</tr>
<tr>
<td>11</td>
<td>0.62</td>
<td>1.29</td>
<td>0.89</td>
<td>0.019</td>
<td>0.006</td>
<td>24.71</td>
<td>34.95</td>
<td>0.93</td>
<td>0.09</td>
</tr>
</tbody>
</table>
microstructure was 20 ml 40 % HNO₃ solution : 5 ml HF. A voltage of 8-i2 was used for a time of 15-20 seconds. A grid measurement method was used to determine the quantities of Cr₇C₃, Cr₂₃C₆ and NbC. The number of image fields per specimen was 20.

3.2.3. Creep Testing

The creep and creep rupture tests were conducted using a uniaxial tensile constant load machine. The amount of creep was measured by means of an extensometer clamped to the shoulders adjacent to the gage section of the specimen. Fig.15 shows the dimensions of creep specimens of HP-Nb heat resistant steel.

3.2.4. Heat Treatment

The microstructures and mechanical properties were determined in both the as-cast condition and after aging at 1100 °C for 10, 100 or 200 hours.
G -- Gauge length : 50.0 ± 0.01 (mm)
D -- Diameter : 12.5 ± 0.25 (mm)
R -- Radius of fillet : 10.0 (mm)
A -- Length of reduced section : 60.0 (mm)

Fig. 15. Creep test sample of HK-40 heat resistant steel.
CHAPTER IV. EXPERIMENTAL RESULTS

4.1 Type 310 Stainless Steel

4.1.1. Microstructural Characterization

The optical microstructures of both the as received and heat-treated samples are shown in Figs. 16 and 17. The remaining twin boundaries were observed in all specimens, but more clearly in the fine-grained specimens. The resultant precipitation, which was visible optically after only 5 hours aging at 1000 °C, 1100 °C and 1200 °C, was predominantly intergranular. No precipitation was observed in the as-received samples.

Further details of these structures were revealed using SEM metallography: see Figs. 18 and 19. For the heat treated samples, the precipitates can be seen both at the grain boundaries and within the grains. As for the optical metallography, no precipitates were seen in the as-received samples: Fig. 16. However, the SEM metallography in conjunction with EDX analysis showed that there was high Cr content phase at the grain boundaries in the heat treated samples: see Fig. 19.

X-ray analysis on the bulk alloy samples showed no evidence for second phases since the particles were too small and too few. Thus, for X-ray diffraction analysis of these second phases, separation of the precipitate particles was required. X-ray diffraction spectra from electrolytically extracted particles showed that these extracted particles were
Fig. 16. Microstructures of 310 stainless steel specimen in as-received condition.
Fig. 17. Microstructures of 310 stainless steel specimens in heat treated conditions.
Fig. 18. SEM micrograph of as received sample of 310 stainless steel specimen: some remaining twin boundaries were observed; no precipitates were identified in grain boundaries and within matrix.
Fig. 19. SEM micrograph of 310 stainless steel sample heat treated for: 1000° C, 72h + 700° C, 15h. Precipitates (M_{23}C_6) were observed at grain boundaries.
of the M$_2$C$_6$ type, see Table 5. (Only after 3 hours heat treatment at any of the temperatures, could the precipitates be observed.)

4.1.2. Activation Energy for Steady-State Creep and Grain Size Effects

After each creep test, a creep curve can be drawn based on the experimental data. Fig. 20 shows the creep curve of both primary and secondary stages of 310 stainless steel (d = 80 µm) tested at $\sigma = 300$ Mpa and $T = 500$ °C.

As mentioned in Chapter II., the following equation can be applied to describe steady state creep behavior [61][62]:

$$\varepsilon = A d^m \sigma^n \exp\left(-\frac{Q_c}{RT}\right)$$

(4.1)

where $A$ is a constant, $d$ the mean grain diameter, $m$ the grain diameter exponent, $\sigma$ the creep stress, $n$ the stress exponent, $Q_c$ the activation energy for creep, $R$ the gas constant, and $T$ is the absolute temperature.

The activation energy for creep, $Q_c$, can be determined by plotting Log $\varepsilon$ against $1/T$ for a set value of $\sigma$. The slope of such a plot is then $-Q_c/R$. Such a plot was made for $\sigma = 300$ MPa and the results for different grain sizes 40 µm and 60 µm are shown in Fig. 21 and 22 respectively. The activation energy ($Q_c$) is calculated as 250 ± 6.4 KJ/mol for $d = 40$ µm and 260 ± 9.2 KJ/mol for $d = 60$ µm. (The second terms of $Q_c$ are
Table 5. The Comparison of Calculated d-Spacing of Precipitate in 310 Stainless Steel to Card 5-0721 of JCPDS.

<table>
<thead>
<tr>
<th>Calculated, ( d ) (Å)</th>
<th>((\text{Cr,Fe,W,Mo})_2\text{C}_6), ( d ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3643</td>
<td>2.375</td>
</tr>
<tr>
<td>2.1551</td>
<td>2.168</td>
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<tr>
<td>2.0377</td>
<td>2.044</td>
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<tr>
<td>1.8740</td>
<td>1.8780</td>
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<td>1.7939</td>
<td>1.7960</td>
</tr>
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<tr>
<td>1.2505</td>
<td>1.2520</td>
</tr>
<tr>
<td>1.2266</td>
<td>1.2270</td>
</tr>
<tr>
<td>1.1623</td>
<td>1.1660</td>
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<tr>
<td>1.0847</td>
<td>1.0840</td>
</tr>
<tr>
<td>1.0647</td>
<td>1.0680</td>
</tr>
</tbody>
</table>
Fig. 20. Creep curve of 310 stainless steel (\(d = 80 \, \mu m\)) tested at \(\sigma = 300 \, \text{Mpa}\) and \(T = 500 \, ^\circ\text{C}\).
Fig. 21. Log (secondary creep rate) vs 1/T for 40 μm grain size samples of 310 stainless steel.
Fig. 22. \( \log ( \text{secondary creep rate} ) \) vs \( 1/T \) for 60 \( \mu \text{m} \) grain size specimens of 310 stainless steel.
standard error of coefficients). The values are close to value given for the activation energy of self-diffusion, namely, $Q_a = 280$ KJ/mol [63]. Thus there appears to be almost no effect of grain size, on the activation energy for steady-state creep, at least over the very limited grain size range that was examined.

4.1.3. Activation Energy for Primary Creep

To determine the strain dependence of activation energy, or the activation energy of primary creep, for the strain-time creep curves of different temperatures ranging from 500°C to 700°C, the activation energy for primary creep can be determined as shown in Fig.23 for 40 μm grain sized specimens. Fig.24 is the variation of activation energy with creep strain for 40 μm grain size specimens, and Fig.25 is that for 60 μm grain size specimens. From Figs.24 and 25, we find that the activation energy for primary creep and secondary creep are almost the same. That means the mechanisms are the same for these two periods of creep.

4.1.4. Stress Dependence of Creep Rate

For the as-received samples, the results for the steady state creep rates, $\dot{\varepsilon}_s$, are summarized in Fig.26, which contains log-log plots of $\dot{\varepsilon}_s$ versus the applied stress, $\sigma$. Although there is some degree of experimental scatter, the data can reasonably well be represented by a straight line on the log-log plot of $\dot{\varepsilon}_s$ vs $\sigma$. 

61
Fig. 23. Variation of activation energy with different creep strain for 40 μm grain size stainless steel.
Fig. 24. Dependence of activation energy for creep $H_c$ on creep strain for 40 µm grain size stainless steel tested at 500-700°C and an applied stress of 300 Mpa.
Fig. 25. Dependence of activation energy for creep $H_c$ on creep stain for 60 $\mu$m grain size stainless steel tested at 500-700 °C and an applied stress of 300 Mpa.
Fig. 26. Dependence of creep rate on applied stress, $\sigma$, for 40 $\mu$m grain sized samples of 310 stainless steel tested at 600 °C.
For $T = 873 \text{ K}$ and $d = 40 \mu\text{m}$, we find the stress exponent, $n$, is equal to $5.9 \pm 0.36$ (±0.36 is the standard error of coefficient). This result is close to the values given by Beere et al [64] and Williams et al [65], who found $n$ to be either 5 or 6 for a grain size of 33 $\mu\text{m}$. A stress exponent $n$, in this range, indicates that 310 stainless steel belongs to the Class II, or metal type of creep alloys.

4.1.5. Grain Size Dependence of Stress Exponent $n$

Similarly, we can also get the values of $n$ of different size samples. Fig.27,28 and 29 are a double-logarithmic plot of the creep rate versus stress at constant grain sizes of 60, 80 and 100 $\mu\text{m}$. Values of $n$ were determined by linear regression analysis. And we get the stress exponent $n = 6.1 \pm 0.34$ at $d = 60\mu\text{m}$ $n = 6.16 \pm 0.28$ at $d = 80 \mu\text{m}$ and $n = 6.3 \pm 0.28$ at $d = 100 \mu\text{m}$. (The second terms of $n$ are the standard error of coefficients). We can see there is a gradual increase in stress exponents with the increase of grain sizes. This is in agreement with previously published values for other stainless steels [56].

4.1.6. Effect of Grain Size on Creep Rate

The influence of grain sizes on creep rate, can be determined by plotting log $\dot{\varepsilon}$ against $d$ for a set value of temperature and stress, and the slope of such a plot is then $m$, the grain diameter parameter. Such plots were made for $\sigma = 250$ Mpa and $\sigma = 300$ MPa at $T = 600^\circ\text{C}$. As seen in Figs.30 and 31. For lower stress ( $\sigma = 250$ Mpa ), $m = -1.68$;
Fig. 27. Dependence of creep rate on applied stress, $\sigma$, for 60 $\mu$m grain sized samples of 310 stainless steel tested at 600 °C.
Fig. 28. Dependence of creep rate on applied stress, $\sigma$, for 80 $\mu$m grain sized samples of 310 stainless steel tested at 600 °C.
Fig. 29. Dependence of creep rate on applied stress, $\sigma$, for 100 $\mu$m grain sized samples of 310 stainless steel tested at 600 $^\circ$C.
Fig. 30. Dependence of steady-state creep rate, \( \dot{\varepsilon} \), on grain size for 310 stainless steel tested at 600°C, 250 Mpa.
Fig. 31. Dependence of steady-state creep rate, $\dot{\varepsilon}$, on grain size for 310 stainless steel tested at 600 °C, 300 MPa.
for higher stress ( \( \sigma = 300 \text{ Mpa} \) ), \( m \) is equal to -1.67.

4.1.7. Primary and Secondary Creep Curve Fitting

Simple graphical representation of creep curves is adequate when tests are performed to establish how certain parameters, such as the time to attain a prescribed creep strain, vary with stress and temperature for any material. However, for many practical and theoretical purpose, it is often desirable to devise equations which describe the rate of strain accumulation with time so that graphical representations can be replaced by analytical procedures which allow the creep curves to be specified in terms of a set of parameters, namely, the numerical values of the coefficients in the strain/time equations employed. Other equations can then be evolved which describe how these parameters vary with stress, temperature or materials variables. In this way, the creep characteristics of a material can be expressed in terms one or more constitutive equations which relate stress-strain-time-temperature.

Based on the experimental data and computer program for curve fitting, for 310 stainless steel, the primary and secondary creep curve can be expressed as the following polynomial equation:

\[
e = a_1 t^{1/3} + a_2 t^{2/3} + a_3 t
\]  
(4.2)
where \( a_1, a_2 \) and \( a_3 \) are the polynomial coefficients which vary with stress, temperature and even grain size.

Table 6 is the list of the \( a_1, a_2 \) and \( a_3 \) parameters determined in the different creep tests. Figs. 32, 33, 34 and 35 are examples of the curve fitting procedures.

4.2. Type HK-40 Heat Resistant Casting Steel

4.2.1. Microstructural Characterizations

In order to assist in the phase identification, the second phase particles (carbides) in the as-cast alloys were electrolytically extracted and used to prepare a sample for X-ray powder diffraction analysis. Fig. 36 shows a typical X-ray diffraction pattern for these extracted carbides. In all four alloys the carbides were a mixture of eutectic \( M_2C_3 \) \([(Cr, Fe)_2C_3]\) and eutectic \( NbC \).

Optical micrographs of all four alloys in the as-cast state are shown in Fig. 37. The "Skeletal" carbide is eutectic \( Cr_7C_3 \) and the "blocky" carbide is \( NbC \). Each carbide has its "own" eutectic area, i.e., they tend to concentrate in areas which are either \( Cr_7C_3 \) or \( NbC \). The variation in the amount of the eutectic carbides as a function of the carbon content of the as-cast alloys is shown in Fig. 38 and Table 7.

The results as illustrated in Figs. 37 and 38 indicate that as the carbon content is increased, the amount of eutectic carbide also increases. The main part of this increase is eutectic \( Cr_7C_3 \), while the eutectic \( NbC \) content remains almost unchanged. Nb is a
Table 6. Coefficients Obtained from Curve Fitting Equation Describing Primary and Secondary Creep Curves for 310 Stainless Steel: $\varepsilon_c = a_1 t^{1/3} + a_2 t^{2/3} + a_3 t$

<table>
<thead>
<tr>
<th>Fitting Method</th>
<th>$\sigma$ (MPa)</th>
<th>$T$ (°C)</th>
<th>$d$ (µm)</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>grapher</td>
<td>300</td>
<td>500</td>
<td>40</td>
<td>4.4x10^{-3}</td>
<td>1.0x10^{-4}</td>
<td>-1.5x10^{-4}</td>
<td>100%</td>
</tr>
<tr>
<td>grapher</td>
<td>300</td>
<td>550</td>
<td>40</td>
<td>-2.4x10^{-4}</td>
<td>2.1x10^{-4}</td>
<td>-2.1x10^{-5}</td>
<td>98%</td>
</tr>
<tr>
<td>grapher</td>
<td>300</td>
<td>650</td>
<td>40</td>
<td>-4.8x10^{-4}</td>
<td>4.2x10^{-4}</td>
<td>-2.6x10^{-5}</td>
<td>99%</td>
</tr>
<tr>
<td>grapher</td>
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<td>700</td>
<td>40</td>
<td>6.8x10^{-4}</td>
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</tr>
<tr>
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<td>60</td>
<td>2.6x10^{-5}</td>
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<td>-2.4x10^{-6}</td>
<td>99%</td>
</tr>
<tr>
<td>grapher</td>
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<td>650</td>
<td>60</td>
<td>4.4x10^{-6}</td>
<td>1.2x10^{-4}</td>
<td>-3.9x10^{-4}</td>
<td>95%</td>
</tr>
<tr>
<td>grapher</td>
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<td>700</td>
<td>60</td>
<td>-2.0x10^{-4}</td>
<td>2.5x10^{-3}</td>
<td>-7.4x10^{-5}</td>
<td>100%</td>
</tr>
<tr>
<td>grapher</td>
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<td>500</td>
<td>80</td>
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<td>3.6x10^{-4}</td>
<td>-4.4x10^{-5}</td>
<td>100%</td>
</tr>
<tr>
<td>grapher</td>
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<td>550</td>
<td>80</td>
<td>6.6x10^{-5}</td>
<td>1.5x10^{-4}</td>
<td>-2.3x10^{-5}</td>
<td>98%</td>
</tr>
<tr>
<td>grapher</td>
<td>300</td>
<td>600</td>
<td>40</td>
<td>2.0x10^{-4}</td>
<td>1.9x10^{-5}</td>
<td>-5.3x10^{-6}</td>
<td>99%</td>
</tr>
<tr>
<td>grapher</td>
<td>250</td>
<td>600</td>
<td>40</td>
<td>1.2x10^{-4}</td>
<td>7.6x10^{-5}</td>
<td>-1.4x10^{-5}</td>
<td>98%</td>
</tr>
<tr>
<td>grapher</td>
<td>350</td>
<td>600</td>
<td>40</td>
<td>5.8x10^{-4}</td>
<td>-3.8x10^{-5}</td>
<td>-1.5x10^{-7}</td>
<td>100%</td>
</tr>
<tr>
<td>grapher</td>
<td>400</td>
<td>600</td>
<td>40</td>
<td>4.2x10^{-4}</td>
<td>-1.7x10^{-5}</td>
<td>8.0x10^{-7}</td>
<td>98%</td>
</tr>
<tr>
<td>grapher</td>
<td>300</td>
<td>600</td>
<td>60</td>
<td>2.6x10^{-4}</td>
<td>5.7x10^{-6}</td>
<td>-2.4x10^{-6}</td>
<td>99%</td>
</tr>
<tr>
<td>grapher</td>
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<td>600</td>
<td>$\infty$</td>
<td>4.6x10^{-5}</td>
<td>1.5x10^{-5}</td>
<td>-1.4x10^{-5}</td>
<td>99%</td>
</tr>
<tr>
<td>grapher</td>
<td>400</td>
<td>600</td>
<td>$\infty$</td>
<td>1.6x10^{-3}</td>
<td>-5.8x10^{-4}</td>
<td>7.3x10^{-5}</td>
<td>99%</td>
</tr>
</tbody>
</table>
Fig.32. Primary and secondary creep data for 310 stainless steel (grain size \( d = 80 \ \mu m \)) for applied stress \( \sigma = 300 \ \text{MPa} \) and \( T = 500 \ ^\circ\text{C} \). Individual points are experimental data and solid line is equation:

\[
\varepsilon_c = -0.0004666 t^{1/3} + 0.000364 t^{2/3} - 0.00004389 t
\]
Fig. 33. Primary and secondary creep data for 310 stainless steel (grain size $d = 40 \, \mu m$) for applied stress $\sigma = 300 \, \text{MPa}$ and $T = 500 \, ^\circ \text{C}$. Individual points are experimental data and solid line is equation:

$$\epsilon_c = 0.000044 t^{1/3} + 0.0001 t^{2/3} - 0.00015 t$$
Fig. 34. Primary and secondary creep data for 310 stainless steel (grain size $d = 40 \, \mu m$) for applied stress $\sigma = 300 \, \text{MPa}$ and $T = 700 \, ^\circ\text{C}$. Individual points are experimental data and solid line is equation:

$$\varepsilon_c = 0.00068 t^{2/3} + 0.0007 t^{2/3} + 0.00013 t$$
Fig. 3.5. Primary and secondary creep data for 310 stainless steel (grain size \( d = 80 \ \mu m \) for applied stress \( \sigma = 300 \) Mpa and \( T = 550 \) °C. Individual points are experimental data and solid line is equation:

\[
\varepsilon_c = 0.000066 t^{1/3} + 0.00015 t^{2/3} - 0.000023 t
\]
Fig. 36. Typical x-ray diffraction spectra from electrolytically extracted carbide particles from as-cast alloys of HP-Nb heat resistant steel.
Fig. 37. Optical micrographs of the four HP-Nb heat resistant alloys in the as-cast condition.
Fig. 38. Variation of the volume fraction $V_v\%$ of the eutectic carbides $\text{Cr}_7\text{C}_3$ and $\text{NbC}$, with the carbon content of the as cast alloys of HP-Nb.
Table 7. Eutectic Carbide Content of As-Cast Alloys of the HP-Nb Heat Resistant Steel

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Carbon Content (wt%)</th>
<th>Carbide Content (wt%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr$_7$C$_3$</td>
<td>NbC</td>
<td>(Cr$_7$C$_3$ + NbC)</td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>1.50</td>
<td>0.74</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.44</td>
<td>2.00</td>
<td>0.78</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.56</td>
<td>2.80</td>
<td>0.80</td>
<td>3.60</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.62</td>
<td>3.20</td>
<td>0.80</td>
<td>4.00</td>
<td></td>
</tr>
</tbody>
</table>
stronger carbide forming element than Cr, thus when the eutectic reaction occurs, Nb combines with C much easier than Cr does. Thus when the carbon content is low, i.e., carbon content is 0.35wt%, eutectic NbC is the main component of the eutectic carbides. Since the Nb content is almost unchanged in the range of alloys studied, after the carbon content is high enough to "use up" the Nb in forming eutectic NbC, then as the carbon content is further increased, there is increased precipitation of eutectic Cr₇C₃, which becomes the main component of the eutectic carbide.

The microstructures of alloy 3 and alloy 7 were determined after aging at 1100°C, and the change in microstructures with aging time is shown in Figs.39 and 40. It can be seen that the eutectic NbC has good stability and its appearance and the amount is almost unchanged upon aging. The eutectic Cr₇C₃ coarsened faster in alloy 3 than in alloy 7, this is because alloy 3 has a higher carbon content. The secondary carbide particles, Cr₂₃C₆, precipitate first among the eutectic carbides, then throughout the whole grain. As the carbon content is increased, there is more Cr₂₃C₆ formed and this Cr₂₃C₆ shows a faster growth (coarsening) rate and hence the particles are larger. After 200 hours aging the eutectic Cr₇C₃ has slowly changed to a "broken chain" morphology and the extent of the coarsening of Cr₂₃C₆ is more readily seen.

4.2.2. Mechanical Properties

4.2.2.1. Creep Rupture Strength
Fig. 39. Optical micrographs of alloy 3 (0.56 wt% C) aged at 1100 °C for 10, 100 and 200 hours.
Fig. 40. Optical micrographs of alloy 7 (0.44 wt% C) aged at 1100 °C for 10, 100 and 200 hours.
The creep rupture properties of the four alloys are shown in Fig.41 and Fig.42 for test temperatures of 870 °C and 950 °C respectively. In order to compare the present results for alloy 3 and 7 (i.e. the intermediate carbon content alloys) with previous results for alloys of the same type, i.e. HP-Nb, produced in Japan [2], a Larson-Miller plot was constructed and shown in Fig.43. It can be readily seen from this plot that the points for alloys 3 and 7 are all on the upper side of the experimental data bands for the Japanese alloys.

4.2.2.2. Creep Rupture Ductility

The creep rupture ductilities of the four alloys at 870 °C and 950 °C under varying applied stress are summarized in Table 8 and Figs.44 and 45. Examination of this table shows that, in general, the creep rupture ductilities are highest for carbon contents between 0.45wt% and 0.56wt%.

4.2.2.3. Creep Rate

The change of creep rate with time for an applied stress of 70 MPa and a temperature of 950 °C is shown in Fig.46 or alloys 3 (0.56wt% C), 4 (0.35wt% C) and 11 (0.62wt% C). Alloy 11 exhibits the slowest creep rate whereas alloy 4 has the highest creep rate. The general trend is that as the carbon content is increased, the creep rate is decreased.
Fig. 41. Creep rupture strength at 870 °C for alloy 4 (0.35 wt% C), 7 (0.44 wt% C), 3 (0.56 wt% C) and 11 (0.62 wt% C).
Fig. 42. Creep rupture strength at 950 °C for alloy 4 (0.35 wt% C), 7 (0.44 wt% C), 3 (0.56 wt% C) and 11 (0.62 wt% C).
Fig. 43. Larson-Miller plot for HP-Nb heat resistant steel, where the solid lines are bands within which the creep properties are defined to be reliable; the symbols are the values of Larson-Miller parameter: $P = 10 \cdot T \cdot (23 + \log t)$ of alloy 3 (0.56 wt% C) and alloy 7 (0.44 wt% C). They are on the upper side of the band.
Table 8. Creep Rupture Ductilities of Four HP-Nb Type Alloys at 870 °C and 950 °C

<table>
<thead>
<tr>
<th>Alloy No. (wt% C)</th>
<th>Creep Rupture Ductilities (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>870 °C</td>
</tr>
<tr>
<td></td>
<td>70 MPa</td>
</tr>
<tr>
<td>4 (0.35)</td>
<td>6.5</td>
</tr>
<tr>
<td>7 (0.44)</td>
<td>50.8</td>
</tr>
<tr>
<td>3 (0.56)</td>
<td>32.7</td>
</tr>
<tr>
<td>11 (0.62)</td>
<td>21.0</td>
</tr>
</tbody>
</table>
Fig. 44. Variation of creep rupture ductility with carbon content of HP-Nb heat resistant steel at 950 °C and 70 Mpa.
Fig. 45. Variation of creep rupture ductility with carbon content of HP-Nb heat resistant steel at 870 °C and 90 Mpa.
Fig. 46. Creep rate-time plots for alloys 4 (0.35 wt% C), 3 (0.56 wt% C) and 11 (0.62 wt% C).
4.2.2.4. Vickers Hardness

The Vickers hardness were determined for both the as-cast alloys and after aging at 1100°C for 10-200 hours. The values are summarized in Table 9. Trends to be noted are that as follows: i). in the as-cast state, an increase in carbon content, and hence an increase in the amount of eutectic carbides, gives a higher hardness; ii). aging of the as-cast alloys, and the precipitation of secondary carbides (Cr$_2$C$_6$), increases the hardness with the maximum hardness being produced after about 100 hours at 1100°C. This increase in hardness due to the precipitation of secondary carbides is higher for alloy 3 (0.56wt% C) than for alloy 7 (0.44wt% C).
Table 9. Vickers Hardness of All Four As-Cast HP-Nb Type Alloys and Selected Alloys Aged at 1100 °C

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Carbon (wt%)</th>
<th>Vickers Hardness Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>As-Cast</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>182</td>
</tr>
<tr>
<td>7</td>
<td>0.44</td>
<td>183</td>
</tr>
<tr>
<td>3</td>
<td>0.56</td>
<td>187</td>
</tr>
<tr>
<td>11</td>
<td>0.62</td>
<td>192</td>
</tr>
</tbody>
</table>
CHAPTER V. DISCUSSION OF RESULTS

5.1. 310 Stainless Steel

5.1.1. Effect of Stress

The establishment of the stress dependence of the primary creep rate is necessary for a more complete understanding of creep. However, it should be pointed out that the primary creep rate, and the primary creep strain, is a difficult quantity to measure. Not only is accurate and sensitive equipment required to measure the initial displacement, but also it is difficult to determine the beginning of time-dependent creep. The interrelationship between primary and steady-state creep rate, predicts that the primary creep rate must depend on stress in a manner similar to secondary creep rate.

As discussed in Chapter II., the effect of the applied stress, $\sigma$, on the secondary creep rate, $\dot{\varepsilon}_s$, is frequently described by a power law of the form:

$$\dot{\varepsilon}_s = A\sigma^n$$  \hspace{1cm} (5.1)
where \( n \) is known as the stress exponent. For austenitic stainless steel, a value of \( n = 4.2 \) (close to 5) has been accepted by researchers [5], based on the data of Garofalo et al. [30]. At high stresses, however, creep rates for many materials begin to increase at a faster rate than predicted by extrapolation of the above equation. According to Sherby and Burke [66], the "breakdown of the power law" occurs at stresses which lead to ratios of \( \dot{\varepsilon} / D = 10^9 \text{ cm}^{-2} \) where \( D \) represents the coefficient of self diffusion for the alloy. An exponential law has been proposed to hold for the high stress region. In many cases, however, creep data determined under conditions of \( \dot{\varepsilon}/D > 10^9 \text{ cm}^{-2} \) can still be fitted to a power law within experimental scatter. This will lead to a higher value of the stress exponent because the above equation must now describe the faster rate of increase of the secondary creep rate with stress.

From Figs.26, 27, 28 and 29, we can see that at test stress as high as \( \sigma = 200-400 \) MPa, the stress exponents are higher than 5, (\( n = 5.9 \) at \( d = 40 \) \( \mu \text{m} \); \( n = 6.1 \) at \( d = 60 \) \( \mu \text{m} \); \( n = 6.16 \) at \( d = 80 \) \( \mu \text{m} \) and \( n = 6.3 \) at \( d = 100 \) \( \mu \text{m} \)), this is perhaps because of the higher test stresses.

Another point worth mentioning is that, for a nitried austenitic stainless steel 20%Cr-25%Ni-1.5%Ti tested by Ecob [66], the stress exponent \( n \) was equal to 11. This steel would have contained a significant fraction of dispersed TiN particles and dispersions are known to produce a significant increase in \( n \) [67]. For the 310 stainless steel, because of the low carbon content, the precipitated carbide's volume fraction is too low to have a significant effect on increasing the stress exponent \( n \). So the slightly increased stress exponents (compared to 5) are mostly due to the higher test stress. (As
high as 400 Mpa, while the tensile strength for 310 stainless steel is 625 Mpa.

5.1.2. Effect of Temperature

Experimental evidence strongly indicates that high temperature creep is diffusion controlled, and in pure metals the controlling mechanism seems to depend on self-diffusion. In the presence of impurities, or in the case of alloys, creep may then depend on the diffusion of an impurity or an added element. For pure metals at high temperatures, which in many cases can be well above 0.5 $T_m$, $\Delta H_c$ is nearly equal to the activation energy for self diffusion, $\Delta H_d$. For alloys and ionic materials, $\Delta H_c$ is nearly equal in many cases to the activation energy for diffusion of one of the elements, usually the one exhibiting the lowest diffusivity.

The activation energy for creep, determined from the present results, i.e., $Q_c = 250$ KJ/mol at $d = 40 \mu m$ and $Q_c = 260$ KJ/mol at $d = 60 \mu m$, is approximately equal to the activation energy for self diffusion of iron in austenitic stainless steel which is given as 280 KJ/mol. It is also in good agreement with $Q_c = 279-298$ KJ/mol determined by Yamane et al [68] for the activation energy for steady-state creep of a 20Ni-25Cr austenitic stainless steel. Values of $Q_c$ of this magnitude, together with the values of $n$ that were measured, suggest that dislocation climb is rate controlling and that the 310 austenitic stainless steel is Class II alloy in Sherby and Burke [5] classification.

From the present study, we can also see that the activation energy for creep, $\Delta H_c$, is independent of creep strain, see Figs.24, 25. This may be taken to mean that $\Delta H_c$ is
the same for primary and secondary creep. This has also been observed in polycrystalline 
\( \alpha \) and \( \beta \) - thallium [69], copper [70] and Ag-Al alloys [71]. A similar conclusion that 
\( \Delta H_c \) is independent of creep strain was reached on the basis of results on stainless steel 
[30] and Mg [72].

In the absence of a change in the mode of deformation, sufficient experimental 
evidence shows that \( \Delta H_c \) remains nearly constant during primary and secondary creep 
and may indicate that the processes controlling creep are the same during primary and 
secondary creep. This evidence can't be taken as conclusive, however, because only a 
very small increase in \( \Delta H_c \) is needed to account for the decrease in creep rate from 
primary to steady state. For a ratio of \( \dot{\varepsilon}_p/\dot{\varepsilon}_s = 10^3 \), which is about an upper limit, the 
change in \( \Delta H_c \) is 1.1 RT J/mol. This change in many cases is of the order of the scatter 
found experimentally. Thus it is also not possible to determine accurately the variation 
in \( \Delta H_c \) with creep deformation by means of the present techniques. However if \( \Delta H_c \) 
varies with deformation, the change is likely to be small unless a change in deformation 
mode occurs.

5.1.3. Effect of Grain Size

It is now well known that fine-grained materials exhibit a grain-size-dependent 
creep rate which increases with decreasing grain size. Two decades ago, Garofalo et al. 
[41] made an extensive study of the effect of grain size on the creep rate of an austenitic 
stainless steel. The study revealed that the steady-state creep rate was essentially
independent of the grain size for coarse grain sizes (greater than or approximately equal to 100 \( \mu m \)). These observations were thought to be due to the abundance of grain boundaries acting as dislocation sources in fine grained materials [72].

As shown in Figs.30 and 31, the steady state creep rates monotonically decrease with the increase in grain size. In the results for \( \sigma = 300 \) MPa for the 310 stainless steel, the grain diameter parameter \( m \) is equal to -1.67, and for \( \sigma = 250 \) Mpa, the grain diameter parameter, \( m \), is decreased slightly to -1.68. Both values are slightly different from a previously published value of \( m = -2 \), which was obtained at a lower applied stress. Similar decrease in the absolute value of \( m \) with increase in \( \sigma \) is found in other papers. For example, Takahashi et al.'s study [57] of a 20Ni-25Cr austenitic stainless steel at \( \sigma = 4.9 \) MPa and \( T = 1171 \) to 1211 K, \( m \) is equal to -2 and the relationship of \( \dot{\varepsilon} \propto d^2 \) is found at all test temperatures. The effect of grain size on steady-state creep rate is poor in the coarse-grained specimens at \( 9.8 \) MPa \( \leq \sigma \leq 19.6 \) MPa, \( m \) gradually increase from -2 to -1/2 with grain size.

The temperature dependence of \( \dot{\varepsilon} \), for grain sizes of 40 \( \mu m \) and 60 \( \mu m \) is shown in Fig.21 and Fig.22. They are almost the same. It has been claimed that \( Q_e \) is essentially insensitive to a change in grain size for the creep in austenitic stainless steels [73]. Also, no grain size effect was found for \( \Delta H_e \) in dilute solid solutions of Mg in Al [74] and in an Fe-17%Cr-14%Ni-1%Mn alloy [41].

With the increase of grain size, there is a slight increase of stress exponent \( n \). Stress exponents in this range ( from 5.9 to 6.3 ) are in reasonable agreement with the work of Linga Murty et al [56] for a 20Ni-25Cr austenitic stainless steel, where the stress
exponent of 4.5 was obtained for \( d = 9 \, \mu m \) and with an increase of grain size to \( d = 150 \, \mu m \), the stress exponent increased to \( n = 5.5 \).

5.1.4. Creep Curve Fitting

Many cases have been reported of creep curves showing irregularities. Creep curves of the S or Sigmoidal type and of the periodic, or oscillating type [75] have been observed in single crystals and polycrystals of metals and alloys. For fine grain size materials, the creep curves tend to be normal ones, while for large grain size materials, the creep curves change to inverted ones.

The polynomial type expressions overestimate early strains. This is observed quite generally for normal creep curves and is due to the fact that the creep rates calculated from polynomial equation tend to infinity as times tend to zero. It is also found that the largest deviations often occur during early primary creep but it is in this region of rapid creep rate that experimental values are least reliable.

Polynomial coefficients from curve fitting equation (Eq.2.12) in Table 6 yield values of \( a_3 \) which do not correspond to the secondary creep rate and, for the polynomial type equation, the values have little physical significance since they are negative. It is generally difficult to ascribe physical meaning to polynomial coefficients and some of them do not behave in a systematic manner with stress. For the present polynomial equation:
\[ \varepsilon_c = a_1 t^{1/3} + a_2 t^{2/3} + a_3 t \]  
(5.2)

with the increase of stress, \( a_2 \) and \( a_3 \) are increased, but no systematic change was found in \( a_1 \). While with an increase of temperature, \( a_2 \) is increased but not \( a_1 \) and \( a_3 \). In all cases, the goodness of fit can be improved by the addition of more parameters to the equation but it then becomes difficult to understand their physical meaning and they behave in an increasingly erratic manner with respect to the testing variables of stress and temperature.

Very many other equations, including that having logarithmic forms \([\varepsilon_c = \varepsilon_0 + \alpha_1 \ln ( \alpha_2 t + 1 )]\), have been suggested in an attempt to provide a consistent approach for the representation of creep curve shape [76]. Yet, while the present polynomial type equation is far from exhaustive, it covers the equation types which have been most widely used in data fitting exercises concerned with normal primary and secondary creep curves. Whichever equation type is chosen, it is necessary to devise an adequate procedure for the unambiguous assignment of numerical values to the coefficients.

5.2. HK-40 Heat Resistant Steel

5.2.1. Effect of Carbon and Carbide on

Microstructures
FCC alloys can be hardened by the addition of carbon in relatively large amounts (0.5 wt%) to give a general carbide precipitation. Carbon may also promote the formation of grain boundary carbides such as $M_23C_6$ and $M_7C_3$ to provide strength in these regions. Some alloys also contain the strong primary carbide forming element Nb. The element produces, in addition to $M_7C_3$ and $M_6C$, an MC phase which has greater high temperature stability. The precipitation of primary NbC carbide occurs on matrix dislocations in some iron-containing alloys [77].

In order to obtain the optimum ductility and creep rupture strength, the carbon content must be controlled so as to lead to a better distribution of carbides both at the grain boundaries and within the matrix grains [77]. If the matrix becomes much stronger than the grain boundaries, premature failure occurs either because stress relaxation is difficult or because of an actual weakness in the grain boundary zone. It is expected that an increased population of secondary carbides ($Cr_{23}C_6$) in the matrix will result in a higher matrix strength and a higher content of more stable, complex eutectic carbides (Cr$_7$C$_3$ and NbC) at the grain boundaries will give a higher grain boundary strength [36].

From the results in Table 7, it can be seen that when Nb content is fixed at about 1 wt%, the carbon content only influences the quantity of Cr$_7$C$_3$, but not NbC. This is because the Nb solubility in austenite is ~ 0.5 wt%. The remaining 0.5 wt% Nb requires 0.065 wt% carbon to form NbC. In our alloys, the carbon content is much greater than 0.065 wt%, thus the quantity of NbC is controlled by the Nb content. Since the Nb content of all four alloys is about 1 wt%, then the amount of NbC is almost the same for the four alloys.
From Figs.39 and 40, we can see that carbon influences the stability of the aged structure. At 1100 °C and after 200 hours aging, eutectic Cr7C3 and eutectic NbC are generally stable. The secondary particles of Cr23C6 particles in alloy 3 (0.56 wt% C) precipitate faster than those in alloy 7 (0.44 wt% C) and tend to be evenly distributed. For aging times of 10 hours to 200 hours, the Cr23C6 particles in alloy 3 are larger than those in alloy 7. This indicates that increasing the carbon content is deleterious to the structural stability of the carbides. However, there is no change in the morphology of the carbides, especially the NbC carbides.

5.2.2. Effect of Carbide on Properties

From Figs.41 and 42, it can be seen that alloy 3 (0.56 wt% C) and alloy 7 (0.44 wt% C) have higher creep rupture strengths than alloys 4 (0.35 wt% C) and 11 (0.62 wt% C) (the creep rupture strengths are similar for alloy 3 and 7). In explaining these observations, it is noted that alloy 4 has the lowest carbon content. Thus both the matrix and the grain boundary contain the least amount of carbides. The strength is thus low and deformation is relatively easy in the matrix and dislocations glide easily to the grain boundaries where cracking can occur. Alloy 11 has the highest carbon content and thus both the matrix and grain boundaries have a higher strength. However, the ductility in the matrix is relatively low (see Table 8) and relaxation of the stresses built up during deformation becomes difficult, and premature failure occurs. Alloy 3 and alloy 7 have a moderate carbon content: the grain boundary has a high enough strength to prevent
cavity formation and the matrix has sufficient ductility to impede crack growth. Thus alloy 3 and alloy 7 have the highest creep rupture strength.

From Fig. 46, it can readily be seen that the higher the carbon content, then the lower the creep rate. As the carbon content is increased, there are more eutectic carbides at the grain boundaries and these carbides are effective obstacles to grain boundary sliding.

By examination of the hardness of alloy 3 and alloy 7 in the aged condition, it can be seen that the higher the carbon content, the higher is the hardness, and the greater is the difference when compared with the initial value for the as cast state. This indicates that upon aging, the higher-carbon content alloy (3) precipitates more Cr₂₃C₆ than the lower carbon content alloy (7). These observations are in agreement with the results of Morris and Harris [78] for precipitation in a 316 stainless steel, where it was concluded that precipitation in a solution-treated type 316 stainless steel during aging at temperatures in the range 525 to 900 °C commences with the very rapid formation of M₆C at the grain boundaries and, subsequently, interagranularly; the extent of the carbide precipitation increases progressively with increasing aging time, and increasing the carbon content of the steel promotes more extensive carbide precipitation.
CHAPTER VI. CONCLUSIONS

310 Stainless Steel

Creep tests on 310 stainless steel at temperatures range from 500-700°C (0.48-0.57 T_m) have shown that:

i. The activation energy for steady state creep, \( Q_c \), determined at grain diameter, \( d = 40 \mu m \) and \( \sigma = 300 \) MPa, is equal to 250 KJ/mol, and when grain size increases to \( d = 60 \mu m \), \( Q_c = 260 \) KJ/mol. These values are approximately that for the volume self-diffusion of iron (280 KJ/mol). Changing the grain size does not significantly change the value of activation energy for creep.

ii. The activation energy for primary creep is the same as that for the secondary creep, that is, for 310 stainless steel, the activation energy is independent of creep strain.

iii. Measured values for the stress-exponent of steady state creep, \( n \), are around 6. With an increase of grain size, the stress exponent, \( n \), also increases slightly.
iv. The grain diameter parameter, $m$, as in the equation of

$$t_s = A \sigma^m d^n \exp \left( -Q_c / RT \right)$$

was determined to be -1.68 for $\sigma = 250$ Mpa and -1.67 for $\sigma = 300$ MPa at $T = 600$ °C. These values are slightly different from previously published value of $m = -2$, which were obtained at lower applied stresses.

v. A constitutive equation has been developed to describe both the primary and secondary creep behavior:

$$e = a_1 t^{1/3} + a_2 t^{2/3} + a_3 t$$

This equation fits the measured creep curves to an accuracy of 95 to 100%.

HP-Nb Cast Alloys

The main conclusions to come from the research of HP-Nb heat resistant steel are as follows:
i. The as-cast structure of the HP-Nb alloys consists of skeletal eutectic carbide, Cr$_2$C$_3$, and blocky eutectic carbide, NbC, in a supersaturated austenite matrix.

ii. Increasing the carbon content from 0.35wt% to 0.62wt% while keeping the Nb content constant at about 1wt%, only increases the amount of eutectic Cr$_2$C$_3$ but not NbC.

iii. The morphology of the eutectic Cr$_2$C$_3$ and NbC does not change with changing carbon content. And the higher the carbon content, the greater amount of the secondary carbides Cr$_{23}$C$_6$.

iv. The creep rupture strength depends on the carbon content and the nature of the carbides. The best creep rupture properties are obtained for carbon content between 0.45 and 0.55 wt%.
CHAPTER VII. REFERENCES


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